COOPERATIVE RESEARCH REPORT

No. 147

REPORTS ON THE RESULTS OF
THE BALTIC SEDIMENT INTERCALIBRATION EXERCISE

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# COOPERATIVE CONTAMINANT-RELATED SEDIMENT STUDIES
## IN THE BALTIC SEA

## RESULTS OF THE ICES INTERCALIBRATION EXERCISE ON GEOCHEMICAL AND SEDIMENTOLOGICAL DETERMINANDS IN BALTIC SEA SEDIMENTS

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## Introduction

During its meeting in 1982, the ICES/SCOR Working Group on the Study of the Pollution of the Baltic Sea (SCOR WG 42) agreed that "Pilot Sediment Studies" should be initiated in its study area. A basic programme proposed by an ad hoc Sediment Group, convened by Dr L. Niemistö, was accepted. This programme was set up in order to investigate several closely related tasks, including

a) problems of contamination history, reflected by contaminant profiles in segmented sediment cores,

b) material fluxes across the water-sediment interface, and

c) geochemical processes in the early stages of diagenesis.

The intercalibration of the different geochemical and sedimento-logical methods in use in the laboratories of potential partici-pants around the Baltic Sea was considered to be a necessary pre-requisite.

At the 1982 Statutory Meeting, the Council adopted these plans by resolution C.Res.1982/4:9. The national Delegates were asked to nominate participants for the intercalibration exercise. For the first part of this exercise not only laboratories from around the Baltic Sea, but laboratories from all ICES member countries were invited to participate.

An intercalibration programme, proposed by its organizer (Prof. L. Brügmann) and the convener of the Sediment Group, was dis-cussed in detail in the beginning of 1983 at meetings of the Mar-ine Chemistry Working Group (MCWG), the ICES/SCOR Working Group on the Study of the Pollution of the Baltic, and the Working Group on Marine Sediments in Relation to Pollution (WGMS). Based on the outcome of these discussions, the final programme was set up and started following confirmation by the ICES Advisory Com-mittee on Marine Pollution in June 1983.

The exercise aimed to cover four aspects:

1) Geochemical methods for such determinands as metals, organic and inorganic carbon, phosphorous, and nitrogen should be intercompared.

2) Together with 1), the elemental composition of sediment reference materials from the Baltic Sea, prepared especially for this intercalibration and to be used later for cooperative sediment studies, should be verified.

3) The capability of laboratories involved in present or future contamination-related investigations on Baltic Sea sediments, comprising the three above-mentioned objectives, to resolve vertical distribution patterns of selected geochemical [see a)] and sedimentological determinands (e.g., grain size, dated age) in segmented cores by accurate and precise measurements, should be examined.

4) Peculiarities of two-dimensional distribution patterns of different determinands on a short transect through a typical net sedimentation area of the western Baltic Sea should be investigated.

To meet aims 1) - 4), two different sets of samples were prepared and distributed in two steps of the exercise:

Step 1 - To perform tasks 1) and 2), two sub-samples of dry homogenized mud material ("ABSS" and "MBSS") were sent out to numerous laboratories in ICES member countries.

Step 2 - For tasks 3) and 4), several laboratories, preferably from countries bordering the Baltic Sea, were each supplied with a freshly taken deep-frozen and segmented core (20 x 1 cm).

A preliminary report on the results of the first step was discussed at the 1984 meeting of the three relevant ICES Working Groups (MCWG, WGMS, ICES/SCOR WG) and, after their review, this report was sent out in May 1984 to the participants for information and further comments. The initial results of the second step were presented at a meeting of geochemists and sedimentologists from all Baltic Sea countries, held 4-6 September 1984 on the Finnish R/V "Aranda" in Rostock, German Democratic Republic and considered in the preparation of plans for joint sediment studies. During that meeting, it was agreed that an additional intercomparison among a small group of laboratories (organizer: Dr A. Jensen, Denmark) should be conducted on analytical problems identified in the determination of mercury and cadmium in sediment samples ABSS and MBSS. Problems related to a proper interpretation of data on sedimentation rates for parallel cores were further considered by correspondence in another group of experts on radiochemical dating, headed by Dr P. Pheiffer-Madsen, Denmark. The outcome of the last-mentioned two activities and the conclusions from the "Aranda Meeting" are included in this report as in the last section (p.85).

The present report summarizes the results of thousands of geo-
chemical and sedimentological analyses carried out in nearly 50
laboratories in 15 countries. The successful execution of this
exercise was made possible only due to the invaluable contri-
butions of the participants (listed in Table 13) and their as-
sistants, the permanent support by the authors' institutions, and
the valuable stimulation provided by the relevant ICES Working
Groups.

REPORT ON THE RESULTS OF STEP 1:

THE INTERCOMPARISON EXERCISE ON REFERENCE SAMPLES ABSS AND MBSS

Sampling and sample preparation

The reference samples were taken from the Arkona Basin, on 9 December 1982, on station "GDR 113" ($54^0$ 55.5'N, $13^0$ 30.0'E, water depth 48.5 m) (ABSS), and from the Mecklenburg Bight on 18 December 1982, on station "110" ($54^0$ 14.4'N, $11^0$ 29.4'E, water depth 24.5 m) (MBSS), respectively.

Sampling was performed with a Van Veen grab. The muddy material was stored dark and cool ($4^0$ C) in plastic bags until further treatment in the land-based laboratory*.

Following wet sieving through a 1 mm net, the samples were washed intensively 5 times with a total amount of about 1.5 $m^3$ distilled water. Between washings, the material was left for three days to settle out, and then decanted. The final densities of the slurried muds were 1.2 $g.cm^{-3}$ (ABSS) and 2.0 $g.cm^{-3}$ (MBSS), respectively. These samples were evaporated to dryness at $70-80^0$ C for 24 hrs. The dry cakes were broken and drying was continued for a further 4 hrs. This material was crushed in a hammer breaker ($<$ 1 mm) and pulverized in a porcelain ball mill for 3 hrs. Dry sieving measurements showed that the fraction greater than 63 μm then represented only 2.2 % (ABSS) and 0.79 % (MBSS) of the total amounts. The mass of porcelain ball material lost during grinding, and consequently mixed with the samples, was only 0.17 % of the total mass of the sediment. Therefore, in no case could an influence on the final composition of the samples be expected, either by contamination due to foreign material or by inhomogeneities caused by the presence of coarser grain size fractions.

To avoid contamination, both samples were further treated very carefully, using only plastic tools. The total yield of dry material was 12 kg (ABSS) and 23 kg (MBSS). The homogenized samples were split into portions of about 50 g (ABSS) and 100 g (MBSS), respectively, and sealed in plastic bags.

The grain size distribution in the original wet samples was investigated using a "Sedigraph 5000". For this purpose, one portion of the wet sieved material <63 μm (ABSS: 99 %; MBSS: 98.2 % of the material <1 mm) was homogenized by ultrasonic agitation, 20 minutes for MBSS and 70 minutes for ABSS, until no further change in the grain size distribution was observed. The "Sedigraph 5000" records (Table 1) show significant differences between the two samples. The ABSS material (20.5 % <0.2 μm) is several times finer than MBSS (5.5 % <0.2μm).

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*The further preparation of the samples was carried out by Dr Sansoni, Akademie der Wissenschaften der DDR, Forschungsinstitut für Aufbereitung, Freiberg/SA.

## Distribution of samples and reporting of results

35 sample sets were sent out in August 1983 in small parcels fol-
lowing a custom declaration formulated at the Institute of Marine
Research, Rostock-Warnemünde. Three laboratories reported leak-
ages in the plastic bags and suggested contamination influences.
They were each supplied with a new set of samples. The deadline
for receipt of results of the analyses on ABSS and MBSS was in-
itially set for 15 November 1983. Because another series of 33
sample sets was distributed later, this deadline was changed to
the end of 1983. Subject to the receipt of information relating
to organizational and/or equipment problems in some laboratories,
later results were also accepted. This was to support the collec-
tion of a greater number of data, necessary for the subsequent
statistical treatment. There were still some laboratories which
reported their data after a preliminary report on the first step
of the intercalibration had been prepared in the first half of
1984. These data were likewise documented because the labora-
tories, separately indicated in Tables 3 - 12, had no previous
access to the preliminary report and expanded the range of ap-
plied methods and of determinands included.

Altogether, 42 laboratories reported data to the organizer; that
represents a response of nearly 62 %. This is an acceptable num-
ber due to the fact that only 28 sample sets were sent out upon
direct request to ICES or to the coordinators. The remaining
sample sets were distributed to laboratories involved in the
second phase of the sediment intercalibration organized under the
Joint Monitoring Group of the Oslo and Paris Commissions (on a
proposal of the organizer, Dr M. Joanny, France) and to labora-
tories dealing with contaminants in Baltic Sea sediments.

## Methods

Every participant was requested to apply a similar reference
method. This method was to be relatively simple and free from
interferences, so that it could be applied without undue problems
by every reasonably equipped laboratory. The results of this part
of the exercise were aimed at obtaining an objective measure of
the analytical ability of the different laboratories dealing with
selected determinands. In addition, the proposed reference method
should propagate the use of weak leaching techniques in contami-
nant studies on sediments.

In the current literature, there are very many methods proposed
for a selective and/or stepwise leaching of metals from sediments
(Brügmann and Hennings, 1982). These methods are mostly taken
from "classic" analytical soil chemistry. They are applied to ob-
tain information on metal binding forms in relation to the subse-
quently leached and/or dissolved mineral phases. However, of pri-
mary interest are those weak treatments which extract only metal
fractions of mainly anthropogenic origin, potentially available
for a re-mobilization by all possible variations of the natural
abiotic environmental conditions (e.g., salinity, temperature, pH
value, redox potential, concentration of inorganic and organic
complexing ligands in the pore water, presence of co-precipitat-
ing, occluding or adsorbing carriers such as Mn/Fe oxides/hydrox-

ides, humic substances, clay minerals, etc.) and which are poten-
tially bioavailable.

The choice of such a leaching agent will always be a compromise
and can only give an operationally defined measure of the con-
taminant fraction concerned. In relation to the very often used
(and misused) term "bioavailability", it must be kept in mind
that the different groups of benthic species show wide differ-
ences in their mechanisms for food intake, in their metabolism,
and in the size and nature of their contact areas with the sedi-
ment. A leaching agent should, therefore, preferably realize con-
ditions for the extraction of selected contaminants which cover
at least those conditions likely to be optimum for species being
most effective in that sense. Unfortunately, information on such
upper limits for extraction conditions simulating most benthic
organisms is not yet available.

There are two acidic extractants frequently in use, namely, 25 %
acetic acid (Loring, 1981; Davies, 1983), and dilute 0.5 N
(Chester and Voutsinou, 1981) or 1.0 N hydrochloric acid (Van
Valin and Morse, 1982). An HCl leaching was preferred, consider-
ing that dilute hydrochloric acid media are very common as basic
solutes for the subsequent AAS analyses. This acid is also
readily available in high purity by sub-boiling distillation.

The following reference method was proposed:

About 0.5 g of the sample is put into a plastic bottle and
treated with 25 ml 1.0 N HCl. Following short taking shaking and
12 hour leaching at ambient conditions, the samples are mixed for
6 hours with medium power on a shaking machine. After settling of
suspended matter, the decanted samples are filtered through a
0.45 µm filter, which has previously been leached for more than 6
days in 1.0 N HCl, washed and dried. Analyses by AAS should be
done using standard solutions in 1.0 N HCl.

In addition, the methods commonly in use in the laboratories were
to be applied. Analyses of the above-mentioned determinands
(metals, organic and inorganic carbon, phosphorus and nitrogen)
were not obligatory, but it was expected that the participants
would use their usual methods applicable to the amount of samples
delivered.

Table 2 summarizes the decomposition procedures and the instru-
mental methods applied for the total analyses. A destruction of
the silicate lattice with hydrofluoric acid was used by only 10
laboratories. Strong attacks of the sediment samples in all cases
but one included nitric acid, alone or together with other strong
oxidants ($HClO_4$, $H_2O_2$), with HCl as _aqua regia_ or with strong
solvents ($H_2SO_4$). In most cases, wet dissolution procedures under
ambient pressure were preferred. Only some laboratories reported
on the use of pressurized digestion bombs. True total methods
without previous dissolution of the sediment samples, such as
neutron activation analyses (NAA) or selected atomic emission
spectrometric (AES) techniques, were applied by five laboratories
(NAA 3, AES 2). One of these laboratories submitted data obtained
from X-ray fluorescence analysis, also.

## Results and discussion

37 laboratories reported results to the organizer on both reference samples by 15 April 1984. After this deadline, four additional data sets were received. As can be seen from Tables 3 - 12, the total number of data submitted for elements (mostly metals) was as follows: Cu (124) - Pb, Zn (116) - Cd (111) - Mn (95) - Fe (86) - Cr, Ni (84) - Hg (51) - Co (42) - C-org. (28) - Al (28) - C-inorg. (18) - P (16) - N (14) - Ti (12) - Ca, Mg, U, V (10) - As (8) - Ba, Be, Cs, K, Na, Rb, Sc (6) - Ga, La, Th, Yb, Zr (4) - B, Ce, Eu, Hf, Lu, Mo, Nb, Nd, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Y (2).

The above order apparently reflects the priorities set in participating laboratories for monitoring metals in sediments or related material. The ability to cover the full range of necessary and/or relevant determinands by laboratory programmes is always limited by the available personnel or instrument capacity. For the content of clay, humic substances (fulvic and humic acids) and radionuclides (137-C, 210-Po, 210-Pb) in both samples, single values were submitted.

A significant difference between the composition of both samples was clearly reflected by the results for many determinands. Following the grain size fractionation, with the portion of very fine materials (<0.2 µm, see Table 1) about 4 times greater in ABSS, the contents of several metals with environmental relevance (Cu, Pb, Zn, Ni, Hg) and of organic carbon and nitrogen are between 210 % (Hg-total) and 40 % (N) higher than in MBSS. This can hardly be explained in relation to any postulated "local anthropogenic influences", because the Mecklenburg Bight samples (MBSS) should, in that case, be more susceptible to contamination due to its proximity to possible contaminant sources. However, this proximity to land seems otherwise to favour the addition of coarser material which dilutes the higher content of relevant contaminants in the finer clay fractions.

The sample ABSS was taken from the central Arkona Basin at a greater distance from land-based sources. Therefore, the relative amount of the finer fractions of the suspended particulate matter with longer residence time in the water column, approaching this area and/or being of local autochthonous origin, should increase significantly.

Using the ratio of the organic carbon contents (C-org.(ABSS)/C-org.(MBSS) = 1.5) to "normalize" the metal contents of both samples equalized the above-mentioned metal ratios (Hg 3.1, Zn 2.0, Cu 1.8, Pb 1.7, Ni 1.5) in only one case.

The ratios of ABSS to MBSS for determinands which are mainly part of the more inert fractions of sediments, e.g., Al, Co, Cr, Ti, were only insignificantly higher than one. The same was the case for C-inorg. and phosphorus. In the case of manganese, the MBSS mean value is slightly higher than for ABSS,. This could be due to the differences in redox conditions observed between these areas. Bottom topography, water depth, and oxygen concentrations in the Mecklenburg Bight favour the formation of Fe/Mn-accumulations on recent deposits. "Micronodules", enriched in the rela-

tively mobile manganese, could be the reason for increased concentrations of this element.

Having in mind the limited number of data and the differences in the analytical experience of participating laboratories, a relative standard deviation of around 15 $\pm$ 5 % (depending on the concentration level found for the determinands) seems to be a reasonable "threshold" for accepting the results of an intercalibration exercise such as this. The application of the two-sigma rule was taken as a necessary procedure for the preliminary rejection of typical outliers. A more sophisticated statistical treatment of the data was considered impractical in view of the lack of information on the quality of submitted data, the very different total procedures and, in particular, the limited numbers of data which resulted from the application of the "reference method".

The fractions of metals available after use of the 1 N HCl "reference method" were between about 100 % (Pb) and only 5 % (Al) of the total amounts. This weak leaching approach seems to be a simple way to gain information rapidly on partially recovered metal fractions from muddy sediments. In some cases (Pb, Zn, Cd), percentages close to the total contents were recovered by this agent. In other cases (e.g., Ni, Cu), only around 50 % became available. Due to its strong binding to organic material (possibly humic substances), mercury should be determined only by procedures which include a preceding strong oxidation step, thereby assuring complete mineralization. One participant reported that analyses after using the 1 N HCl leach resulted in repeated observations of higher lead contents than those observed after total digestion including HF treatment. The author has made similar observations on sediments from the southwestern Baltic Sea, whereas in other areas of the Baltic Sea the lead behaved more "regularly". This phenomenon could be caused by precipitation or co-precipitation of lead fluorides and an incomplete re-dissolution of the digested and dried salts for the final AAS measurement.

The first purpose of this intercalibration exercise was to characterize both sediment samples (ABSS and MBSS) so that they could be used as reference materials in future Baltic sediment studies. Therefore, it was acknowledged that some laboratories, in addition to applying the 1 N HCl leaching method, should apply several different "total" procedures to the samples. The results from one of these laboratories, which is known to be experienced in the preparation of standardized marine materials for trace metals,* were used as reference values indicated by a cross in Figures 1 - 9. In most cases, the mean value of the data received from all laboratories (having previously rejected outliers) was close to this reference value. In these figures, the only data considered were those received prior to the deadline set before the preparation of the preliminary report, which was presented at

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*Dr S. Berman, National Research Council Canada, Division of Chemistry, Marine Analytical Chemistry Standards Programme, Ottawa, Canada.

the ICES Working Group meetings in early 1984. Therefore, these mean values may sometimes deviate from those given in Tables 3 - 12, in which subsequently submitted data were included. In any event, any such differences are statistically insignificant.

The procedure for reporting the results submitted by the different laboratories correspond with the procedures agreed in the meetings of the relevant ICES Working Groups and the ACMP in 1984. It was agreed that laboratories should be identified together with their data as far as those data did not belong to the category of outliers. This was done to facilitate further exchange of information between the participants on details of the applied analytical procedures. In addition, it follows the practice used in most ICES intercalibrations.

COPPER (Table 3)

ABSS(MBSS)

29(29) laboratories submitted quantitative results for copper, leachable by 1 N HCl, and 33(33) for "total Cu". Rejecting typical outliers, mean values of 28 ± 3 (13 ± 2) $\mu g \cdot g^{-1}$ for the more mobile fractions and 51 ± 6 (29 ± 3) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

55(45) % of the total Cu contents were dissolved using the weak leaching procedure. The relationship between the copper concentration in ABSS and that in MBSS was 2.2 for the more mobile fraction and 1.8 for the total amounts.

For the weakly leachable fraction, Figure 1a shows that about 60(76) % of the results were between $\overline{x}$ ± 1 sigma (broken lines); for the total amounts, 57(61) % were within this range (Figure 1b).
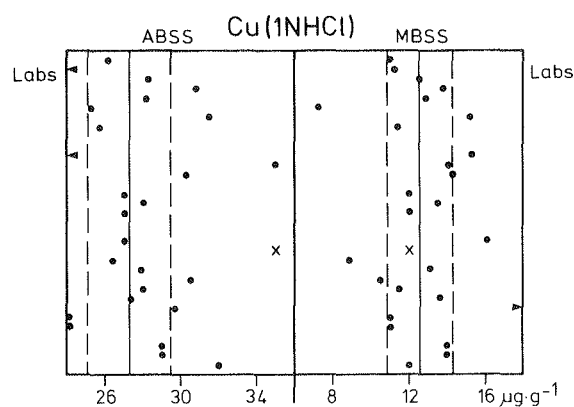


Figure 1a
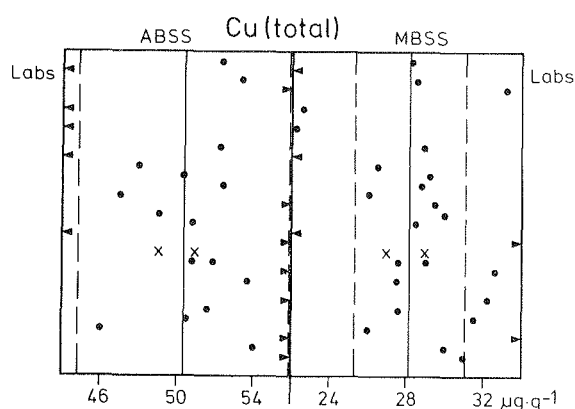


Figure 1b

The relative standard deviation (R.S.D.) is acceptably low. A relationship between the recovery for "total" contents and the completeness of the dissolution of the silicate lattice was not visible (statistically significant).

## LEAD (Table 4)

### ABSS(MBSS)

29(29) laboratories submitted quantitative results for lead, leachable by 1 N HCl, and 29(29) for "total Pb". Rejecting typical outliers, mean values of 94 ± 9 (52 ± 8) $\mu g \cdot g^{-1}$ for the more mobile fractions and 94 ± 11 (54 ± 5) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

Using the weak leaching procedure 100 (96) % of the total Pb contents were dissolved. The ratio of lead concentrations in ABSS and those in MBSS was 1.8 for the more mobile fraction and 1.7 for the total amounts.

For the weakly leachable fraction, Figure 2a shows that about 63(81) % of the results were between $\bar{x}$ ± 1 sigma (broken lines); for the total amounts, 69(69) % were within this range (Figure 2b).
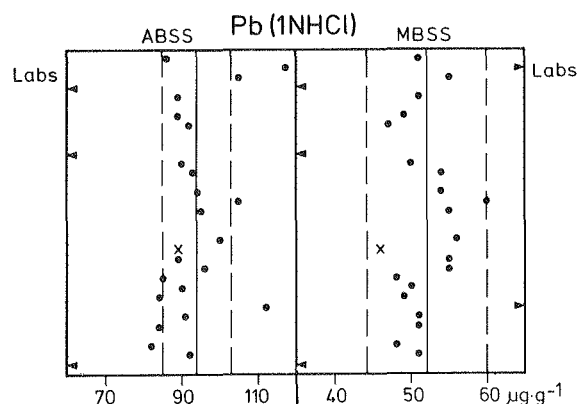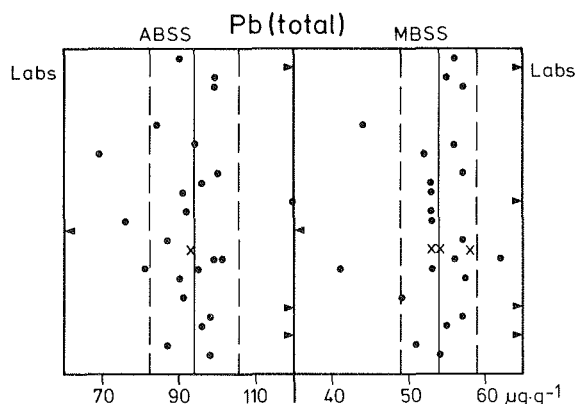


Figure 2a                    Figure 2b

The relative standard deviation is acceptably low (the higher R.S.D. for MBSS 1 N HCl fractions was due to the inclusion of exceptionally high or low values, just within the rejection threshold of $\bar{x}$ ± 2 sigma). The data for the "total" amounts do not seem to depend on the completeness of the dissolution of the silicate lattice.

ZINC (Table 5)


ABSS(MBSS)

27(27) laboratories submitted quantitative results for zinc, leachable by 1 N HCl, and 31(31) for "total Zn". Rejecting typical outliers, mean values of 261 $\pm$ 23 (119 $\pm$ 18) $\mu g \cdot g^{-1}$ for the more labile fractions and 307 $\pm$ 25 (154 $\pm$ 17) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

85(77) % of the total Zn contents were dissolved using the weak leaching procedure. The relationship between zinc concentrations in ABSS and those in MBSS was 2.2 for the more mobile fraction and 2.0 for the total amounts.

For the weakly leachable fraction, Figure 3a shows that about 61(57) % of the results were between $\overline{x} \pm 1$ sigma (broken lines); for the total amounts, 70(81) % were within this range (Figure 3b).
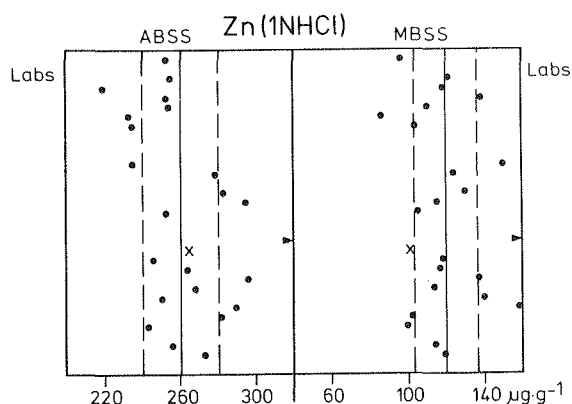


Figure 3a
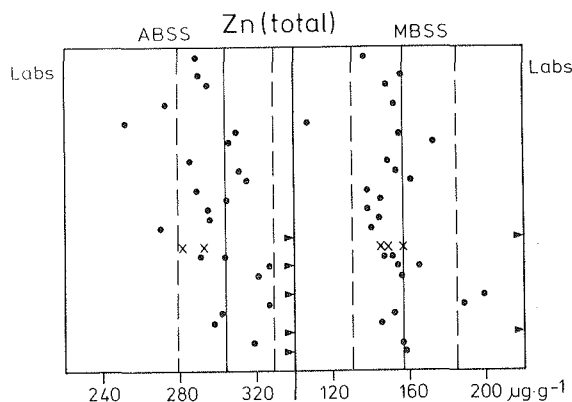
Figure 3b

The relative standard deviation is acceptably low. A significant relationship between the data for "total" contents and the different decomposition procedures used was not noticeable.

CADMIUM (Table 6)


ABSS(MBSS)

25(26) laboratories submitted quantitative results for cadmium, leachable by 1 N HCl. 30(30) laboratories submitted results for "total Cd", 29(29) of them quantitative, the others indicated as "less than". Rejecting typical outliers, mean values of 0.96 $\pm$ 0.35 (0.60 $\pm$ 0.22) $\mu g \cdot g^{-1}$ for the more labile fractions and 0.99 $\pm$ 0.45 (0.74 $\pm$ 0.47) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

Using the weak leaching procedure, 102(81) % of the total Cd contents were dissolved. The relationship between cadmium in ABSS and MBSS was 1.6 for the more mobile fraction and 1.3 for the total amounts.

For the weakly leachable fraction, Figure 4a shows that about 57(68) % of the results were between $\bar{x} \pm 1$ sigma (broken lines); for the total amounts, 56(63) % were within this range (Figure 4b).



Figure 4a
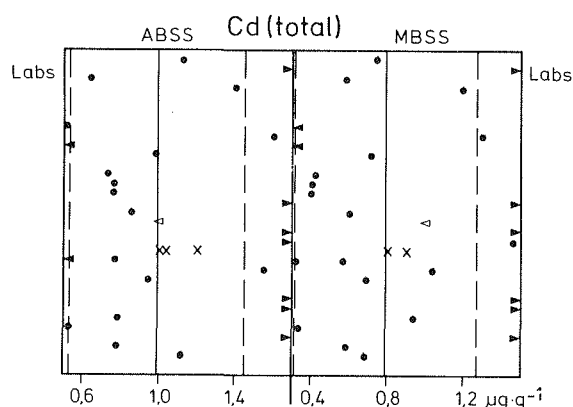


Figure 4b

The (R.S.D.) is acceptably high. A significant relationship between the data for the "total" contents and the completeness of the digestion was not observed.

MANGANESE (Table 7)


ABSS(MBSS)

21(21) laboratories submitted quantitative results for manganese, leachable by 1 N HCl, and 27(27) for "total Mn". Rejecting typical outliers, mean values of 106 ± 19 (140 ± 18) $\mu g \cdot g^{-1}$ for the more labile fractions and 365 ± 40 (381 ± 34) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

Using the weak leaching procedure, only 29(37) % of the total Mn contents were dissolved. The ratio between manganese concentrations in ABSS and MBSS was 0.76 for the more mobile fraction and 0.96 for the total amounts.

For the weakly leachable fraction, Figure 5a shows that about 58(53) % of the results were between $\bar{x} \pm 1$ sigma (broken lines); for the total amounts, 50(50) % were within this range (Figure 5b).
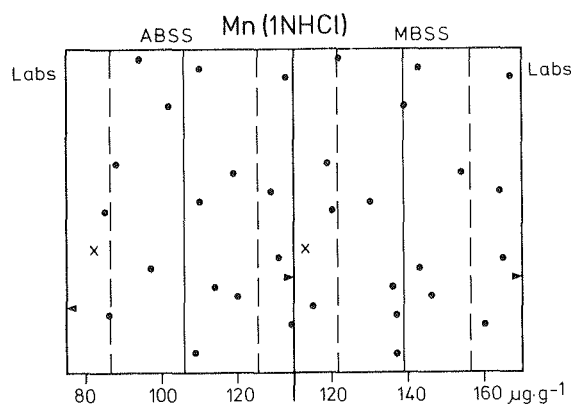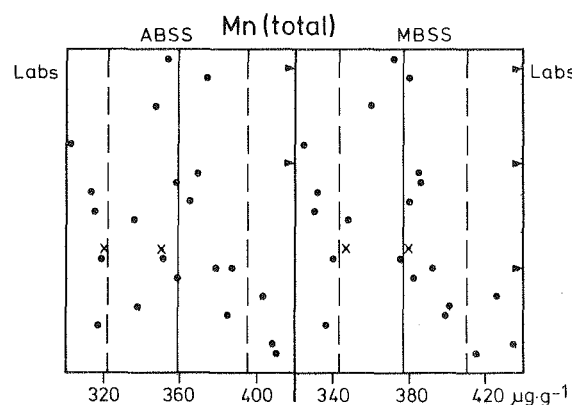


Figure 5a                    Figure 5b


The R.S.D. is acceptably low. There was a trend towards higher values for the "total" concentrations using HF digestion procedures, but this was not statistically significant.

IRON (Table 8)


ABSS(MBSS)

18(18) laboratories submitted quantitative results for iron, leachable by 1 N HCl, and 25(25) for "total Fe". Rejecting typical outliers, mean values of 1.01 ± 0.22 (0.60 ± 0.16) % for the more labile fractions and 3.52 ± 0.49 (2.94 ± 0.44) % for the total amounts were calculated.

Only 29(20) % of the total Fe contents were dissolved using the weak leaching procedure. The relationship between iron concentrations in ABSS and MBSS was 1.7 for the more mobile fraction and 1.2 for the total amounts.

For the weakly leachable fraction, Figure 6a shows that about 53(53) % of the results were between $\bar{x}$ ± 1 sigma (broken lines); for the total amounts, 43(48) % were within this range (Figure 6b).
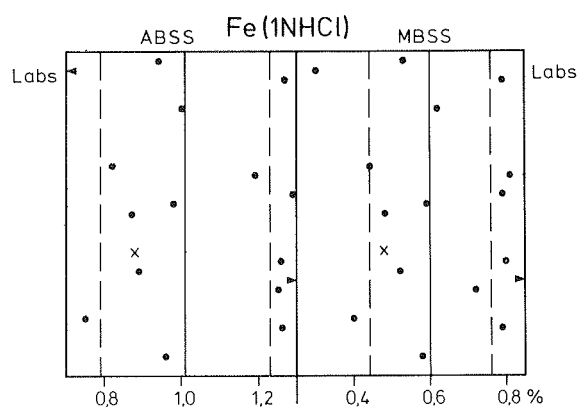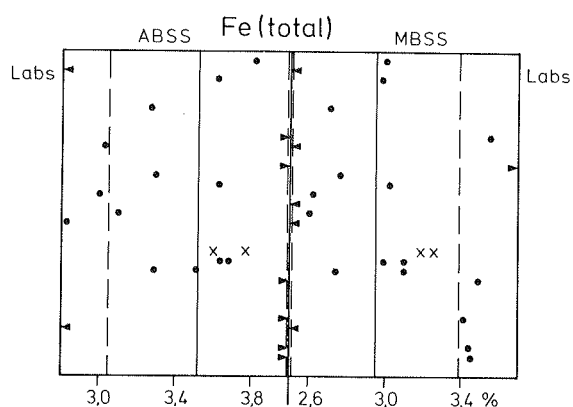


Figure 6a                    Figure 6b


The R.S.D. for the total extraction is acceptably low, but it is unsatisfactory in the case of 1 N HCl extraction. A "total" digestion of the sediment samples seems to result in slightly higher values.

## CHROMIUM (Table 9)

### ABSS(MBSS)

17(18) laboratories submitted quantitative results for chromium, leachable by 1 N HCl, and 25(24) for "total Cr". Rejecting typical outliers, mean values of 14 $\pm$ 4 (10 $\pm$ 4) $\mu g \cdot g^{-1}$ for the more labile fractions and 58 $\pm$ 20 (49 $\pm$ 19) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

Using the weak leaching procedures, only 24(20) % of the total Cr contents were dissolved. The relationship between chromium in ABSS and MBSS was 1.4 for the more mobile fraction and 1.2 for the total amounts.

For the weakly leachable fraction, Figure 7a shows that about 73(75) % of the results were between $\bar{x} \pm 1$ sigma (broken lines); for the total amounts, 60(58) % were within this range (Figure 7b).
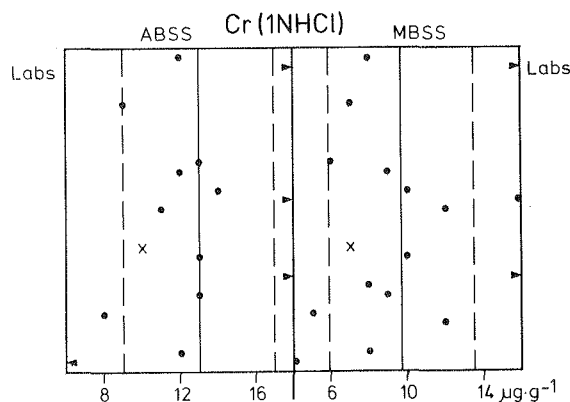
**Figure 7a**
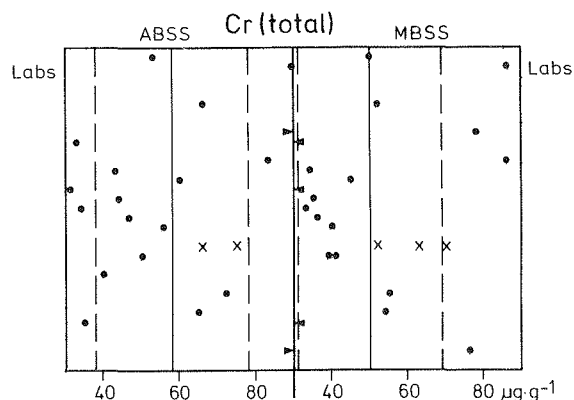
**Figure 7b**

The R.S.D. is unacceptly high. Therefore, an expected significant relationship between the completeness of the digestion and the measured "total" values could not be verified.

NICKEL (Table 10)

ABSS(MBSS)

17(17) laboratories submitted quantitative results for nickel, leachable by 1 N HCl, and 25(25) for "total Ni". Rejecting typical outliers, mean values of 18 ± 4 (11 ± 2) µg·g$^{-1}$ for the more labile fractions and 37 ± 6 (25 ± 5) µg·g$^{-1}$ for the total amounts were calculated.

49(44) % of the total Ni contents were dissolved using the weak leaching procedure. The relationship between ABSS and MBSS for nickel was 1.6 for the more mobile fraction and 1.5 for the total amounts.

For the weakly leachable fraction, Figure 8a shows that about 73(75) % of the results were between $\bar{x} \pm 1$ sigma (broken lines); for the total amounts, 60(58) % were within this range (Figure 8b).
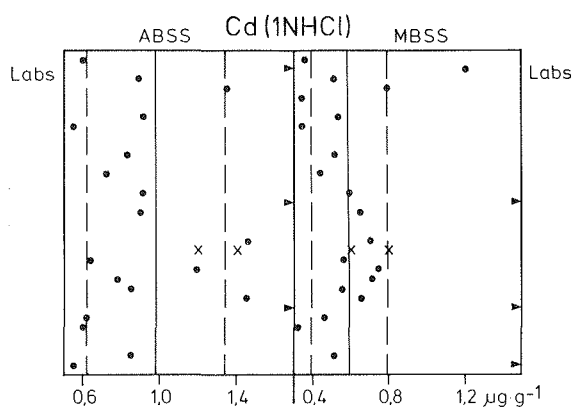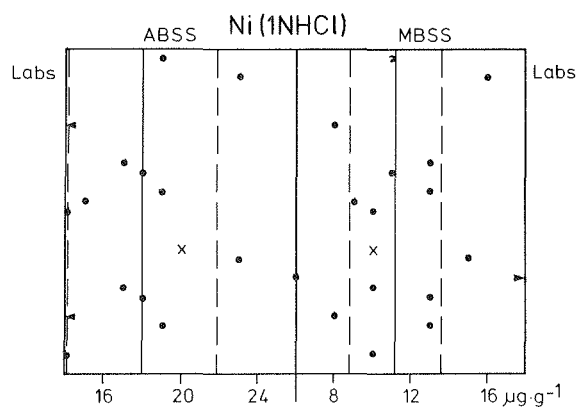


Figure 8a
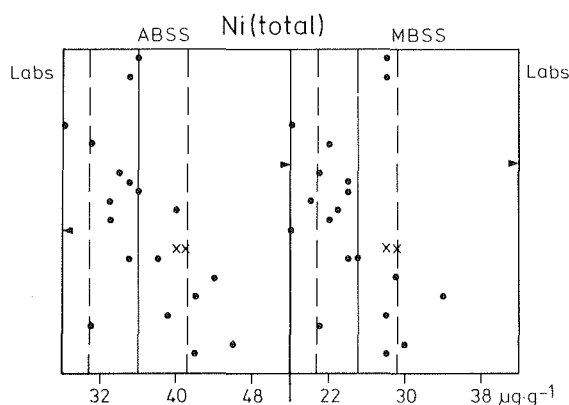


Figure 8b

A relative standard deviation around ± 20 % could be considered still satisfactory. A significant relationship between the completeness of the digestion and the "total" values was not visible.

MERCURY (Table 11)

ABSS(MBSS)

Only 6(6) laboratories submitted results for mercury, leachable by 1 N HCl, 5(5) of them were quantitative. 20(19) laboratories submitted results for "total Hg", 19(18) of which were quantitative. Rejecting outliers, mean values of $59(32)_1$ ng·g$^{-1}$ for the more labile fractions and 256 ± 99 (82 ± 33) ng·g$^{-1}$ for the total amounts were calculated.

Using the weak leaching procedure, only 23(39) % of the total Hg contents were dissolved. The relationship between mercury in ABSS and MBSS was 1.8 for the more mobile fraction and 3.1 for the total amounts.

For the weakly leachable fraction, Figure 9a shows that about 50(66) % of the results were between $\bar{x}$ ± sigma (broken lines); for the total amounts, 68(67) % were within this range (Figure 9b).
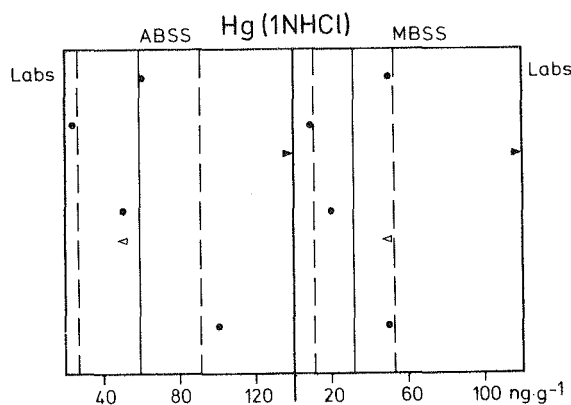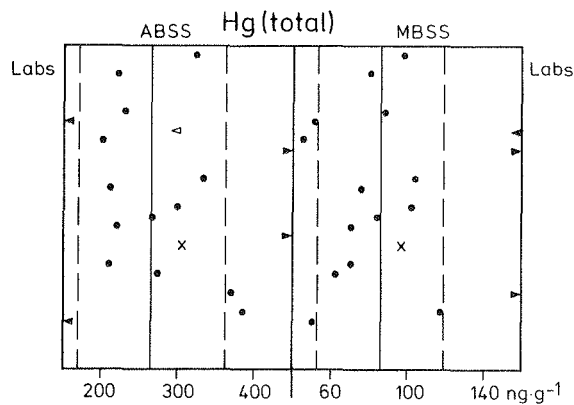


Figure 9a                    Figure 9b

The relative standard deviation was unacceptably high.

## COBALT (TABLE 12)

### ABSS(MBSS)

6(6) laboratories submitted quantitative results for cobalt, leachable by 1 N HCl, and 15(15) for "total Co". Mean values of 6.1 ± 1.2 (5.8 ± 1.1) $\mu g \cdot g^{-1}$ for the more labile fractions and 12 ± 2 (11 ± 2) $\mu g \cdot g^{-1}$ for the total amounts were calculated.

51(53) % of the total Co contents were dissolved by the weak leaching procedure. The relationship between cobalt concentrations in ABSS and MBSS was 1.1 both for the more mobile fraction and for the total amounts. R.S.D. values between 10 % and 20 % are acceptable. No significant dependence of the total amounts on the completeness of the digestion was observed.

## ALUMINIUM (Table 12)

### ABSS(MBSS)

7(6) laboratories submitted quantitative results for aluminium, leachable by 1 N HCl, and 8(8) laboratories for "total Al". Rejecting typical outliers, mean values of 0.38 ± 0.09 (0.27 ± 0.06) % for the more labile fractions and 5.6 ± 0.8 (5.1 ± 0.8) % for the total amounts were calculated.

Only 6.8(5.3) % of the total Al contents were dissolved using the weak leaching procedure. The ratio of aluminium concentrations between ABSS and MBSS was 1.4 for the more labile fraction and 1.1 for the total amounts.

A total digestion by HF resulted in obviously higher Al values.

## ORGANIC CARBON (Table 12)

### ABSS(MBSS)

14(14) laboratories submitted quantitative results for C-org. Mean values of 5.9 ± 0.9 (4.0 ± 0.8) % were calculated. The relationship between C-org. in ABSS and MBSS was 1.5.

Relative standard deviations lower than or equal to ± 20 % are acceptable.

## INORGANIC CARBON (Table 12)

### ABSS(MBSS)

9(9) laboratories submitted quantitative results for the inorganic carbon content. Mean values of 0.14 ± 0.08 (0.14 ± 0.09) % were calculated. There was no difference between ABSS and MBSS in inorganic carbon concentration.

The R.S.D. was more than ± 50 %. This could be due to the relatively low concentrations in both samples. Another reason could be that the wide variety of terms used for inorganic carbon ("carbonate-carbon", "carbonates", "$CaCO_3$-C", "$CO_3^{2-}$-C", "inorg.-C", etc.) could have led to an incorrect interpretation by the Coordinator (or the designation used by the submitting laboratory was incorrect).

## PHOSPHORUS (Table 12)

### ABSS(MBSS)

8(8) laboratories submitted quantitative results for the total phosphorus content. Mean values of 0.11 ± 0.03 (0.10 ± 0.02) % were calculated. The relationship between phosphorus in ABSS and MBSS was 1.1

Relative standard deviations around ± 20 % were just considered acceptable.

## NITROGEN (Table 12)

### ABSS(MBSS)

7(7) laboratories submitted quantitative results for the nitrogen content. Mean values of 0.68 ± 0.18 (0.48 ± 0.22) % were calculated. The ratio of nitrogen concentrations between ABSS and MBSS was 1.4

Relative standard deviations between ± 26 % and ± 46 % are unacceptably high.

## Conclusions

The results reported by the laboratories participating in this part of the exercise indicate that

a) The reference samples distributed appear to have been adequately homogenized and not unduly contaminated during the various steps leading to their preparation. There was likewise no indication that single samples were contaminated during packing or shipping. There were several cases where laboratories reported values which were omitted later as "outliers", but this had to be done regularly for both independent samples ABSS and MBSS, presumably reflecting improper treatment during the analytical procedures.

b) Due to their now well-documented concentrations of many en-
   vironmentally relevant metals and broad information on other
   determinands, the samples ABSS and MBSS are suitable to be
   used further as reference materials for Baltic Sea sediment
   studies. Their composition, e.g., in relation to Hg and Cd
   concentrations, should be continously verified and refined.

c) The comparability of the data for many determinands (Zn, Cu,
   Pb, Mn, Fe, Ni, C-org., Al, Co) was satisfactory. The devia-
   tions in the reported results for Hg, Cd, Cr, and C-inorg.
   were unacceptably high.

d) The approach of using a simple and rapid weak leaching method
   to obtain an idea of the potential partially available frac-
   tions of metals in organic-rich fine-grained sediments was
   found to be useful. For elements relevant from the toxicolo-
   gical point of view, such as Pb, Cd, and Zn, almost the entire
   contents present in the samples could be extracted by 1 N HCl.
   For metals fixed primarily in the silicate lattice (e.g., Al,
   Cr) or requiring strong reducing conditions for their dissol-
   ution (e.g., Mn, Fe) only between about 5 % and 30 % were
   released by this agent. Intermediate amounts (40-60 %) became
   available for Cu, Ni, and Co.

e) With the exception of the primarily lattice-bound elements
   (e.g., Al, Cr, Ti), most of the oxidizing procedures used ap-
   peared to release equivalent amounts of metals in relation to
   procedures including HF.

## REFERENCES

Brügmann, L., Hennings, U. 1982. Stratigraphie und Spezifizierung
   von Metallen in Sedimenten der westlichen Ostsee. Acta hydro-
   chim. hydrobiol., 10:41-53.

Chester, R., Voutsinou, F.G. 1981. The initial assessment of
   trace metal pollution in coastal sediments. Mar. Poll. Bull.,
   12: 84-91.

Davies, I.M. 1983. The detection of anthropogenic inputs and po-
   tential bio-availability of metals on sewage sludge dumping
   grounds. ICES, C.M.1983/E:41.

Loring, D.H. 1981. Potential bio-availability of metals in east-
   ern Canadian estuarine and coastal sediments. Rapp. P.-v.
   Reun. Cons. int. Explor. Mer, 181:93-101.

Loring, D.H. 1987. ICES First Intercalibration for Trace Metals
   in Marine Sediments (1/TM/MS). Coop. Res. Rep. No. 145.

Van Valin, R., Morse, I.W. 1982. An investigation of methods com-
   monly used for the selective removal and characterization of
   trace metals in sediments. Mar. Chem., 11:535-564.

Table 1  Grain size distribution (<63 µm).

| Fraction (µm) | | | "MBSS" (%) | "ABSS" (%) |
|---|---|---|---|---|
| 40 | – | 63 | 2 | – |
| 31.5 | – | 40 | 3 | – |
| 25 | – | 31.5 | 5.5 | 3 |
| 20 | – | 25 | 8 | 2.5 |
| 16 | – | 20 | 7.5 | 5 |
| 12.5 | – | 16 | 6.5 | 4 |
| 10 | – | 12.5 | 4.5 | 4 |
| 8 | – | 10 | 3.5 | 5 |
| 6.3 | – | 8 | 5 | 6 |
| 5 | – | 6.3 | 7 | 6.5 |
| 4 | – | 5 | 3 | 4.5 |
| 3.15 | – | 4 | 5 | 6 |
| 2.5 | – | 3.15 | 4 | 5 |
| 2 | – | 2.5 | 3 | 3 |
| 1.6 | – | 2 | 3 | 3 |
| 1.25 | – | 1.6 | 3 | 3 |
| 1 | – | 1.25 | 3 | 2.5 |
| 0.8 | – | 1 | 1 | 2.5 |
| 0.63 | – | 0.8 | 3 | 3 |
| 0.5 | – | 0.63 | 2 | 2 |
| 0.4 | – | 0.5 | 2 | 2 |
| 0.315 | – | 0.4 | 2 | 2 |
| 0.25 | – | 0.315 | 3 | 3 |
| 0.2 | – | 0.25 | 5 | 2 |
| <0.2 | | | 5.5 | 20.5 |

Table 2 Decomposition procedures and instrumental methods for
the determination of "total" metal contents in "ABSS"
and "MBSS".

| Lab. No. | Method | Decomposition procedure |
|---|---|---|
| 0 | AAS | $HCl/HNO_3/HF/HClO_4$ |
| 1[1] | AAS | |
| 2 | AAS | $HNO_3/H_2O_2$ |
| 3 | AAS | $HNO_3/HClO_4$ |
| 4 | AAS | |
| 5 | AAS | 5 N $HNO_3/120^0 C$, 2 atms. |
| 6 | NAA | |
| 7 | AAS | $HNO_3$ |
| 8 | NAA | |
| 9 | AAS | $HNO_3$ (4 ml/1 g) |
| 10 | AAS | $HNO_3/HCl(H_2O_2/HNO_3/HF/HClO_4$ for Ca, Mg, Al) |
| 11 | AAS,RFA,AES | $HF/H_2SO_4$ |
| 12 | AAS | $HNO_3$ (1:1), 40 ml/2 g |
| 13 | AAS | $HNO_3$ (1:1), 10 ml/0,5 g |
| 14 | AAS | $HNO_3$ ("hot"), 12 h |
| 15 | AAS | 4 N $HNO_3$, 20 ml/0.6 - 0.8 g |
| 16 | AAS | $HCl/HNO_3$ (JMG) |
| 17 | AAS | $HNO_3$, 5 ml/1 g |
| 18 | AAS | $HNO_3$, 20 ml/4 g |
| 19[1] | | |
| 20 | ICP/AES,IDMS | $HNO_3/HClO_4/HF$ |
| 21 | AAS | $HNO_3$ (1:1), 20 ml/0.5 g |
| 22 | AAS | $HNO_3/HF/HClO_4$ ; $HNO_3$ (1:1) |
| 23 | AAS | 6 N $HNO_3$, 20 ml/1 g |
| 24[1] | | |
| 25 | AAS,Pol | $HCl/HNO_3$ (JMG) |
| 26 | AAS | $HCl/HNO_3$ (JMG) |
| 27 | AAS | $HNO_3/HCl$ |
| 28 | AAS | $HNO_3$ |
| 29 | AAS | $HNO_3/HF/HClO_4$ |
| 30 | AAS | $HNO_3/HCl/HF$ |

(cont'd)

Table 2 (cont'd)

| Lab. No. | Method | Decomposition procedure |
|---|---|---|
| 31 | AAS | $HNO_3$/HCl (Cd, Pb); $H_2SO_4$/$HNO_3$/$HClO_4$ (Al, Cr, Cu, Fe, Mn, Ni, P, Zn) |
| 32[1] | AAS | |
| 33[1] | DPASV | |
| 34 | IDAS | $HNO_3$/HF |
| 35[1] | AAS | |
| 36[1] | | |
| 37 | AAS | $HNO_3$, autoclave |
| 38 | AAS | |
| 39 | NAA | |
| 40 | ICP/AES | $HNO_3$/HF/$HClO_4$ |
| 41 | AAS,AES | $HNO_3$/HF (As,Cd,Co,Cu) |

[1] Only use of the "reference method" or no description given for the "total procedure".

| | |
|---|---|
| AAS | Atomic Absorption Spectrometry |
| AES | Atomic Emission Spectrometry |
| DPASV | Differential Pulse Anodic Stripping Voltammetry |
| ICP | Inductively Coupled Plasma |
| IDAS | Isotope Dilution Alpha-Spectrometry |
| IDMS | Isotope Dilution Mass Spectrometry |
| NAA | Neutron Activation Analysis |
| Pol | Polarography |
| RFA | X-Ray Fluorescence Analysis |
| (JMG | Method proposed for the sediment intercalibration of the "Joint Monitoring Group" (Coordinator Dr M. Joanny, France) |

Table 3  COPPER ($\mu g.g^{-1}$)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 26.2 | 52.3 | 11.0 | 28.3 |
| 1 | - | 36.3 | 11.3 | - |
| 2 | 28.3 | 53.4 | 12.6 | 28.6 |
| 3 | 30.8 | 57.4 | 13.8 | 33.2 |
| 4 | 28.2 | - | 12.9 | - |
| 5 | 25.2 | 42.2 | - | 22.6 |
| 6 | - | - | - | - |
| 7 | 25.7 | 41.9 | 11.4 | 22.2 |
| 8 | - | - | - | - |
| 9 | - | 52.3 | - | 29.0 |
| 10 | 22.1 | - | 15.2 | 21.3 |
| 11 | - | 48 | 14 | 26.5 |
| 12 | 30.3 | 50.3 | 14.3 | 29.2 |
| 13 | - | 52.4 | - | 28.8 |
| 14 | 27 | 47 | 12 | 26 |
| 15 | 28 | 59 | 13.5 | 29.5 |
| 16 | 27 | 49 | 12 | 30 |
| 17 | - | 50.8 | - | 28.5 |
| 18 | 21[2] | 37;52[2] | 10[2] | 29[2] |
| 19 | 27 | - | 16.1 | - |
| 20 | - | 51;53 | 12 | 27;29 |
| 21 | 26.4 | 50.8;51.9 | 8.9 | 27.6;29 |
| 22 | 27.9 | 58 | 13.1 | 32.6 |
| 23 | 30.5 | 53.7 | 10.5 | 27.5 |
| 24 | 28 | - | 11.5 | - |
| 25 | 27.3 | 57.6 | 13.6 | 32.2 |
| 26 | 29.7 | 51.6 | - | 27.6 |
| 27 | 24 | 50.5 | 11 | 31.5 |
| 28 | 24 | 46 | 11 | 26 |
| 29 | - | - | - | - |

(cont'd)

Table 3   (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | 29 | 54 | 14 | 30 |
| 31 | 29 | 58 | 14 | 31 |
| 32 | 32 | – | 12 | – |
| 33 | 31.5 | – | 15.2 | – |
| 34 | – | – | – | – |
| 35 | 29.9 | – | 12.4 | – |
| 36 | – | 61 | – | – |
| 37[2] | – | 55.9 | – | 30.0 |
| 38[2] | – | 55 | – | 33 |
| 39 | – | – | – | – |
| 40[2] | – | 48 | – | 26 |
| 41[2] | – | 52 | – | – |
| ICES 1/TM/MS[4] | – | – | 10.0 | 30.3(32.2)[3] |
| Total Range | 19 – 35 | 30 – 76 | 7.2 – 19 | 16 – 43 |
| No. of Labs | 29 | 33 | 29 | 33 |
| Range red.[1] | 21 – 32 | 36 – 61 | 8.9 – 16 | 21 – 33 |
| No. of Labs | 26 | 30 | 27 | 28 |
| Mean[3] | 28 | 51(53) | 13 | 29(28) |
| R.S.D. ($\pm$%) | 10 | 12 | 14 | 10 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987, Table 4).

<u>Table 4</u>   LEAD ($\mu g.g^{-1}$)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 86 | 90 | 51 | 56 |
| 1 | 117 | – | 76 | – |
| 2 | 105 | 99 | 55 | 55 |
| 3 | – | 99 | – | 57 |
| 4 | 89 | – | 51 | – |
| 5 | – | – | – | – |
| 6 | – | – | – | – |
| 7 | 92 | 84 | 47 | 44 |
| 8 | – | – | – | – |
| 9 | – | 94 | – | 56 |
| 10 | – | 69 | 29 | 52 |
| 11 | 90 | – | 50 | – |
| 12 | 93 | 100 | 54 | 57 |
| 13 | – | 96 | – | 53 |
| 14 | 94 | 91 | 54 | 53 |
| 15 | 105 | 120 | 60 | 68 |
| 16 | 95 | 92 | 55 | 53 |
| 17 | – | 76 | – | 53 |
| 18 | – | 94[2] | 41[2] | 54[2] |
| 19 | 100 | 87 | 56 | 57 |
| 20 | 89 | 93;96 | 46 | 54;58 |
| 21 | 89 | 101;99 | 55 | 62;56 |
| 22 | 96 | 81;95 | 55 | 41;53 |
| 23 | 85 | 90 | 48 | 55 |
| 24 | 90 | – | 50 | – |
| 25 | 84 | 91 | 49 | 49 |
| 26 | 112 | 128 | – | – |
| 27 | 91 | 98 | 51 | 57 |
| 28 | 84 | 96 | 51 | 55 |
| 29 | – | – | – | – |

(cont'd)

Table 4  (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | 82 | 87 | 48 | 51 |
| 31 | 92 | 98 | 51 | 54 |
| 32 | – | – | – | – |
| 33 | 89 | – | 49 | – |
| 34 | – | – | – | – |
| 35 | 109 | – | 69 | – |
| 36 | – | – | – | – |
| 37[2] | – | 110 | – | – |
| 38[2] | – | 82 | – | 52 |
| 39 | – | – | – | – |
| 40 | – | – | – | – |
| 41[2] | 91 | – | 53 | – |
| ICES 1/TM/MS[4] | – | – | 46.9 | 55.8(56.7)[3] |
| Total Range | 25 – 117 | 29 – 140 | 10 – 78 | 19 – 94 |
| No. of Labs | 29 | 29 | 29 | 29 |
| Range red.[1] | 82 – 117 | 69 – 128 | 29 – 76 | 41 – 68 |
| No. of Labs | 25 | 26 | 26 | 25 |
| Mean[3] | 94 | 94(88) | 52 | 54(54) |
| R.S.D. (±%) | 10 | 12 | 16 | 9 |

[1] reduced range without outliers (outside $\bar{x}$ ± 2 sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 5   ZINC ($\mu g.g^{-1}$)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| O | 253 | 289 | 96 | 136 |
| 1 | -- | -- | -- | -- |
| 2 | 255 | 290 | 121 | 156 |
| 3 | 219 | 295 | 118 | 148 |
| 4 | 253 | -- | 138 | -- |
| 5 | 254 | 273 | 110 | 152 |
| 6 | -- | -- | -- | -- |
| 7 | 235 | 252 | 104 | 107 |
| 8 | -- | 310 | -- | 155 |
| 9 | -- | 306 | -- | 173 |
| 10 | -- | -- | -- | -- |
| 11 | 235 | 286 | 150 | 149 |
| 12 | 279 | 311 | 124 | 153 |
| 13 | -- | 315 | -- | 161. |
| 14 | 283 | 289 | 130 | 138 |
| 15 | 295 | 305 | 115 | 145 |
| 16 | 253 | 295 | 105 | 138 |
| 17 | -- | 296 | -- | 144 |
| 18 | $243^{2}$ | $270;308^{2}$ | $117^{2}$ | $140;160^{2}$ |
| 19 | -- | -- | -- | -- |
| 20 | 265 | 293;318 | 101 | 149;157 |
| 21 | 246 | 304;291 | 118 | 151;147 |
| 22 | 264 | 327;361 | 117 | 165;154 |
| 23 | 296 | 321 | 137 | 156 |
| 24 | 268 | -- | 114 | -- |
| 25 | 250 | 363 | 140 | 199 |
| 26 | 290 | 327 | 158 | 189 |
| 27 | 282 | 302 | 102 | 152 |
| 28 | 243 | 298 | 100 | 145 |
| 29 | -- | -- | -- | -- |

(cont'd)

Table 5  (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | 256 | 319 | 114 | 157 |
| 31 | 273 | 347 | 119 | 158 |
| 32 | – | – | – | – |
| 33 | 233 | – | 86 | – |
| 34 | – | – | – | – |
| 35 | 256 | – | 112 | – |
| 36 | – | 306 | – | 150 |
| 37[2] | – | 317 | – | 148 |
| 38[2] | – | 336 | – | 196 |
| 39 | – | – | – | – |
| 40[2] | – | 305 | – | 150 |
| 41[2] | 305 | – | 144 | – |
| ICES 1/TM/MS[4] | – | – | 98.8 | 147(159)[3] |
| Total Range | 219-536 | 252-529 | 86-235 | 107-255 |
| No. of Labs | 27 | 31 | 27 | 31 |
| Range red.[1] | 219-305 | 252-363 | 86-158 | 107-199 |
| No. of Labs | 26 | 29 | 26 | 29 |
| Mean[3] | 261 | 307(313) | 119 | 154(152) |
| R.S.D. (±%) | 9 | 8 | 15 | 11 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 6  CADMIUM ($\mu g.g^{-1}$)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 0.6 | 1.12 | 0.36 | 0.74 |
| 1 | 1.8 | – | 1.2 | – |
| 2 | 0.89 | 0.64 | 0.51 | 0.58 |
| 3 | 1.35 | 1.40 | 0.79 | 1.20 |
| 4 | – | – | 0.34 | – |
| 5 | – | – | – | – |
| 6 | – | – | – | – |
| 7 | 0.55 | 0.50 | 0.34 | 0.27 |
| 8 | – | 1.6 | – | 1.3 |
| 9 | – | 0.27 | – | 0.17 |
| 10 | 0.83 | 0.98 | 0.51 | 0.71 |
| 11 | – | – | – | – |
| 12 | 0.72 | 0.73 | 0.44 | 0.42 |
| 13 | – | 0.76 | – | 0.40 |
| 14 | 0.91 | 0.76 | 0.59 | 0.40 |
| 15 | – | – | – | – |
| 16 | 0.90 | 0.85 | 0.65 | 0.60 |
| 17 | – | <1.0 | – | <1.0 |
| 18 | $0.8^2$ | $2.2;0.6^2$ | $<0.4^2$ | $1.8;<0.4^2$ |
| 19 | 1.46 | – | 0.70 | 1.46 |
| 20 | 1.4;1.2 | 1.2;1.03 | 0.8;0.6 | 0.8;0.68 |
| 21 | 0.64 | 0.77;0.41 | 0.56 | 0.32;0.57 |
| 22 | 1.19 | 1.55 | 0.74 | 1.03 |
| 23 | 0.78 | 0.94 | 0.71 | 0.69 |
| 24 | 0.85 | – | 0.55 | – |
| 25 | 1.45 | 1.8 | 0.65 | – |
| 26 | – | – | – | – |
| 27 | 0.62 | 0.78 | 0.46 | 0.93 |
| 28 | 0.60 | 0.53 | 0.32 | 0.33 |
| 29 | – | – | – | 2.1 |

(cont'd)

Table 6 (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | – | 0.78 | – | 0.58 |
| 31 | 0.85 | 1.11 | 0.51 | 0.68 |
| 32 | 0.55 | – | – | – |
| 33 | 0.91 | – | 0.53 | – |
| 34 | – | – | – | – |
| 35 | 1.18 | – | 1.05 | – |
| 36 | – | – | – | – |
| 37[2] | – | 0.90 | – | 0.58 |
| 38[2] | – | 0.7 | – | 0.5 |
| 39 | – | – | – | – |
| 40 | – | – | – | – |
| 41[2] | – | 0.36 | – | 0.22 |
| ICES 1/TM/MS[4] | – | – | 0.49 | 0.56(0.73)[3] |
| Total Range | 0.55-5.47 | 0.27-6.2 | 0.32-5.66 | 0.17-6.9 |
| No. of Labs | 25 | 30 | 26 | 30 |
| Range red.[1] | 0.55-1.8 | 0.27-2.2 | 0.32-1.2 | 0.17-2.1 |
| No. of Labs | 23 | 25 | 23 | 25 |
| Mean[3] | 0.96 | 0.94(1.11) | 0.60 | 0.74(0.76) |
| R.S.D. (±%) | 36 | 48 | 36 | 63 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 7   MANGANESE ($\mu g.g^{-1}$)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 94 | 353 | 122 | 372 |
| 1 | 110 | — | 143 | — |
| 2 | 133 | 374 | 167 | 380 |
| 3 | — | — | — | — |
| 4 | — | — | — | — |
| 5 | 102 | 347 | 139 | 360 |
| 6 | — | — | — | — |
| 7 | — | — | — | — |
| 8 | — | — | — | — |
| 9 | — | 302 | — | 325 |
| 10 | — | — | — | — |
| 11 | 88 | 450 | 119 | — |
| 12 | 119 | 369 | 154 | 385 |
| 13 | — | 358 | — | 386 |
| 14 | 129 | 313 | 164 | 332 |
| 15 | 110 | 365 | 130 | 380 |
| 16 | 85 | 315 | 120 | 330 |
| 17 | — | 336 | — | 348 |
| 18 | — | — | — | — |
| 19 | — | — | — | — |
| 20 | 82 | 350 | 113 | 380 |
| 21 | 131 | 351;319 | 165 | 375;340 |
| 22 | 97 | 387;378 | 143 | 442;392 |
| 23 | — | 358 | — | 382 |
| 24 | 114 | — | 136 | — |
| 25 | 120 | 403 | 146 | 426 |
| 26 | 71 | 338 | 115 | 401 |
| 27 | 86 | 385 | 137 | 399 |
| 28 | 135 | 317 | 160 | 336 |
| 29 | — | — | — | — |

(cont'd)

Table 7 (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | – | 408 | – | 435 |
| 31 | 109 | 410 | 137 | 415 |
| 32 | – | – | – | – |
| 33 | – | – | – | – |
| 34 | – | – | – | – |
| 35 | 114 | – | 150 | – |
| 36 | – | 450 | – | 400 |
| 37 | – | – | – | – |
| 38 | – | – | – | – |
| 39 | – | – | – | – |
| 40[2] | – | 384 | – | 424 |
| 41 | – | – | – | – |
| ICES 1/TM/MS[4] | – | – | 114 | 396(397)[3] |
| Total Range | 71–290 | 71–533 | 113–310 | 78–486 |
| No. of Labs | 21 | 27 | 21 | 27 |
| Range red.[1] | 71–135 | 302–450 | 113–167 | 325–442 |
| No. of Labs | 19 | 23 | 19 | 22 |
| Mean[3] | 106 | 365(388) | 140 | 381(404) |
| R.S.D. (±%) | 18 | 11 | 13 | 9 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 8 IRON (%)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 0.94 | 3.81 | 0.53 | 3.00 |
| 1 | 0.54 | 2.60 | 0.30 | 2.22 |
| 2 | 1.27 | 3.62 | 0.79 | 2.98 |
| 3 | — | — | — | — |
| 4 | — | — | — | — |
| 5 | 1.00 | 3.27 | 0.62 | 2.71 |
| 6 | — | — | — | — |
| 7 | — | — | — | — |
| 8 | — | 4.2 | — | 3.5 |
| 9 | — | 3.03 | — | 2.44 |
| 10 | — | — | — | — |
| 11 | 0.82 | 4.40 | 0.44 | 3.78 |
| 12 | 1.19 | 3.29 | 0.81 | 2.76 |
| 13 | — | 3.63 | — | 3.02 |
| 14 | 1.29 | 3.00 | 0.79 | 2.62 |
| 15 | 0.98 | 2.8 | 0.59 | 2.4 |
| 16 | 0.87 | 3.1 | 0.48 | 2.6 |
| 17 | — | 2.83 | — | 2.30 |
| 18 | — | — | — | — |
| 19 | — | — | — | — |
| 20 | 0.88 | 3.6 | 0.48 | 3.26 |
| 21 | 1.26 | 3.64;3.68 | 0.80 | 3.10;2.99 |
| 22 | 0.89 | 3.51;3.29 | 0.52 | 3.10;2.74 |
| 23 | — | 4.41 | — | 3.49 |
| 24 | 1.25 | — | 0.72 | — |
| 25 | — | — | — | — |
| 26 | — | — | — | — |
| 27 | 0.75 | 4.07 | 0.40 | 3.42 |
| 28 | 1.26 | 2.78 | 0.79 | 2.29 |
| 29 | — | — | — | — |

(cont'd)

Table 8 (cont'd)

| Lab. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| No. | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | – | 4.05 | – | 3.44 |
| 31 | 0.96 | 4.15 | 0.58 | 3.45 |
| 32 | – | – | – | – |
| 33 | – | – | – | – |
| 34 | – | – | – | – |
| 35 | 1.02 | – | 0.58 | – |
| 36 | – | 3.71 | – | 3.02 |
| 37[2] | – | 3.21 | – | 2.76 |
| 38[2] | – | 3.41 | – | 2.61 |
| 39[2] | – | 3.92 | – | 3.43 |
| 40 | – | – | – | – |
| 41 | – | – | – | – |
| ICES 1/TM/MS[4] | – | – | 0.31 | 2.79(3.23)[3] |
| Total Range | 0.54-1.93 | 2.60-4.41 | 0.30-1.32 | 2.22-3.78 |
| No. of Labs | 18 | 25 | 18 | 25 |
| Range red.[1] | 0.54-1.29 | 2.60-4.41 | 0.30-0.81 | 2.22-3.78 |
| No. of Labs | 17 | 25 | 17 | 25 |
| Mean[3] | 1.01 | 3.52(3.78) | 0.60 | 2.94(3.22) |
| R.S.D. ($\pm$%) | 22 | 14 | 27 | 15 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 9   CHROMIUM $(\mu g \cdot g^{-1})$

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 12 | 48 | 8 | 50 |
| 1 | – | 90 | – | 86 |
| 2 | – | – | – | – |
| 3 | – | – | – | – |
| 4 | – | – | – | – |
| 5 | 9 | 66 | 7 | 52 |
| 6 | – | – | – | – |
| 7 | – | – | – | – |
| 8 | – | 93 | – | 78 |
| 9 | – | 33 | – | 23 |
| 10 | – | – | – | – |
| 11 | 13 | 83 | 12 | 86 |
| 12 | 12 | 43 | 9 | 34 |
| 13 | – | 60 | – | 45 |
| 14 | 14 | 31 | 10 | 23 |
| 15 | 19 | 44 | 16 | 35 |
| 16 | 11 | 34 | 12 | 33 |
| 17 | – | 47 | – | 36 |
| 18 | $20^2$ | $56;63^2$ | $14^2$ | $40;50^2$ |
| 19 | – | – | – | – |
| 20 | 10 | 75;84 | 7 | 63;70 |
| 21 | 13 | 50;50 | 10 | 41;39 |
| 22 | – | – | – | – |
| 23 | 24 | 40 | 19 | – |
| 24 | – | – | 8 | – |
| 25 | 13 | 72 | 9 | 55 |
| 26 | – | – | – | – |
| 27 | 8 | 65 | 5 | 54 |
| 28 | 17 | 35 | 12 | 28 |
| 29 | – | – | – | – |

Table 9 (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | — | — | — | — |
| 31 | 12 | 96 | 9 | 76 |
| 32 | — | — | — | — |
| 33 | — | — | — | — |
| 34 | — | — | — | — |
| 35 | — | — | — | — |
| 36 | — | 56 | — | 57 |
| 37[2] | — | 39 | — | 30 |
| 38[2] | — | 40 | — | 31 |
| 39 | — | — | — | — |
| 40[2] | — | 87 | — | 69 |
| 41 | — | 51 | — | 51 |
| ICES 1/TM/MS[4] | — | — | 3.68 | 33.1(63.3)[3] |
| Total Range | 4-60 | 31-96 | 4-51 | 23-86 |
| No. of Labs | 17 | 25 | 18 | 24 |
| Range red.[1] | 8-24 | 31-96 | 5-19 | 23-86 |
| No. of Labs | 15 | 25 | 16 | 24 |
| Mean[3] | 14 | 58(82) | 10 | 49(72) |
| R.S.D. (±%) | 32 | 34 | 35 | 38 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 10   NICKEL ($\mu g \cdot g^{-1}$)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | 19 | 36 | 11 | 28 |
| 1 | – | – | – | – |
| 2 | 23 | 35 | 16 | 28 |
| 3 | – | – | – | – |
| 4 | – | – | – | – |
| 5 | – | – | – | – |
| 6 | – | – | – | – |
| 7 | 12 | 28 | 8 | 18 |
| 8 | – | – | – | – |
| 9 | – | 31 | – | 22 |
| 10 | – | – | – | – |
| 11 | 17 | – | 13 | – |
| 12 | 18 | 34 | 11 | 21 |
| 13 | – | 35 | – | 24 |
| 14 | 19 | 36 | 13 | 24 |
| 15 | 15 | 33 | 9 | 20 |
| 16 | 14 | 40 | 10 | 23 |
| 17 | – | 33 | – | 22 |
| 18 | $19^2$ | $26;38^2$ | $13^2$ | $18;27^2$ |
| 19 | – | – | – | – |
| 20 | 20 | 41;42 | 10 | 28;29 |
| 21 | 23 | 38;35 | 15 | 25;24 |
| 22 | – | – | – | – |
| 23 | 26 | 44 | – | 29 |
| 24 | 17 | – | 10 | – |
| 25 | 18 | 42 | 13 | 34 |
| 26 | – | – | – | – |
| 27 | 13 | 39 | 8 | 28 |
| 28 | 19 | 31 | 13 | 21 |
| 29 | – | – | – | – |

Table 10 (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | – | 46 | – | 30 |
| 31 | 14 | 42 | 10 | 28 |
| 32 | – | – | – | – |
| 33 | – | – | – | – |
| 34 | – | – | – | – |
| 35 | – | – | – | – |
| 36 | – | 45 | – | 38 |
| 37[2] | – | 25 | – | 14 |
| 38[2] | – | 35 | – | 22 |
| 39 | – | – | – | – |
| 40[2] | – | 46 | – | 35 |
| 41[2] | – | 42 | – | 27 |
| ICES 1/TM/MS[4] | – | – | 7.39 | 27.1(29.0)[3] |
| Total Range | 12–26 | 25–82 | 8–19 | 14–71 |
| No. of Labs | 17 | 25 | 17 | 25 |
| Range red.[1] | 12–26 | 25–46 | 8–16 | 14–38 |
| No. of Labs | 17 | 24 | 16 | 24 |
| Mean[3] | 18 | 37(42) | 11 | 25(30) |
| R.S.D. (±%) | 21 | 16 | 21 | 21 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] numbers in parentheses: mean values of data resulting after "total" (HF) dissolution.

[4] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 11   MERCURY  $(ng \cdot g^{-1})$

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 0 | – | 324 | – | 98 |
| 1 | – | – | – | – |
| 2 | 60 | 220 | 50 | 80 |
| 3 | – | – | – | – |
| 4 | – | – | – | – |
| 5 | – | – | – | – |
| 6 | – | 231 | – | 88 |
| 7 | 24 | 117 | 9 | 51 |
| 8 | – | <300 | – | <300 |
| 9 | – | 202 | – | 45 |
| 10 | – | 470 | – | – |
| 11 | – | – | – | – |
| 12 | – | – | – | – |
| 13 | – | 336 | – | 104 |
| 14 | – | 210 | – | 75 |
| 15 | – | – | – | – |
| 16 | <50 | 300 | 20 | 102 |
| 17 | – | 265 | – | 84 |
| 18 | – | 220;257[2] | – | 70;68[2] |
| 19 | <50 | – | <50 | – |
| 20 | – | 304 | – | 97 |
| 21 | – | – | – | – |
| 22 | – | 210 | – | 70 |
| 23 | – | 273 | – | 62 |
| 24 | – | – | – | – |
| 25 | – | 370 | – | 180 |
| 26 | – | – | – | – |
| 27 | – | 383 | – | 117 |
| 28 | 100 | 80 | 50 | 50 |
| 29 | – | – | – | – |

Table 11  (cont'd)

| Lab. No. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|
| | 1 N HCl | "total" | 1 N HCl | "total" |
| 30 | – | – | – | – |
| 31 | – | – | – | – |
| 32 | – | – | – | – |
| 33 | – | – | – | – |
| 34 | – | – | – | – |
| 35 | – | – | – | – |
| 36 | – | – | – | – |
| 37[2] | – | 100 | – | 40 |
| 38 | – | – | – | – |
| 39 | – | – | – | – |
| 40 | – | – | – | – |
| 41 | – | – | – | – |
| ICES 1/TM/MS[3] | – | – | – | 90 |
| Total Range | 24–380 | 80–662 | 9–250 | 40–450 |
| No. of Labs | 6 | 20 | 6 | 19 |
| Range red.[1] | 24–100 | 8–470 | 9– 50 | 40–180 |
| No. of Labs | 4 | 18 | 4 | 17 |
| Mean | 59 | 256 | 32 | 82 |
| R.S.D. ($\pm$%) | 54 | 39 | 66 | 40 |

[1] reduced range without outliers (outside $\bar{x} \pm 2$ sigma).

[2] submitted after deadline (15 April 1984).

[3] "excluded mean values" as found in ICES intercalibration 1/TM/MS (Loring, 1987).

Table 12  OTHER DETERMINANDS

| Determinand | Lab no. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|---|
| | | 1 N HCl | "total" | 1 N HCl | "total" |
| Co $(\mu g \cdot g^{-1})$ | 0 | 6.2 | 13 | 5.4 | 11 |
| | 8 | – | 13 | – | 11 |
| | 9 | – | 8 | – | 8 |
| | 11 | – | 15 | – | 9 |
| | 14 | 7.0 | 11 | 7.0 | 10 |
| | 15 | 5.5 | 12 | 5.6 | 12 |
| | 16 | 5.0 | 9 | 5.5 | 10 |
| | 20 | – | 12 | – | 10 |
| | 27 | 5.0 | 14 | 4.0 | 12 |
| | 28 | 8.0 | 11 | 7.0 | 10 |
| | 30 | – | 15 | – | 13 |
| | 38[1] | – | 11 | – | 10 |
| | 39[1] | – | 13 | – | 12 |
| | 40[1] | – | 15 | – | 14 |
| | 41[1] | – | 13 | – | 11 |
| Mean | | 6.1±1.2 | 12±2(14) | 5.8±1.1 | 11±2(11) |
| Range | | (5.8-8.0) | (8-15) | (4.0-7.0) | (8-14) |
| Al (%) | 0 | 0.35 | 5.82 | 0.28 | 5.20 |
| | 5 | 0.46 | – | 0.31 | – |
| | 10 | 0.47 | 4.64 | – | 5.31 |
| | 11 | 0.31 | 6.69 | – | 5.93 |
| | 20 | 0.30 | 5.80 | 0.21 | 5.36 |
| | 27 | 0.25 | 6.19 | 0.19 | 5.43 |
| | 31 | – | 4.74 | – | 3.60 |
| | 35 | 0.49 | – | 0.34 | – |
| Mean | | 0.38±0.09 | 5.6±0.8(5.7) | 0.27±0.06 | 5.1±0.8(5.5) |
| Range | | (0.25-0.49) | (4.6-6.7) | (0.19-0.34) | 3.6-5.9) |
| 1/TM/MS[1] | | – | – | 0.15 | 5.22 |
| C org. (%) | 0 | | 6.75 | | 4.17 |
| | 1 | | 6.15 | | 4.27 |
| | 7 | | 6.08 | | 4.26 |
| | 11 | | 5.79 | | 3.80 |
| | 14 | | 6.6 | | 5.0 |
| | 16 | | 7.0 | | 5.2 |
| | 18 | | 5.96 | | 4.04 |
| | 21 | | 6.04 | | 4.03 |
| | 25 | | 6.81 | | 4.85 |
| | 26 | | 4.51 | | 2.89 |
| | 28 | | 4.12 | | 2.51 |
| | 30 | | 5.51 | | 3.97 |
| | 35 | | 5.50 | | 3.67 |
| | 36 | | 5.17 | | 3.29 |
| Mean | | | 5.9±0.9 | | 4.0±0.8 |
| Range | | | (4.1-7.0) | | (2.5-5.2) |

(cont'd)

Table 12 (cont'd)

| Determinand | Lab no. | "ABSS" 1 N HCl | "ABSS" "total" | "MBSS" 1 N HCl | "MBSS" "total" |
|---|---|---|---|---|---|
| C inorg. (%) | 0 | | 0.25 | | 0.28 |
| | 1 | | 0.08 | | 0.25 |
| | 7 | | 0.06 | | 0.04 |
| | 9 | | 0.065 | | 0.07 |
| | 11 | | 0.23 | | 0.17 |
| | 14 | | 0.20 | | 0.18 |
| | 25 | | 0.08 | | 0.072 |
| | 35 | | 0.06 | | 0.09 |
| | 36 | | 0.21 | | 0.26 |
| Mean | | | 0.14±0.08 | | 0.14±0.09 |
| Range | | | (0.06-0.25) | | (0.04-0.28) |
| P (%) | 0 | | 0.13 | | 0.12 |
| | 11 | | 0.11 | | 0.13 |
| | 20 | | 0.11 | | 0.084 |
| | 25 | | 0.18 | | 0.13 |
| | 28 | | 0.10 | | 0.085 |
| | 31 | | 0.11 | | 0.089 |
| | 36 | | 0.10 | | 0.08 |
| | 37 | | 0.078 | | 0.077 |
| Mean | | | 0.11±0.03 | | 0.10±0.02 |
| Range | | | (0.10±0.18) | | (0.08±0.13) |
| N (%) | 0 | | 0.46 | | 0.33 |
| | 1 | | 1.05 | | 0.96 |
| | 18 | | 0.66 | | 0.43 |
| | 21 | | 0.68 | | 0.45 |
| | 25 | | 0.62 | | 0.33 |
| | 28 | | 0.67 | | 0.42 |
| | 37 | | 0.65 | | 0.43 |
| Mean | | | 0.68±0.18 | | 0.48±0.22 |
| Range | | | (0.46-1.05) | | (0.33-0.96) |
| Ti (%) | 11 | | 0.36 | | 0.32 |
| | 20 | 0.011 | 0.44 | 0.008 | 0.39 |
| | 36 | | 0.40 | | 0.38 |
| | 40[1] | | 0.38 | | 0.35 |
| | 41[1] | | 0.37 | | 0.37 |
| Mean | | | 0.39 | | 0.36 |
| ICES 1/TM/MS[3] | | | | | 0.34 |
| As ($\mu$g·g$^{-1}$) | 6 | | 15 | | 20 |
| | 8 | | 27 | | 24 |
| | 20 | | 20 | | 19 |
| | 41[1] | | 10 | | 12 |
| U ($\mu$g·g$^{-1}$) | 8 | | 4 | | 5 |
| | 10 | | 5.2 | | 3.6 |
| | 34 | 2.5 | 4.9 | 1.6 | 3.4 |
| | 39[1] | | 4.0 | | 3.5 |

(cont'd)

Table 12   (cont'd)

| Determinand | Lab no. | "ABSS" | | "MBSS" | |
|---|---|---|---|---|---|
| | | 1 N HCl | "total" | 1 N HCl | "total" |
| V ($\mu g \cdot g^{-1}$) | 11 | | 112 | | 97 |
| | 20 | 33 | 102 | 18 | 85 |
| | 40[1] | | 104 | | 84 |
| | 41[1] | | 104 | | 91 |
| Ba ($\mu g \cdot g^{-1}$) | 39[1] | | 328 | | 329 |
| | 40[1] | | 375 | | 368 |
| | 41[1] | | 393 | | 485 |
| Be ($\mu g \cdot g^{-1}$) | 16 | | 1.7 | | 0.9 |
| | 40[1] | | 2.5 | | 2.0 |
| | 41[1] | | 1.8 | | 1.3 |
| Ca (%) | 10 | 0.34 | 0.75 | 0.70 | 1.01 |
| | 20 | 0.55 | 0.80 | 0.54 | 0.90 |
| | 30 | | 0.86 | | 0.96 |
| Cs ($\mu g \cdot g^{-1}$) | 1 | | 5.0 | | 4.1 |
| | 8 | | 5.9 | | 4.6 |
| | 39[1] | | 6.5 | | 5.5 |
| K (%) | 10 | | 1.01 | | 0.71 |
| | 24 | 0.26 | | 0.20 | |
| | 36 | | 2.39 | | 2.19 |
| Li ($\mu g \cdot g^{-1}$) | 11 | | 40 | | 32 |
| | 30 | | 44 | | 35 |
| | 40[1] | | 39 | | 32 |
| Mg (%) | 10 | 0.37 | 1.19 | 0.46 | 0.56 |
| | 20 | 0.52 | 1.26 | 0.39 | 1.00 |
| | 30 | | 1.30 | | 1.02 |
| Rb ($\mu g \cdot g^{-1}$) | 1 | | 106 | | 82 |
| | 39[1] | | 106 | | 100 |
| | 41[1] | | 110 | | 120 |
| Sc ($\mu g \cdot g^{-1}$) | 8 | | 12.6 | | 10.3 |
| | 39[1] | | 12.2 | | 10.3 |
| | 40[1] | | 11.6 | | 9.6 |
| Ga ($\mu g \cdot g^{-1}$) | 11 | | 16 | | 14 |
| | 41[1] | | 17 | | 17 |
| La ($\mu g \cdot g^{-1}$) | 39[1] | | 39.8 | | 32.4 |
| | 40[1] | | 43 | | 35 |
| Na (%) | 20 | 0.55 | 1.08 | 0.41 | 1.00 |
| | 36 | | 1.36 | | 1.22 |

Table 12 (cont'd)

| Determinand | Lab no. | "ABSS" 1 N HCl | "ABSS" "total" | "MBSS" 1 N HCl | "MBSS" "total" |
|---|---|---|---|---|---|
| Th ($\mu g \cdot g^{-1}$) | 10 | | 2.8 | | 2.0 |
| | 39[1] | | 11.6 | | 9.7 |
| Yb ($\mu g \cdot g^{-1}$) | 11 | | 3.7 | | 3.3 |
| | 39[1] | | 3.2 | | 2.6 |
| Zr ($\mu g \cdot g^{-1}$) | 11 | | 175 | | 250 |
| | 41[1] | | 250 | | 230 |
| B ($\mu g \cdot g^{-1}$) | 41[1] | | 305 | | 278 |
| Ce ($\mu g \cdot g^{-1}$) | 39[1] | | 78.3 | | 66.7 |
| Eu ($\mu g \cdot g^{-1}$) | 39[1] | | 1.5 | | 1.3 |
| Hf ($\mu g \cdot g^{-1}$) | 39[1] | | 6.8 | | 9.0 |
| Lu ($\mu g \cdot g^{-1}$) | 39[1] | | 0.55 | | 0.50 |
| Mo ($\mu g \cdot g^{-1}$) | 41[1] | | 3 | | 3.3 |
| Nb ($\mu g \cdot g^{-1}$) | 41[1] | | 19 | | 18 |
| Nd ($\mu g \cdot g^{-1}$) | 39[1] | | 37.2 | | 29.5 |
| Sb ($\mu g \cdot g^{-1}$) | 8 | | 1.7 | | 1.3 |
| Se ($\mu g \cdot g^{-1}$) | 8 | | 1.6 | | 1.3 |
| Si (%) | 11 | | 28.7 | | 24.7 |
| Sm ($\mu g \cdot g^{-1}$) | 39[1] | | 6.6 | | 5.7 |
| Sn ($\mu g \cdot g^{-1}$) | 41[1] | | 8 | | 7.8 |
| Sr ($\mu g \cdot g^{-1}$) | 40[1] | | 122 | | 119 |
| Ta ($\mu g \cdot g^{-1}$) | 39[1] | | 1.3 | | 1.0 |
| Tb ($\mu g \cdot g^{-1}$) | 39[1] | | 0.7 | | 0.72 |
| Y ($\mu g \cdot g^{-1}$) | 40[1] | | 29.3 | | 24 |
| $^{137}$Cs ($mBq \cdot g^{-1}$) | 1 | | 17.6 | | 21.3 |
| $^{210}$Po ($mBq \cdot g^{-1}$) | 1 | | 82.3 | | 74.0 |
| $^{210}$Pb ($mBq \cdot g^{-1}$) | 34 | 108 | 117.3 | 55 | 68.5 |
| Humic substances (%) | 1 | | 2.60 | | 2.04 |
| Fulvic acids | 1 | | 0.81 | | 0.78 |
| Humic acids | 1 | | 1.79 | | 1.26 |
| Clay (%) | 1 | | 9.0 | | 6.8 |

[1] submitted after deadline (15 April 1984).
[2] 'excluded mean values' as found in ICES intercalibration 1/TM/MS (Loring, 1987)

Table 13    Laboratories Participating in Step 1 of the Intercalibration (numbers
of the labs reflect the sequence in which the organizer received the
results).

| | | | |
|---|---|---|---|
| BELGIUM | (33) | Institut de Chimie<br>Laboratoire Océanologie<br>Université de Liège<br>Sart Tilman<br>4000  Liége | G. Gillain |
| CANADA | (20) | Division of Chemistry<br>National Research Council<br>Montreal Rd.<br>Ottawa, Ontario K1A OR9 | S. Berman |
| | (30) | Atlantic Oceanographic Laboratory<br>Bedford Institute of Oceanography<br>P.O. Box 1006<br>Dartmouth, N.S. B2Y 4A2 | D.H. Loring<br>R.T.T. Rantala |
| DENMARK | (23) | Marine Pollution Laboratory<br>Jægersborg Allé 1B<br>DK-2920  Charlottenlund | A. Jensen |
| | ( 6) | Danish Isotope Centre<br>Skelbækgade 2<br>DK-1717  Copenhagen V | P. Madsen<br>I. Drabæk |
| | (12) | Superfos A/S<br>Frydenlundsvej 30<br>DK-2950  Vedbæk | L. Rasmussen |
| FINLAND | (28) | Institute of Marine Research<br>Asiakkaankatu 3<br>P.O. Box 33<br>SF-00931  Helsinki 93 | L. Niemistö |
| | (38) | National Board of Waters<br>Kyläsaarenkatu 10<br>SF-00550  Helsinki | K. Haapala<br>I. Mäkinen |
| FRANCE | ( 4) | IFREMER<br>B.P. 1049<br>44037  Nantes Cédex | Y. Thibaud |
| | (16) | Institut Pasteur de Lille<br>Service Chimie Analytique<br>Domaine du Certia<br>369 rue Jules Guesde<br>59650  Villeneuve d'Ascq Cédex | A. Phillipo |
| | (25) | Faculté de Pharmacie<br>Université d'Aix-Marseille II<br>Laboratoire d'Hydrologie<br>27 boulevard Jean Moulin<br>13385  Marseille Cédex 4 | A. Arnoux |

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Table 13 (cont'd)

| FRANCE (cont'd) | (27) | Laboratoire Municipal<br>29 rue Bourg l'Abbé<br>76000   Rouen | .. Gervaise |
|---|---|---|---|
| | (35) | Laboratoire de Sédimentologie et<br>Geochemie Marines<br>Université de Perpignan<br>Avenue de Villeneuve<br>66025   Perpignan | J.P. Cambon |
| GERMAN DEMOCRATIC REPUBLIC | ( 0) | Institut für Meereskunde der AdW<br>der DDR<br>Seestrasse 15<br>DDR-2530   Rostock-Warnemünde | L. Brügmann<br>D. Lange |
| | (34) | Bergakademie Freiberg<br>Sektion Physik<br>Bernhard von Cotta-Strasse 4<br>DDR-9200   Freiberg | K. Fröhlich<br>R. Gellermann |
| | (32) | Wasserwirtschaftsdirektion Küste<br>Badenstrasse 18<br>DDR-2300   Stralsund | P. Berend |
| | (39) | Karl-Marx-Universität Leipzig<br>Sektion Physik<br>Talstrasse 35<br>DDR-7010   Leipzig | G. Just |
| | (40) | Zentralinstitut für Physik<br>der Erde der AdW der DDR<br>Telegrafenberg<br>DDR-1500   Potsdam | P. Vogler |
| | (41) | Bergakademie Freiberg<br>Sektion Geowissenschaften<br>DDR-9200   Freiberg | W. Schrön |
| FEDERAL REPUBLIC OF GERMANY | ( 8) | Bundesanstalt für Gewässerkunde<br>Kaiserin-Augusta-Anlagen 15<br>D-5400   Koblenz | F. Ackermann |
| | (22) | Deutsches Hydrographisches<br>Institut<br>Bernhard-Nocht-Strasse 78<br>D-2000   Hamburg 4 | H. Albrecht |
| NETHERLANDS | (31) | Institute for Soil Fertility<br>Postbus 30003<br>9750   Ra Haren | A.J. De Groot |

Table 13 (cont'd)

| | | | |
|---|---|---|---|
| NORWAY | (37) | Norwegian Institute for Water Research-NIVA P.P. Box 333 Blindern 3 Oslo 3 | H. Hovind |
| PORTUGAL | (26) | Instituto Hidrographico Rua das Trinas 49 1296 Lisboa | T. Vinhas |
| POLAND | (10) | Institute of Meteorology and Water Management Maritime Branch Washyngtona 42 81-342 Gdynia | A. Trzosinska E. Andrulewicz L. Felkier |
| | (19) | Morski Instytut Rybacki (MIR) Aleja Zjednoczenia 1 81-345 Gdynia | A. Ropelewski K. Siudzinski |
| | ( 1) | Institute of Oceanology Polish Academy of Sciences P.O. Box 68 81-967 Sopot | J. Pempkowiak B. Skwarzec D. Knapinska-Skiba |
| | (29) | Institut Oceanografii Uniwersytet Gdanski ul. Czolgistow 46 81-378 Gdynia | K. Pecherzewski |
| SPAIN | ( 2) | Laboratorio Oceanografico Magallanas, s/n$^0$ San Pedro del Pinatar (Murcia) | A. Rodriguez de Leon J. Guerrero |
| | ( 9) | Instituto Quimico de Sorria Barcelona - 17 | J. Obiols Salvat D. Luis Peiró Mir |
| SWEDEN | ( 5) | University of Stockholm Department of Geology P.O. Box 6801 S-11386 Stockholm | R. Hallberg E. Billeryd |
| | (15) | Swedish Environment Protection Board Laboratory for Coastal Research S-17011 Drottningholm | I. Gustavsson |
| UNITED KINGDOM | (14) | DAFS, Marine Laboratory Victoria Road Box 101 Aberdeen AB9 8DB | I.M. Davies P.W. Balls |

Table 13 (cont'd)

| UNITED KINGDOM (cont'd) | (18) | MAFF, Fisheries Laboratory<br>Remembrance Avenue<br>Burnham-on-Crouch<br>Essex CMO 8 HA | R. Law<br>J.E. Portmann<br>D. Harper |
|---|---|---|---|
| | (21) | Welsh Water Authority<br>Tremains House<br>Coychurch Road<br>Bridgend<br>Mid Glamorgan CF31 2AR | C. Pattinson |
| | (24) | Yorkshire Water Authority<br>Skeldergate<br>York | R. Hill |
| | (17) | Severn Trent Water Authority<br>Lower Trent Divisional Laboratory<br>Meadow Lane<br>Nottingham NG2 3HN | D. Gelsthorpe<br>J.D. Foster |
| | ( 7) | Forth Purification Board<br>Port Edgar<br>South Queensferry<br>West Lothian EH30 9SO | T.M. Leatherland |
| | (13) | Anglian Water Authority<br>Regional Standards Laboratory<br>Great House<br>Clarendon Road<br>Cambridge CS2 2BL | C.R. Whitfield |
| USSR | ( 3) | Institute of Thermophysics and<br>Electrophysics<br>Paldiski-Street 1<br>200031  Tallinn | H. Jankovski |
| | (11) | Institute of Oceanology<br>"Shirshov Institute"<br>ul. Krasikova 23<br>117218  Moscow | V.V. Gordeev<br>N.J. Tolmacheva<br>V.N. Lukashin<br>T. Kuzmina<br>N.I. Zavadskaya<br>L. Golitzina |
| | (36) | Institute of Oceanology<br>Atlantic Department<br>Prospekt Mira<br>236000  Kaliningrad-obl. | E. Emelyanov<br>Yu. O. Shajdurov<br>N.B. Vlasenko |

REPORT OF RESULTS OF AN ADDITIONAL INTERCOMPARISON EXERCISE FOR
THE DETERMINATION OF CADMIUM AND MERCURY IN SEDIMENTS FOR
THE BALTIC SEA SEDIMENT STUDY GROUP

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                    DENMARK

## Introduction

During the meeting held in September 1984 on the Finnish R/V
"Aranda" in Rostock, German Democratic Republic, it was agreed
that the analyses of cadmium and mercury in the first step of the
sediment intercalibration exercise should be repeated. This was
due to the fact that the relative standard deviations calculated
from the values submitted for both elements were in an unaccept-
able range of more than 40%.

Therefore, sets of six different samples were distributed to ob-
tain more information on possible reasons for these poor results
and to check the capabilities of Baltic laboratories to analyse
cadmium and mercury relative to all participants in the first
step and in relation to the needs of a critical assessment of the
contamination of Baltic sediments.


## Sample preparation

It was agreed that the following samples should be prepared and
distributed to laboratories around the Baltic Sea:


## Sample No. 1

In an autoclave, 7.3233 g of the sediment sample ABSS were di-
gested in a closed volumetric flask at $120^0$ C, 1 ato for 30 min-
utes with 100 ml of half-concentrated nitric acid. After dilution
with deionized water to 500 ml, the solution was filtered and
subsampled into polyethylene bottles, with about 30 ml for each
participant.


## Sample No. 2

7.3540 g of the sediment sample MBSS was treated as described for
Sample No. 1.


## Sample No. 3

1.0092 g of the Canadian sediment reference sample MESS-1, with a
certified concentration of cadmium, was treated for Sample No. 1.
Due to the smaller amount of the material used, the volume of the
acid and of the final solution were reduced to one-fifth. Only
about 10 ml were distributed with each set of samples.

Sample No. 4

About 30 ml blank solution, prepared as for Sample Nos. 1 - 3 but without addition of sediment, were distributed.


Sample No. 5

A 1000 mg/l cadmium standard solution acidified to pH 1 - 2 with nitric acid was distributed, with about 30 ml in each set.


Sample No. 6

50.24 g of ABSS and 91.75 g of MBSS were mixed together by shaking intensively for 12 hours in a 500 ml PE bottle. About 10 g of this mixture were distributed in PE bottles.


Distribution of samples and reporting of results

Sets of the above-described samples were distributed to 14 Baltic laboratories in the beginning of November 1985 without informing them of the origin of Sample Nos. 1, 2, 3, and 6 and setting a deadline for submission of results by the end of January 1985. Sample Nos. 1, 2, 3, 4, and 6 were to be analysed for cadmium and No. 6 also for mercury. Sample No. 5 was to be used for preparing a calibration curve together with the normal calibration curve used in the laboratory. Participants were requested to carry out the analyses at least in triplicate and to provide details about the analytical methods used, including standard curves and in- strument type.

Eleven out of the 14 laboratories submitted data. The addresses and the code numbers for the laboratories are identical to those used in the first step (see Table 13).


Methods

The digestion methods for Sample No. 6, the general principle of the instrumental analytical procedure and the equipment used are summarized in Table 14.

All laboratories except one have used the flameless atomic ab- sorption technique, predominantly using stannochloride as a re- ducing agent. Two laboratories have collected mercury in a gold trap. One laboratory (No. 6) has used a neutron activation tech- nique from which the results should be accurate.

It can be seen from Table 14 that all laboratories have used graphite furnace atomic absorption spectroscopy for analysing cadmium. All laboratories have injected the sample directly into the graphite furnace. Two laboratories have used a L'vov platform with matrix modifier. Presumably the other laboratories have used a normal graphite tube.

## Results and discussion

Eight laboratories reported results on mercury and ten laboratories on cadmium. The results for mercury are presented in Table 15 and for cadmium in Table 16.

From Table 15, it can be seen that the results are scattered, with a percent relative standard deviation (% R.S.D.) of 55%. Even by excluding the lowest result (No. 38), the R.S.D. decreases only to 40%. In Table 15 is also shown for comparison the results of the different laboratories from Step 1 of this exercise and the theoretical concentration in the mixture (Sample No. 6) has been calculated on the basis of the results from the first step. The agreement between the analysed and the calculated results is not very good. Generally the R.S.D. is at the same level of about 40%, which also was found in the first step. This means that if the results are normally distributed, 95% of the results are within a range of a factor of 10. There is no evident difference between the results from the different techniques used.

The results for cadmium are shown in Table 16. The results for the predigested samples (Nos. 1, 2, and 3) have been reported by the laboratories in µg/l. The organizer has calculated the results in ng/g dry sediment to make these results comparable with those from the first step. It can be seen that the R.S.D. was between 40% and 70%. By excluding 5 laboratories (Nos. 3, 5, 10, 11, and 28), which have reported values too high or too low for the standard reference material (MESS-1), the R.S.D. is reduced to 10 -25%, which is an improvement compared with the first step, where the R.S.D. for the same samples was from 48 - 63%, as shown in Table 16. The results for the Canadian standard reference sediment are near to the certified value if the same 5 laboratories are excluded. The results from the first step and from this exercise on sediment samples ABSS and MBSS are in most cases quite different, as shown in Table 16. The blank sample (No. 4) distributed contained no significant amounts of cadmium, except in one case where the blank has been subtracted. Most laboratories have used the distributed cadmium standard. Six laboratories reported that the standard gave the same result as their own standard. However, four laboratories reported that it gave higher results than their own standard. All results are reported on the basis of the normal standard in the laboratory.

The results for cadmium in the solid sample (No. 6, a mixture of sediment ABSS and MBSS) are similar to those for the liquid samples, with the R.S.D. about 25% (Table 16). If three results are excluded (lab Nos. 3, 5, and 28), the R.S.D. is 10% which is a relatively good result. However, looking at the analyses and the results calculated on the basis of the results from the first step of the intercalibration, the agreement is not as good as might have been expected.

Because a standard reference material has been included in the distributed samples, the results for cadmium in Table 16 have been normalized on the basis of the certified value. It can be seen that the R.S.D. for all results is reduced to 24 - 30% when the results have been normalized. By excluding 2 - 3 results, the relative standard deviation is further reduced to 6 - 15%. This

means that the problems with the analysis of cadmium are asso-
ciated with the measurement in the graphite furnace where the
interference problems have not been resolved.

It is not possible to see any difference in the results due to
the different techniques used.

Generally it can be concluded from the results for both mercury
and cadmium that the intra-laboratory variability is low compared
with the variability between laboratories. It was surprising that
the variability was greater in the results on the distributed
solutions than on the solid samples. This indicates that the dif-
ferent matrices can increase the variability and that it is not
the digestion step, but rather the measurement step which intro-
duces the variability.


Conclusion

It can be concluded that this intercalibration exercise has not
improved the comparability for analysing mercury in sediments
compared with the first step of this intercalibration exercise.
The relative standard deviation is still around 40 - 55%. This is
not satisfactory because this means that there is a factor of 10
between the lowest and highest results if they are normally dis-
tributed. It is not possible to give any explanation for this
variability in relation to the different techniques used in the
different laboratories.

The relative standard deviations for cadmium in the distributed
solutions are the same as that found in the first step. This is
about 50%. However, if 3 out of 9 results are excluded, the rela-
tive standard deviation for the solid sample is reduced to 10%.
It is surprising that the variation is not lower for the liquid
samples because the digestion step is excluded. This indicates
that the problems with the analysis of cadmium are associated
with the atomic absorption graphite furnace measurement and not
with the digestion step. This has further been confirmed by nor-
malizing the results on the basis of the certified value of the
distributed standard reference material, whereby the relative
standard deviation is reduced to 6 - 15% by excluding only 3 re-
sults.

Table 14  Sample amount and digestion procedures for the solid Sample 6 and the equipment used for all determinations of cadmium and mercury.

| Lab No. | Mercury | | | Cadmium | | |
| | Amount (g) | Digestion method | Equipment | Amount (g) | Digestion/ reduction method | Equipment |
|---|---|---|---|---|---|---|
| 0 | 0.1 | $HNO_3$, in teflon bomb, $KMnO_4$, $NH_2OH$, Sn(II) | Coleman MAS 50 | 0.5 | 1 N HCl | PE-4000, HGA-400, AS-40, L'vov platform, matrix modifier |
| 3 | No results | | | No method description | | |
| 5 | No results | | | 1.0 | "Autoclave" | Varian AA-1275, HGA CTA-95 |
| 6 | 0.3 | Neutron activation | | No results | | |
| 10 | 0.5 | Closed teflon tube $HNO_3$ + $H_2SO_4$, 120-130$^0$C, Sn(II), no $KMnO_4$ | LDC spectrophotometer | 0.5 | Closed teflon tube $HNO_3$, HCl, 120-130$^0$C | Beckmann AAS-1275, CNA accessory and Hassmann cuvette |
| 11 | 0.5-1.5 | $H_2SO_4$-$HNO_3$, Sn(II), no $KMnO_4$ | Home-made AAS, cold vapor | 1.0 | HF-$H_2SO_4$-$HNO_3$, dilution $HCl^3$ | PE-403, HGA 74, BG gasstop |
| 12 | No results | | | 1.0 | "Autoclave" | PE-5000, HGA-400, AS-40 |
| 15 | 0.3 | "Autoclave", $KMnO_4$, $NH_2OH$, Sn(II) | LDC spectrophotometer | 0.3 | "Autoclave" | PE-5000, HGA-500 |
| 23 | 1.0 | "Autoclave" $KMnO_4$, $NH_2OH$ | PE-403, MHS-20 gold trap | 1.0 | "Autoclave" | PE-5000, HGA-500, AS-40 |
| 28 | 1.0 | "Autoclave" $KMnO_4$, Sn(II) | PE-300, MHS-20 | 1.0 | "Autoclave" | PE-4000, HGA-400, AS-40, pyrocoated + L'vov platform, matrix modifier |
| 38 | 0.5 | "Autoclave" $KMnO_4$, $NH_2OH$, Sn(II) | Colemann MAS 50 | 1.0 | "Autoclave" | PE-400, HGA-400 |

The "Autoclave" method is a standard procedure used in the Scandinavian countries. 1 g sediment is autoclaved 0.5 h with 20 ml $HNO_3$ (1:1) at 120$^0$C in a closed flask. This solution is usually diluted to 100 ml.

Table 15  Results of the analyses of mercury in the solid
ABSS/MBSS mixture (Sample No. 6) (in $ng \cdot g^{-1}$ dry
matter).

| Lab No. | Sample No. 6 ABSS/MBSS | | ABSS[1] | MBSS[1] | ABSS/MBSS[2] |
|---|---|---|---|---|---|
| 0 | 254±13 | 259 257 243 239 270 | 324 | 98 | 178 |
| 6 | 162±2 | 160 163 | 231 | 88 | 139 |
| 10 | 63±7 | 56 70 63 | 470 | No results | |
| 11 | 119±3 | 120 122 117 116 | 223 | 63 | 120 |
| 15 | 232±30 | 204 227 264 | No results | | |
| 23 | 157±10 | 147 167 158 | 273 | 62 | 137 |
| 28 | 144±13 | 153 147 157 142 123 | 80 | 50 | 60 |
| 38 | 19±3 | 19 22 16 | No results | | |
| n | 8 | | 6 | 5 | 5 |
| Mean | 144±79 | | 267±129 | 72±20 | 127±43 |
| R.S.D. | 55 | | 48 | 28 | 34 |
| n[3] | 7 | | 5 | | |
| Mean | 162±65 | | 304±65 | | |
| R.S.D. | 40 | | 33 | | |

[1]Results obtained during the first step of the intercali-
bration exercise.

[2]Relation calculated from (1) (35.38% ABSS and 64.42%
MBSS).

[3]Excluding laboratories Nos. 38 (Sample No. 6) and 28
(ABSS), respectively.

Table 16　Results of the analysis of cadmium in the pre-digested samples (Sample Nos. 1-3) and in the solid sample (Sample No. 6) (in µg·g$^{-1}$ dry matter).

| Lab No. | Sample 1 ABSS | Norm. | Sample 2 MBSS | Norm. | Sample 3 MESS-1 | Sample 6 ABSS/MBSS | Norm. | Single |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.87 (1.12)[1] | 0.79 | 0.62 (0.74)[1] | 0.57 | 0.64 | 0.49+0.02 (0.87)[2] | 0.45 | 0.50 0.51 0.47 |
| 3 | 1.16 (1.40)[1] | 0.77 | 0.82 (1.20)[1] | 0.54 | 0.89 | 0.90 (1.27)[2] | 0.60 | |
| 5 | 1.17 | 0.32 | 1.13 | 0.31 | 0.22 | 1.11 | 0.30 | |
| 10 10[3] | 0.11 (0.76) (0.98)[1] | 0.33 (0.72) | 0.10 (0.33) (0.71)[1] | 0.29 (0.32) | 0.20 (0.62) | -- (0.67) (0.81)[2] | -- (0.64) | |
| 11 | 0.98 0.48[4] | 0.67 | 0.72 0.43[4] | 0.49 | 0.86 | 0.57+0.04 0.46[4] | 0.39 | 0.52 0.60 0.58 |
| 12 | 0.78 (0.73)[1] | 0.82 | 0.56 (0.42)[1] | 0.59 | 0.56 | 0.52 (0.53)[2] | 0.55 | |
| 15 | 0.50 | 0.62 | 0.29 | 0.36 | 0.48 | 0.47±0.04 | 0.58 | 0.52 0.45 0.44 |
| 23 | 0.61 (0.94)[1] | 0.68 | 0.50 (0.69)[1] | 0.56 | 0.53 | 0.61±0.01 (0.78)[2] | 0.72 | 0.62 0.61 0.61 |
| 28 28[5] | 1.44 (0.85) (0.53)[1] | 0.89 (0.71) | 0.90 (0.69) (0.33)[1] | 0.56 (0.57) | 0.95 (0.71) | 1.16±0.02 (0.50±0.02) (0.40)[2] | 0.72 (0.42) | 1.15 1.17 1.14 1.18 1.18 |
| 38 | 0.70 (0.70)[1] | 0.76 | 0.48 (0.50)[1] | 0.52 | 0.55 | 0.50±0.03 (0.57)[2] | 0.54 | 0.47 0.53 0.49 |
| n | 10 | 10 | 10 | 10 | 10 | 9 | 9 | |
| Mean | 0.83 (0.94)[6] | 0.66 | 0.61 (0.74)[6] | 0.47 | 0.78 (0.59±0.10)[7] | 0.70 (0.81)[2] | 0.53 | |
| S.d. | 0.38 | 0.20 | 0.30 | 0.12 | 0.53 | 0.28 | 0.13 | |
| R.S.D. | 46 (48)[6] | 30 | 49 (63)[6] | 24 | 68 | 40 | 25 | |
| n | 5 | 8 | 5 | 7 | 5 | 6 | 7 | |
| Mean | 0.69 | 0.75 | 0.49 | 0.55 | 0.55 | 0.53 | 0.59 | |
| S.d. | 0.14 | 0.09 | 0.13 | 0.03 | 0.06 | 0.13 | 0.09 | |
| R.S.D. | 21 | 12 | 26 | 6 | 11 | 10 | 15 | |

(cont'd)

Table 16 (cont'd)

$$\text{Norm.: The normalized result} = \frac{\text{result of sample}}{\text{results of MESS-1}} \times 0.59$$

[1] Results obtained during the first step of the intercalibration exercise.

[2] Relation calculated from (1) (35.38% ABSS and 64.62% MBSS).

[3] Analysed in the solid sample by atomization in the graphite furnace of a mixture of dry sediment and graphite powder.

[4] New results sent after receipt of report.

[5] The lab has changed analytical procedure. These results were received after report was distributed. They are analysed with the old procedure.

[6] Overall mean and R.S.D. from participants of the final step.

[7] Certified reference value for MESS-1.

REPORT ON THE RESULTS OF STEP 2:

THE INTERCOMPARISON OF ANALYSES OF SLICED WET CORES

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Niemistö, L.        Finnish Institute of Marine Research,
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                    SF-00931  Helsinki 93,
                    FINLAND.

Sampling and sample preparation

For the second step of the intercalibration, the necessary number of cores was taken during the expedition POLEX '83 of the German Democratic Republic R/V "A. v. Humboldt" in the Arkona Basin, 5 July 1983, on station "GDR 113" (54°55.5' N/13°30.0' E), water depth 48.5 m. Before coring, the area around the station was investigated as to its bottom topography by echo-sounding profiles. This was performed in two sections of 2 nautical miles each, in north/south and west/east directions across the sampling location. Coordinates of the station were determined by Decca navigation (chain E = 20.15, chain B = 68.80). In the west/east direction, no change of water depth or thickness of the mud layer (about 7 m) was observed. The same was true for the water depth on the north/south section. However, in this case the mud layer increased from about 5.5 m (1 mile north of the station) to 7 m at "GDR 113", being then constant. The ship was anchored at the central position with 3.5 chain lengths (87.5 m). The wind speed during sampling was 2.1 - 4.8 m·s$^{-1}$ from southwesterly directions (230-280°). The ship moved with 10-15° at the chain. After every third coring, 0.25 chain lengths (about 6.25 m) were added. Finally, the ship had moved by this procedure about 110 m from its first position. The maximum sampling area was estimated to 2,200 m$^2$.

At first, 36 cores were taken identically with a modified Niemistö corer (Niemistö, 1974). Immediately after sampling, the top 20 cm of these cores were dissected into 20 slices of nearly 1 cm diameter using a special splitting device (Niemistö, 1974). The exact length of these sub-sampled cores was between 20.8 cm and 22.0 cm (mean: 21.2 ± 0.2 cm).

The slices were transferred into plastic petri dishes, which were carefully sealed with a tape and stored deep-frozen until shipping and further preparations in the different laboratories.

To perform other background investigations (e.g., redox potential and radionuclide measurements, composition of interstitial waters, intercomparison of different corer types), ten additional cores were taken with two different modifications of the Niemistö corer and with an Olausson box corer. These cores were split into slices of 0.76 to 2 cm. The total number of sub-samples was 875. (Core sampling and splitting was performed by a group of six per-

sons in which the two authors were involved and additionally G. Bublitz, D. Fritsch, G. Nickel (Institut für Meereskunde, Rostock-Warnemünde), and K. Fröhlich (Bergakademie Freiberg, German Democratic Republic).)

## Distribution of samples and reporting of results

Sixteen of the 36 cores which were taken for the main intercali-bration exercise were distributed before 15 March 1984. Most par-ticipants had received their samples during autumn 1983. Within the German Democratic Republic, six sample sets were sent out deep-frozen in special cooling boxes. Six laboratories from other countries took the samples directly from the deep-freezer of the R/V "A. v. Humboldt" or from other vessels which were used for shipping under proper conditions. Transportation by air freight was necessary for four sample sets. Home-made polystyrene boxes with thick walls and an optimized capacity for the 20 sub-samples plus dry-ice were used in those cases. The minimum time during which the samples should maintain their frozen state was esti-mated to be about 3 days. From the ten cores which were taken separately for the background investigations, five were distri-buted to other laboratories and five kept in the Institut für Meereskunde, Rostock-Warnemünde.

Before April 1985, eleven laboratories from six Baltic countries (German Democratic Republic 3; Denmark, Finland, and Poland 2; Sweden and USSR 1) submitted results. Three participants carried out only geochemical investigations, three only the radiochemical dating, and five participants performed both types of measure-ments.

At the ICES/SCOR Working Group Meeting held 1-3 April 1985 in Helsinki, Finland, it was agreed that in the report on this second step, the participants would not be identified together with their submitted results. This was opposite to the procedure used for the report on the first step of the intercalibration exercise. However, it was deemed to be necessary due to the rela-tively low number of widely scattered results. Instead, the dif-ferent results should be coded through the core numbers which were assigned in accordance with the sampling sequence.

The participants were asked to use the 10 even sample numbers of the sediment segments for geochemical investigations and the 10 odd-numbered segments for dating. This recommendation was fol-lowed by most of the participants. In addition, some of them per-formed dating and/or geochemical investigations on all 20 samples.

## Methods

In most cases, the laboratories applied the methods previously used during the first step of the intercalibration (Table 2). Two cores (17, 18) were investigated only on the "total contents" and one core (28) for Pb, Cu, and Cd only on that part which could be extracted by 1 N HCl (Table 17). Before the whole intercali-bration exercise was launched, there had been some discussion in the ICES Working Group on Marine Sediments in Relation to Pollu-

tion on the most useful acid strength for the weak leaching pro-
cedure. The mean values in Table 18 reflect no significant dif-
ferences for 10 metals which were leached in parallel by 0.5 N
and 1 N HCl. Otherwise, looking at the single data and the metal
profiles obtained by both extractants (Figure 10), the 1 N HCl
procedure produced distributions which were less scattered than
those for the weaker acid (see standard deviations in Table 18).
These differences could be due to analytical details. For in-
stance, one could expect for the weaker acid treatment a more
pronounced relationship between the leaching efficiency and the
conditions of the analysis (leaching time, temperature, shaking
strength, etc.). This would favour the 1 N HCl. However, the more
scattered profiles with 0.5 N HCl leaching could also reflect
natural variabilities. Minor changes in the mineral composition,
overlooked with 1 N HCl extraction, would possibly influence the
leaching efficiency. Therefore, valuable information could be
gained from the weaker extractant. Further studies are necessary
to decide upon the usefulness of both extractants and other
agents.


Results and discussion

According to the number of data sets submitted on total concen-
trations and/or on fractions extracted by 1 N HCl, the determi-
nands can be grouped as follows:

| | |
|---|---|
| Cu | 13 |
| Cr, Zn | 12 |
| Pb | 11 |
| Mn | 10 |
| Cd | 9 |
| Fe, Ni, dating by the Pb-210 technique | 8 |
| Al, Co, Hg, dry matter content | 6 |
| Cs-137 | 5 |
| C org. | 4 |
| N, P, clay minerals | 3 |
| Ca, Li, Mg, particle fractionation | 2 |
| Cs, Ga, Rb, V, Yb, Zr, carbonates | 1 |

The data received were treated in four different ways:

a) Mean values and relative standard deviations (R.S.D.) were
   calculated over all segments of the cores, separately for the
   total contents and the weakly extractable fractions of the
   different determinands.

b) The single concentration values, which were reported by the
   participants for the different core segments, were related to
   the corresponding mean values from (a). The resulting 'normal-
   ized' vertical profiles were plotted.

c) Sedimentological and geochemical background data and other
   supplementary information, which were submitted for selected
   cores in numbers not sufficient for intercomparison purposes,
   were plotted, using the dimensions of the original data or
   those received from the 'normalization procedure' of (b).

d) The dating results were compiled by P. Pfeiffer Madsen
   together with a small group of experts. Their revised report
   is included as the last report in this volume.

Table 19 presents the mean total concentrations of 15 determi-
mands (dry matter, organic carbon, nitrogen, phosphorus, Al, Fe,
Mn, Zn, Pb, Cr, Cu, Ni, Co, Cd, Hg), which were calculated from
the data sets submitted. Eight cores (GDR 113/17, 18, 21, 22, 25,
27, 28, 30) were investigated. The distance between the first
(17) and the last core (30) was only about 24 m. Therefore, bear-
ing in mind the even and undisturbed echo-sounding profiles, we
would not a priori expect significant natural differences between
the sampling spots ("sediment patchiness"). For a better compari-
son, in the first column of Table 19 are listed the mean results
of the first step for reference sample ABSS, which was taken at
the same station by a grab sampler (sampling depth about 10-15
cm). In addition, the calculated mean values of the core segments
were corrected taking into consideration the results of the par-
ticipants in the preceding intercalibration step. The corrected
values are added in brackets. The deviations found between the
laboratories are in about the same order of magnitude as for step
one. There are again some outliers, e.g., the mercury value for
core 28, cadmium for core 30, and organic carbon for core 22 (the
latter deviation was compensated by the procedure used for cor-
rection of data).

There was no systematic trend visible for statistically signifi-
cant changes over the 24 m sampling distance. Increasing chromium
contents with continuous sampling were compensated by application
of the correction procedure.

In Table 20 the mean values for the 1N HCl extracts are pre-
sented. Similar comments can be made for these values as for the
total concentrations. There is again observed for many determi-
nands the expected similarity to the bulk reference sample ABSS,
especially for Al, Cr, and Cu. However, as already noted regard-
ing the total concentrations, for some determinands, e.g., Zn and
Cd, higher levels were found in ABSS. This could be caused either
by contamination during sampling and further preparation of the
reference sample or by the stronger enrichment of these elements
in the top layers of the sediment cores. The grab sample, whose
material was not 'diluted' by material from deeper layers with
lower metal contents, caused an enrichment effect.

The relative standard deviations (Table 21), which were calcu-
lated for both types of data sets submitted and which reflected
the sum of the analytical and natural variability of element
concentrations along the cores, were often at about the same
level or below the R.S.D. values obtained during step 1 of the
intercalibration. This could be due mainly to two reasons: (a)
the analytical capabilities in Baltic laboratories may be far
better in relation to the total number of participants in the

first step, and/or (b) the variation in most of the determinands
is some times only minor along the cores.

We will leave now the statistical data and consider more the de-
tailed plots of the different determinands. Despite the use of
the normalization procedure (only the relative values with re-
spect to the mean concentrations of determinands in slices of the
same core are plotted), relatively large differences are ob-
served, probably caused in most cases by the analytical proce-
dures. Even such a simple parameter as the determination of dry
weight (Figure 11) seems to cause problems (cores 17, 25). How-
ever, the general shapes of the different profiles are similar.
The organic carbon seems to be distributed rather evenly along
the cores. This was confirmed by 4 laboratories. Two outlying
single values for core 25 could reflect analytical artefacts or
insufficient homogenization. The latter explanation seems to be
more likely, because in the relevant segments, 10 and 15, the
nitrogen profile also showed pronounced maxima. Both fractions of
Al seem to be distributed rather evenly through the cores. Only
the Al data for core 28 are irregularly scattered. For total man-
ganese (Figure 12), all laboratories found an increasing trend
with depth. However, the profiles for the 1 N HCl fraction of
this element have again very different shapes. This could be due
to analytical reasons, because the weakly extracted Mn fractions
seem to depend strongly on the conditions of the leaching pro-
cedure. This is in correspondence with an observation resulting
from the first step of the intercalibration, which showed rela-
tively high standard deviations for the 1 N HCl fraction compared
with the total amounts. For Cu, Pb (Figure 13) and Zn (Figure
14), a clearly decreasing concentration for the 1 N HCl fractions
with increasing depth below about 6 - 10 cm was confirmed by most
participants. The total values for these elements are more scat-
tered than the weakly extracted fractions due to the increasing
problems associated with higher blanks and the complicated di-
gestion procedures. Another reason could be the effect of the
more inert fractions, which are included in the total fraction
and 'dilute' the easily available parts. Bearing in mind the poor
results for Cd, Hg and Cr during the first step of the intercali-
bration, and during the additional Cd/Hg exercise, there were now
at least some similarities between the shapes of profiles ob-
tained by the different laboratories for those elements (see,
e.g., cores 22 and 27 for Hg; cores 17 and 22 for total-Cd; cores
19, 22 and 25 for total-Cr). However, the deviations observed be-
tween the different core mean values (Table 19) were still rela-
tively large. From the results of the investigations on back-
ground sediment characteristics, which were performed by some
laboratories, and from Figures 15 to 17, the following descrip-
tion can be derived:

- Redox potential measurements, carried out on 0.76 cm slices of
  core 40, show a sharp decrease from about +150 mV to values
  around -25 mV during the first 4 cm (Bågander and Niemistö,
  1978). Another remarkable decrease of the $E_h$ down to -140 mV
  occured below 12 cm sediment depth. This would be in approxi-
  mate agreement with the mean mixing depth (see the last report
  in this volume).

Two years later, in April 1985, the redox potential measure-
ments were repeated twice at nearly the same sampling position.

In both cases, the sharp decrease in the upper part of the sediment cores was confirmed. For one of the cores, the second $E_h$ jump below 12 cm could also be found again.

- Particle size analyses were carried out on three cores (25, 26, 30). The results show that the investigated material consisted mainly (more than 95%) of clay and silt. The different particle size fractions are distributed evenly along the 20 cm cores. However, there is a decreasing trend for the smaller fractions with increasing depth, possibly due to consolidation/aggregation effects. Because of the differences in the technique applied and in the nomenclature used for size fraction boundaries, the results obtained by the three laboratories are not directly comparable.

- Analyses on the mineral composition of the samples were performed by two laboratories (cores 25 and 26). However, in one case (25) the samples were fractioned by sieving before the X-ray diffractometric measurements (2 fractions: 0.05 - 0.1 mm and smaller than 0.05 mm). For the smaller fraction only some qualitative information was submitted, e.g., "even distribution of clay minerals, quartz, and feldspar through the core". The coarser fraction of core 25 was split further into the light and heavy minerals. The mineral composition of core 26 is given in Figure 15. There are no pronounced differenes visible. The mean contents of the identified minerals are as follows (all values in %):

Quartz ....................................... 34.7 (32 - 37)

Feldspar         . K-feldspar .................... 9.4 ( 7 - 12)
                 . plagioclase ................... 9.9 ( 8 - 11)

Clay minerals    . chlorite ...................... 6.0 ( 2 -7.5)
                 . illite, montmorillonite, 'mixed
                 layers' ........................ 28.4 (24 - 33)

Dolomite/calcite ............................. 1.7 (1.5-3.5)

Pyrite ....................................... 2.8 ( 2 - 4)

There seems to be a trend towards an inverse relationship between clay minerals and feldspar. The increasing clay mineral contents with the sediment depth could possibly be due to a conversion of feldspar into clay, which is accompanied by a release of alkaline and alkaline earth metals from the feldspar.

- On core 35 Moessbauer spectroscopic investigations were applied to determine the Fe(II)/Fe(III) relationship as an indicator of the redox conditions of the sediment samples. The results seem to reflect that the Fe(III) fraction (mean: 70.2 ± 0.03 is relatively evenly distributed along the core. However, the detailed profile (Figure 16) shows a pronounced Fe(II) maximum (Fe-III minimum) in the upper layer between about 3 and 7 cm. This could be a reflection of the position of the 'redoxcline', where after oxygen consumption, nitrate, and manganese(IV) reduction, the Fe(III) pool will also be partly used up as an oxidizing agent. In this reduction/oxidation coupling, the more amorphous iron oxide/hydroxides should preferably be included

and not the metal fraction which is fixed in the silicate lattice (e.g., in the clay mineral 'chlorite', a Mg-Fe-silicate).

- The profiles of some metal concentrations in the combined pore waters of cores 38 and 39 (Figure 17) confirm the results of the redox potential and Moessbauer spectroscopic measurements with regard to the existence and position of a reducing zone in the upper sediment layer. This is especially true for Fe and Mn and for metals (Cd, Cu, Ni, Pb) which are possibly fixed by iron and manganese oxides/hydroxides or which show similar geochemical behaviour as their carriers/scavengers. The reason for another peak in the profiles of Pb, Ni, and Cd at about 14 - 15 cm depth is not so clear. Further studies could investigate the question of whether this is due to analytical artefacts or can be related to certain characteristics of the sediment samples. (At the lower level of the mixing zone, the onset of stronger reducing conditions with remobilization effects could be expected.)


Summary and conclusions

The background conditions for this second step of the intercalibration exercise were more complicated than expected due to the relatively strong mixing of the sediment cores. (According to Gosselck (1985), in 1983 in the Arkona Basin on the Baltic Monitoring Programme stations "BY 1" and "BY 2", 58 and 21 individuals of soft bottom macrozoobenthos per 0.1 m$^2$ were counted, respectively.) Most of the determinands were obviously influenced by this mixing effect, which was probably mainly caused by bioturbation. However, the influence of anthropogenic activities can not be excluded entirely.

Because it is likely that these mixing factors acted heterogeneously, given the spatial scale of the coring, a certain degree of mainly natural 'sediment patchiness' must be expected.

Taking these limitations into account, the outcome and most of the analytical results are acceptable, particularly:

- the total number of responding laboratories was relatively high,

- it was the first time that so many participants took part in a Pb-210 dating on natural sediment samples. (They demonstrated the readiness to produce reproducible and accurate dating results for this type of material under complicated conditions. With the application of an algorithm, which took into consideration the mixing terms, comparable values on linear and mass accumulation rates could be obtained.),

- all laboratories were able to resolve vertical distribution patterns for one or another determinand. (However, some participants were obviously unable to do so for certain elements.),

- in spite of the disturbing effect of the sediment patchiness, partially corresponding normalized profiles were found, for several determinands by different laboratories,

- the differences between the mean values of the sub-samples of the cores, calculated from the original results submitted, were very small for several determinands.

Further investigations, aimed at studying the phenomena of 'sediment patchiness' in selected basins of the Baltic Sea (with permanent oxic, frequently changing, and more or less permanent anoxic conditions), should be initiated. These studies should include, in the first step, two-dimensional and later on also three-dimensional surveys. Necessary steps towards coordinated and contamination-related sediment investigations in the Baltic Sea area would be

- to unify further the sampling equipment, methods, and strategies,

- to use on a regular basis suitable reference samples and to undertake other measures for the quality assurance of the analyses, and

- to continue the search for a simple and rapid leaching procedure for the extraction of environmentally relevant contaminant fractions.

## References

Bågander, L.E., and Niemistö, L., 1978. An evaluation of the use of redox measurements for characterizing recent sediments. Estuar. Coastl. Mar. Sci., 6, 127-134.

Gosselck, F., 1985. Zoobenthos, Soft bottom macrozoobenthos in the period 1978-1983, in: HELCOM/GEA: The background document for the first periodic assessment. Doc. GEA 5/2e, 1985.

Niemistö, L., 1974. A gravity corer for studies of soft sediments. Merentutkimuslait.Julk./Havsforskningsinst. Skr. 238, 33-38.

Table 17  Determinands for which quantitative results were reported by
the participants in the second step of the intercalibration
exercise.

x - 'total' contents
+ - fractions, leached by 1.0 N NCl

| Determinand | Core No. GDR 113 | | | | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 17 | 18 | 21 | 22 | 23 | 25 | 27 | 28 | 29 | 30 | 33 | 35 |
| Particle fractionation | | | | | | x | x | | | | | |
| Clay minerals | | | | | | x | x | | | x | | |
| Dry matter | x | | x | x | | | x | x | | x | | |
| Carbonates | | | | | | | x | | | | | |
| C org. | | | | x | | x | x | | | x | | |
| N | | | | | | x | x | x | | | | |
| P | | | | x | | | x+ | | | | | |
| Al | | | | | | x+ | x+ | x+ | | | | |
| Fe | | | | x+ | | x+ | x+ | | | x+ | | |
| Mn | | | x+ | x+ | | x+ | x+ | | | x+ | | |
| Zn | x | x | x+ | x+ | | x+ | x+ | | | x+ | | |
| Pb | x | x | | x+ | | x+ | x+ | + | | x+ | | |
| Cr | x | x | x+ | x+ | | x+ | x+ | | | x+ | | |
| Cu | x | x | x+ | x+ | | x+ | x+ | + | | x+ | | |
| Ni | x | x | | x+ | | x+ | x+ | | | | | |
| Co | | | | x+ | | x+ | x+ | | | | | |
| Cd | x | x | | x+ | | | x+ | + | | x+ | | |
| Hg | x | | | x+ | | | x | x+ | | | | |
| Ca, Mg | | | | | | | | x+ | | | | |
| Rb, Cs | | | | | | | | | | x | | |
| Li | | | | | | x+ | | | | | | |
| Ga, V, Yb, Zr | | | | | | x | | | | | | |
| 210-Pb(-Po, -Bi) | | x | | x | x | x | | | x | x | x | x |
| 137-Cd | | x | | | x | | | | x | x | x | |

Table 18  Recoveries of metals from the segmented core GDR 113/27
using different leaching agents (mean values of 20 sub-
samples).

| Determinand | | 1.0 N HCl | 0.5 N HCl |
|---|---|---|---|
| Al | % | 0.32 ± 0.02 | 0.36 ± 0.05 |
| Fe | % | 0.65 ± 0.05 | 0.67 ± 0.11 |
| Zn | $\mu g \cdot g^{-1}$ | 79.00 ± 28.00 | 72.00 ± 24.00 |
| Pb | $\mu g \cdot g^{-1}$ | 62.00 ± 20.00 | 63.00 ± 19.00 |
| Mn | $\mu g \cdot g^{-1}$ | 61.00 ± 14.00 | 63.00 ± 16.00 |
| Cu | $\mu g \cdot g^{-1}$ | 20.00 ± 4.50 | 16.00 ± 5.80 |
| Cr | $\mu g \cdot g^{-1}$ | 16.00 ± 1.30 | 15.00 ± 2.80 |
| Ni | $\mu g \cdot g^{-1}$ | 11.00 ± 3.50 | 15.00 ± 6.40 |
| Co | $\mu g \cdot g^{-1}$ | 7.00 ± 1.20 | 8.20 ± 1.20 |
| Cd | $\mu g \cdot g^{-1}$ | 0.22 ± 0.10 | 0.22 ± 0.10 |

Table 19  Mean 'total' concentrations of 15 determinands in 8 cores (in brackets: corrected values which take into consideration the results of the laboratories obtained for the reference sample "ABSS").

| Determinand | | ABSS | Core No. GDR 113 chain length (m) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 17 (113) | 18 (113) | 21 (119) | 22 (131) | 25 (131) | 27 (131) | (137) | 30 (137) |
| Dry matter | % | – | 24.1 | – | 23.2 | 22 | 25 | 24.2 | 23.5 | 22.3 |
| Corg. | % | 5.9 ± 0.9 | – | – | – | 4.6 (6.5) | 7.3 (7.4) | 7.1 (6.2) | – | 6.5 (6.2) |
| N | % | 0.68 ± 0.18 | – | – | – | 0.71 (0.72) | 0.74 (0.71) | – | – | – |
| P | % | 0.11 ± 0.03 | – | – | – | 0.12 (0.13) | – | 0.092 (0.078) | – | – |
| Al | % | 5.6 ± 0.8 | – | – | – | – | 5.2 (4.4) | – | 5.6 (6.8) | – |
| Fe | % | 3.5 ± 0.5 | – | – | – | 3.0 (3.7) | 3.3 (2.7) | 2.1 (1.9) | – | 2.4 (3.3) |
| Mn | $\mu g \cdot g^{-1}$ | 365 ± 40 | – | – | 286 (301) | 287 (330) | 302 (245) | 265 (274) | – | 240 ( – ) |
| Zn | $\mu g \cdot g^{-1}$ | 307 ± 25 | 157 (150) | 188 (180) | 172 (193) | 188 (194) | 213 (229) | 157 (167) | – | 190 ( – ) |
| Pb | $\mu g \cdot g^{-1}$ | 94 ± 11 | 88 (92) | 101 (106) | – | 102 (100) | 126 ( – ) | 65 (68) | – | 87 ( – ) |
| Cr | $\mu g \cdot g^{-1}$ | 58 ± 20 | 36 (52) | 35 (51) | 37 (33) | 35 (58) | 51 (36) | 69 (83) | – | 58 (37) |
| Cu | $\mu g \cdot g^{-1}$ | 51 ± 6 | 40 (38) | 43 (41) | 39 (47) | 41 (45) | 49 (52) | 36 (35) | – | 44 (62) |
| Ni | $\mu g \cdot g^{-1}$ | 37 ± 6 | 26 (22) | 29 (25) | – | 29 (35) | 35 ( – ) | 27 (28) | – | – |
| Co | $\mu g \cdot g^{-1}$ | 12 ± 2 | – | – | – | 8.6 (9.4) | 23 (18) | 10 (8.6) | – | – |
| Cd | $\mu g \cdot g^{-1}$ | 0.94 ± 0.45 | 0.77 (0.77) | 0.85 (0.85) | – | 0.60 (1.1) | – | 0.84 (0.71) | – | 1.4 ( – ) |
| Hg | $ng \cdot g^{-1}$ | 256 ± 100 | 245 (230) | – | – | 318 ( – ) | – | 240 (190) | 45 (25) | – |

Table 20 Mean concentrations of 11 metals leached by 1 N HCl from 6 cores (in brackets: corrected values which take into consideration the results of the laboratories obtained for the reference sample "ABBS").

| Determinand | ABSS | Core No. GDR 113 chain length (m) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 21 (119) | 22 (119) | 25 (131) | 27 (131) | 28 (137) | 30 (137) |
| Al % | 0.38 ± 0.09 | – | – | 0.37 (0.45) | 0.32 (0.35) | 0.71 (0.57) | – |
| Fe % | 1.01 ± 0.22 | – | 1.70 (1.36) | 0.84 (1.03) | 0.65 (0.70) | – | 0.85 (1.59) |
| Zn $\mu g \cdot g^{-1}$ | 261 ± 23 | 141 (145) | 161 (173) | 136 (151) | 79 (81) | – | 182 ( – ) |
| Pb $\mu g \cdot g^{-1}$ | 94 ± 9 | – | 93 (104) | 120 (125) | 62 (68) | 37 ( – ) | 77 (62) |
| Mn $\mu g \cdot g^{-1}$ | 106 ± 19 | 88 (91) | 149 (117) | 82 (99) | 61 (69) | – | 59 (57) |
| Cu $\mu g \cdot g^{-1}$ | 28 ± 3 | 28 (31) | 32 (37) | 29 ( – ) | 20 (21) | 18 (23) | 33 ( – ) |
| Cr $\mu g \cdot g^{-1}$ | 14 ± 4 | 11 (17) | 17 (14) | 13 (14) | 16 (19) | – | – |
| Ni $\mu g \cdot g^{-1}$ | 18 ± 4 | – | 20 (19) | 10 (11) | 11 (10) | – | – |
| Co $\mu g \cdot g^{-1}$ | 6.1 ± 1.2 | – | 7.5 (5.7) | 6.9 ( – ) | 7.0 (6.9) | – | – |
| Cd $\mu g \cdot g^{-1}$ | 0.96 ± 0.35 | – | 0.70 (1.12) | – | 0.22 (0.35) | 0.74 (0.86) | – |
| Hg $ng \cdot g^{-1}$ | 59 ± 32 | – | 69 (41) | – | – | 24 ( – ) | – |

Table 21 Relative standard deviations (± %) obtained by the different laboratories for 'total' contents and fractions leached by 1 N HCl (in brackets) from samles of segmented cores (n = 20).

| Determinand | Core No. GDR 113 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | ABSS | 17 | 18 | 21 | 22 | 25 | 27 | 28 | 30 |
| Dry matter | - | 21 | - | 11 | 14 | 10 | 14 | 14 | 11 |
| C org. | 15 | - | - | - | 7 | 25 | 4 | - | 5 |
| N | 26 | - | - | - | 7 | 9 | - | - | - |
| P | 27 | - | - | - | 42 | - | 20 | - | - |
| Al | 14(24) | - | - | - | - | 2(8) | 6(6) | 12(19) | - |
| Fe | 14(22) | - | - | - | 9(15) | 9(27) | 9(8) | - | 10(13) |
| Mn | 11(18) | - | - | 20(7) | 18(23) | 9(33) | 13(23) | - | 22(8) |
| Cu | 12(10) | 26 | 18 | 13(16) | 30(25) | 6(14) | 12(23) | -(6) | 14(15) |
| Zn | 8(9) | 33 | 16 | 11(16) | 21(19) | 7(8) | 30(36) | - | 13(14) |
| Cr | 34(32) | 43 | 42 | 11(7) | 11(10) | 6(20) | 8(8) | - | 21 |
| Co | 17(20) | - | - | - | 8(13) | 17(41) | 10(18) | - | - |
| Ni | 16(21) | 19 | 20 | - | 6(3) | 6(20) | 3(31) | - | - |
| Pb | 12(10) | 36 | 17 | - | 23(20) | 6(10) | 33(33) | -(14) | 30(32) |
| Cd | 48(36) | 25 | 14 | - | 28(26) | - | 27(45) | -(16) | 21 |
| Hg | 39(54) | 57 | - | - | 36(77) | - | 45 | 31(33) | - |
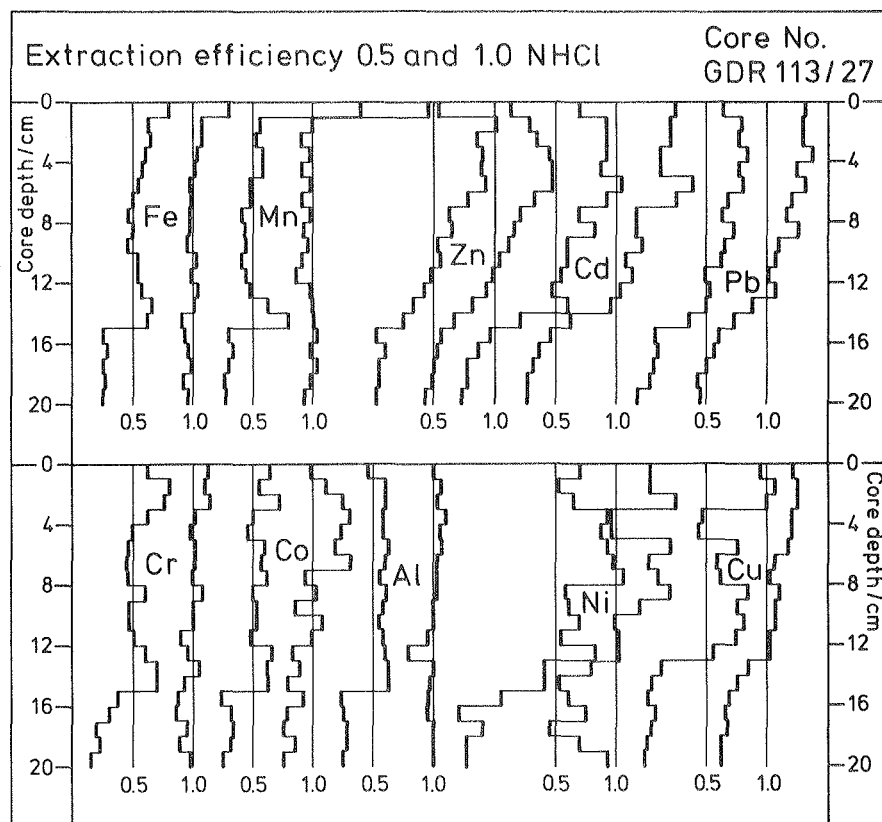
Figure 10    Extraction efficiency of 0.5 N
             and 1.0 N HCl for metals in
             core No. 27.
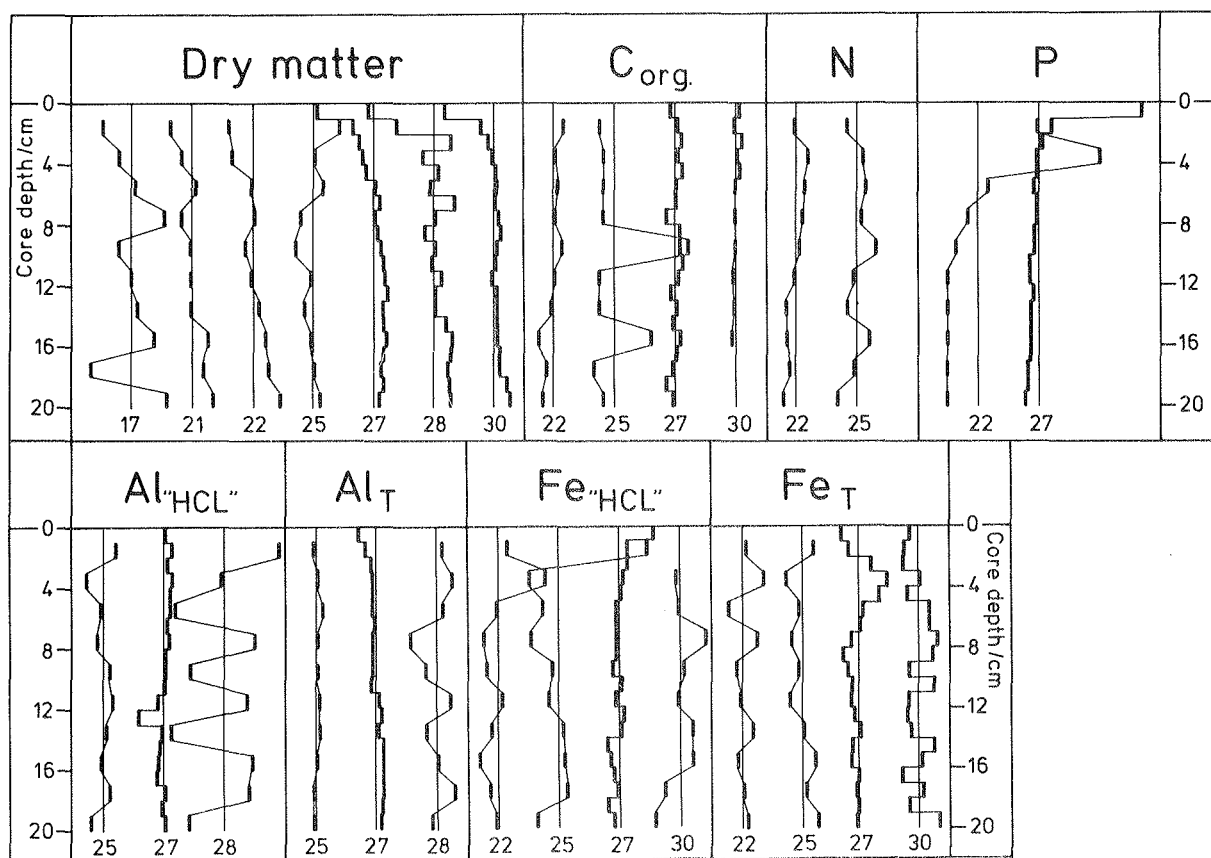


Figure 11    Profiles for the contents of dry matter, organic carbon, nitrogen,
             phosphorus, 'total' (T) and 1.0 N HCl ("HCl") extracted Al and Fe
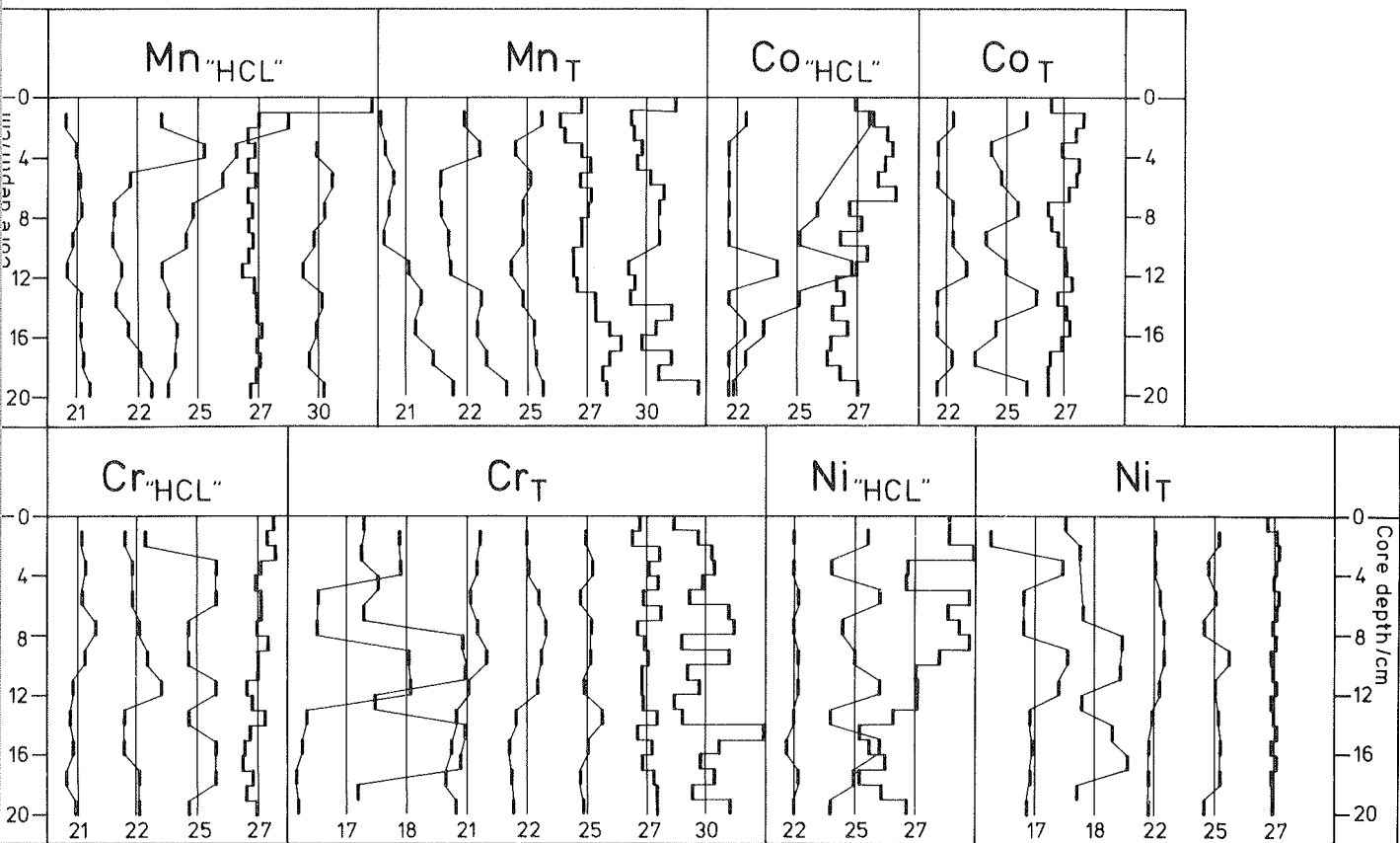             in parallel cores.

Figure 12   Profiles for the contents of 'total' (T) and 1.0 N HCl extracted ("HCl") Mn, Co, Cr, and Ni in parallel cores.
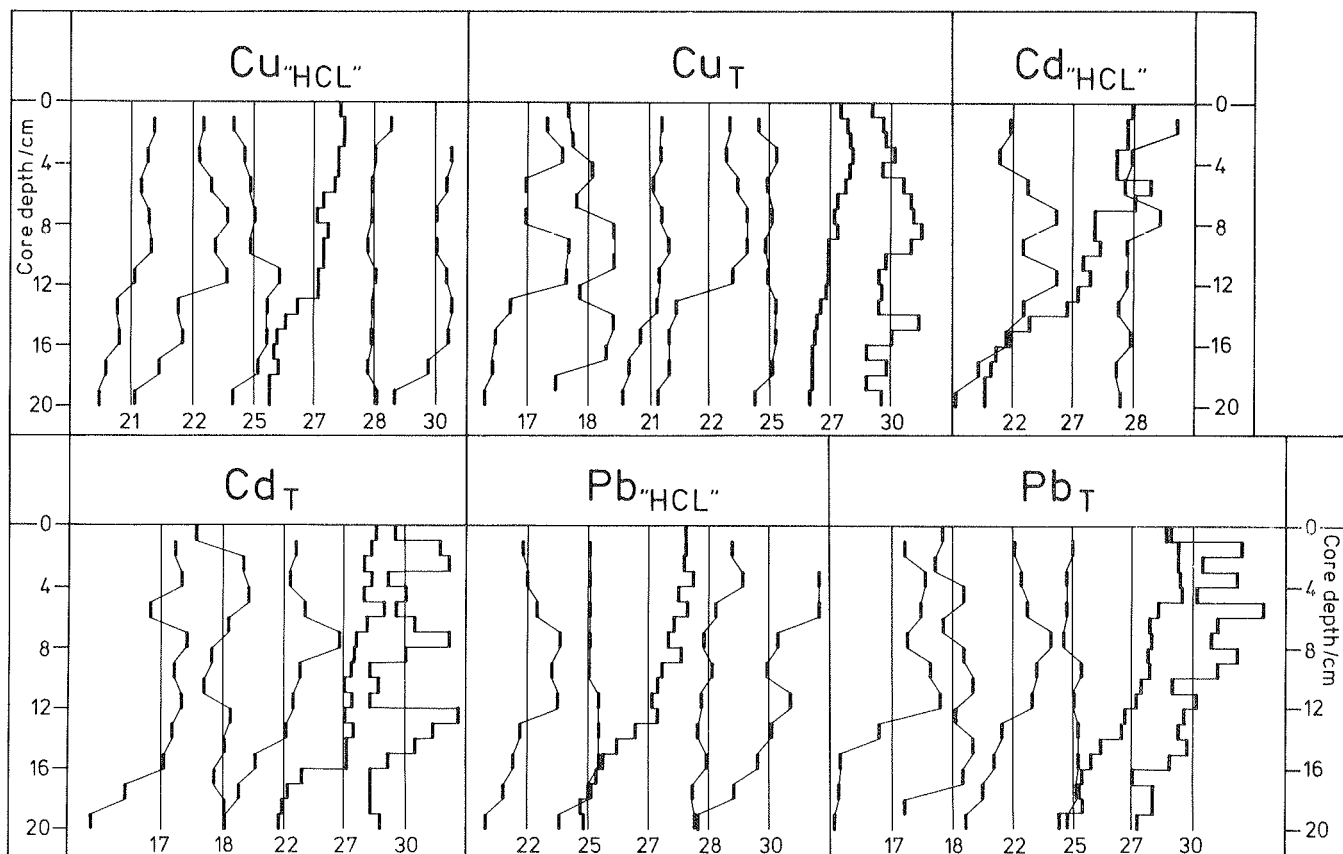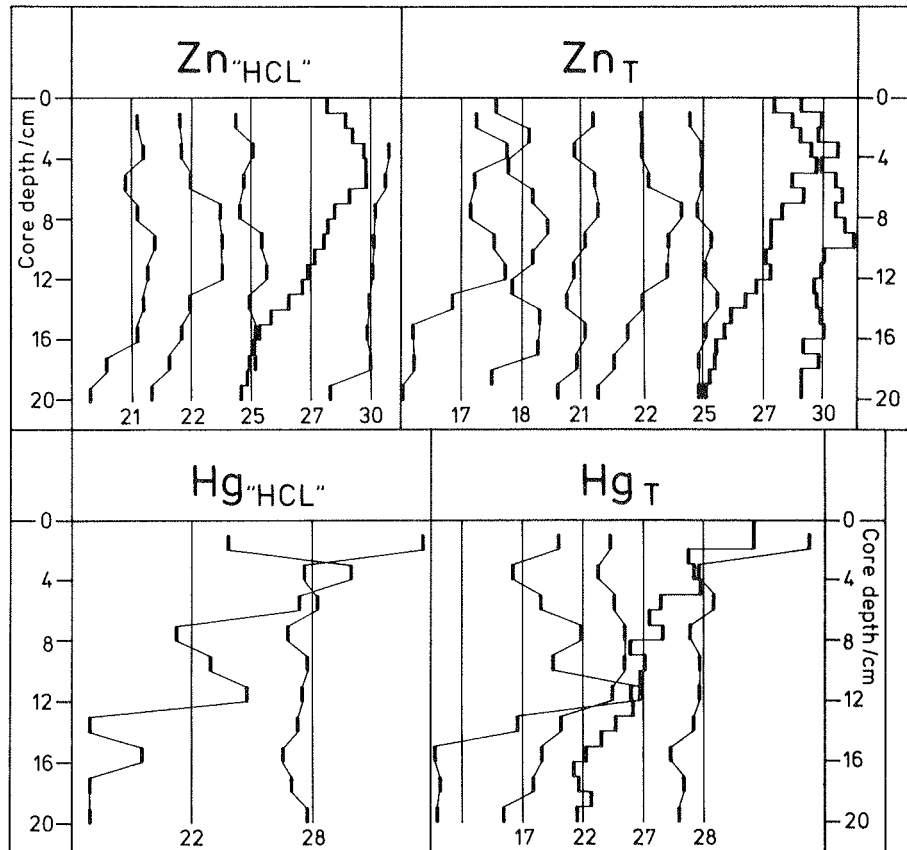


Figure 13   Profiles for the contents of 'total' (T) and 1.0 N HCl extracted ("HCl") Cu, Cd, and Pb in parallel cores.

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Figure 14   Profiles for the contents of 'total' (T) and
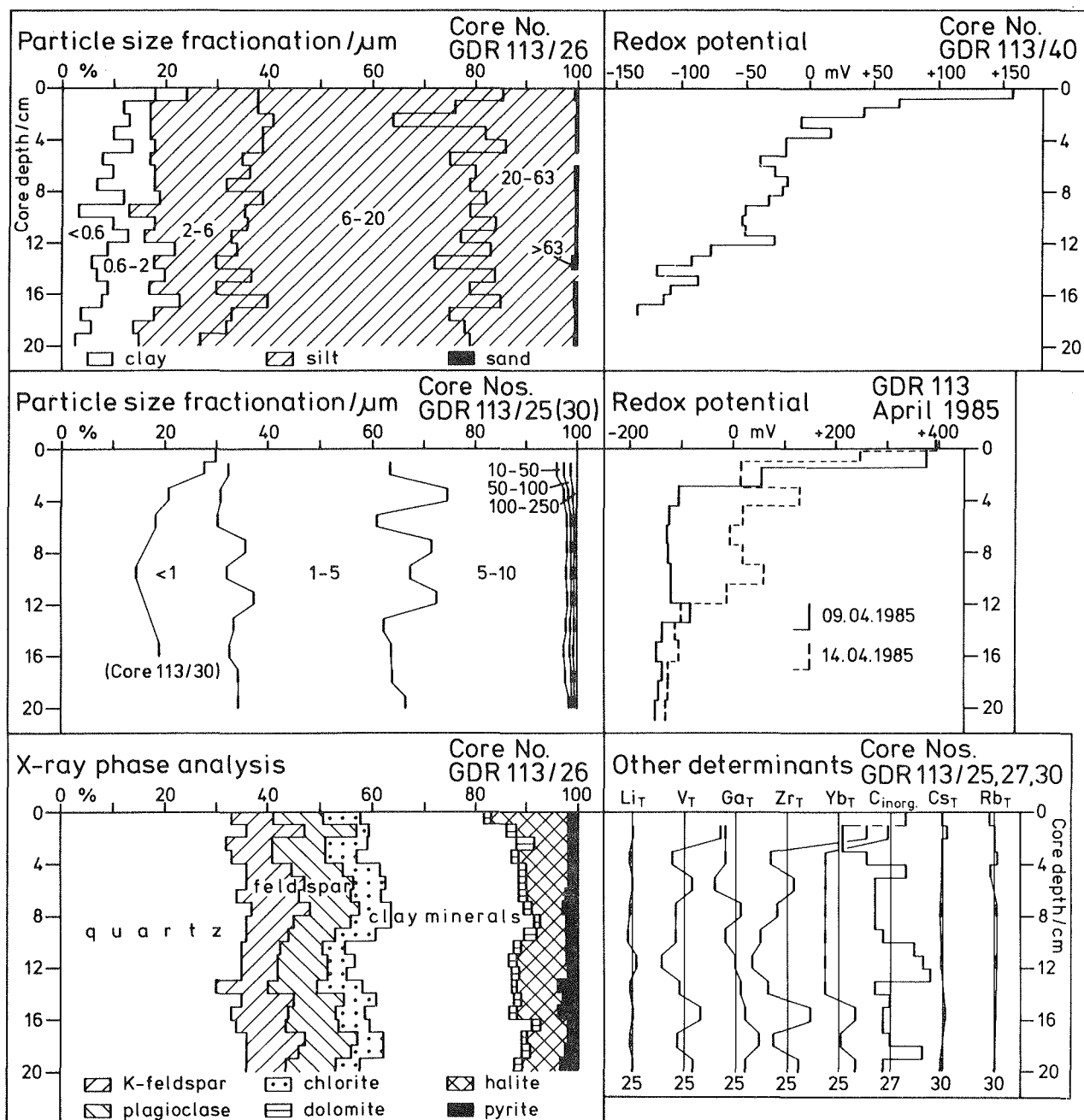1.0 N HCl extracted ("HCl") Zn and Hg in
parallel cores.

Figure 15   Profiles for the 'total' (T) contents of other determinands (Li, V,
Ga, Zr, Yb, Cs, Rb, inorganic carbon), for the particle size frac-
tionation, redox potential, and for the mineral composition in
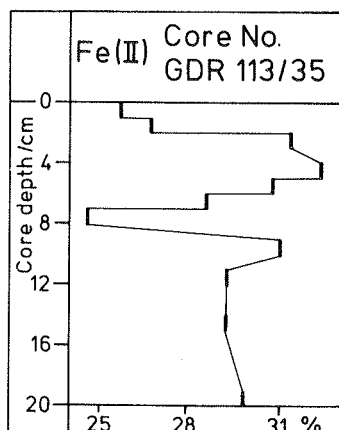parallel cores.

Figure 16   Profile for the percentage
            of Fe(II) in relation to
            the total iron content in
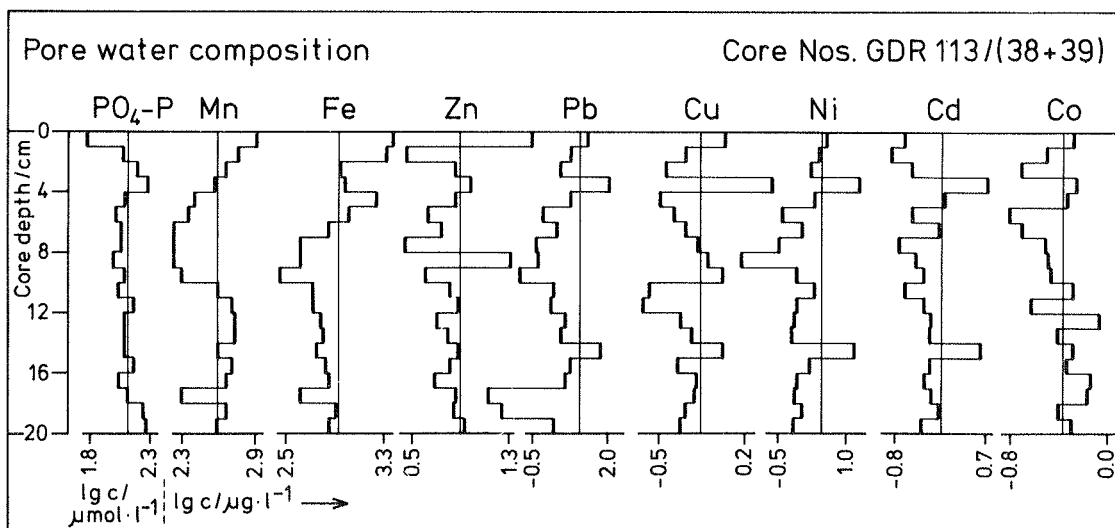            core 35.



Figure 17   Profiles for the contents of 8 metals and phosphate in
            the combined pore water solutions of cores 38 and 39.

Table 22   Participants in the second step of the intercalibration exercise.


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REPORT ON THE RESULTS OF THE RADIOCHEMICAL DATING PART OF
THE SEDIMENT INTERCALIBRATION EXERCISE

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Introduction

The dating of sediments was an essential part of the second  step
of  this  intercalibration  exercise.  The  results  of  the different
participants were discussed during the meeting held in  September
1984  on  the  Finnish R/V "Aranda" in Rostock, German Democratic
Republic. A small sub-group of five persons from laboratories  in
which  cores have been dated for this exercise reached the follo-
wing conclusions:

- The Pb-210 method in its different modifications  can  be  used
  successfully to date Baltic mud sediments. Valuable support can
  be obtained from the measurement of Cs-137 and  other  radionu-
  clides.

- The  five laboratories determined Pb-210 via Po-210 in the same
  principal way. However, some differences exist  in  the  shapes
  obtained  for  the  Pb-210  profiles  (Pb-210  activity  versus
  depth). It could not be decided whether  or  not  and  how  far
  these differences originated from the fact that different cores
  were used. Differences in the calculated accumulation rates  of
  sediments  were  related  to  difficulties  in  estimating  the
  supported Pb-210 values and to the use of different  algorithms
  for the calculation.

- For  the  sampling  site,  a  core length of 20 cm was not suf-
  ficient to cover background values for Pb-210. However, correc-
  tions were possible through additional Ra-226 measurements.

- It  was suggested that another core should be dated by at least
  one laboratory to decide upon the reason for the observed  dif-
  ferences  (natural  variability  or  variabilities caused by the
  whole dating procedure).

- The participants decided to exchange their primary data at  the
  end  of  October  1984  and to continue the discussion on their
  interpretation intersessionally by correspondence.

- The author agreed to prepare a report on the compilation of the
  dating  results by 31 January 1985. Contributions were made for
  this  work  by  K.  Fröhlich,  R.  Gellermann,  A.  Liehu,   J.
  Pempkowiak, and D. Weiss.

## Experimental details

Each of the participants received one core, consisting of the up-
per 20 cm of deep frozen sub-samples as mentioned in the previous
report in this volume. At least every second sample (odd numbers)
was dated. The principle of the Pb-210 method is described else-
where (Häsänen, 1977, Pheiffer-Madsen, and Sørensen, 1979). In
addition to the specific activity, the dry matter content and the
loss on ignition were determined. Altogether, 8 cores were dated
(GDR 113/18, 22, 23, 25, 29, 30, 33, 35). For five of these cores
(18, 23, 29, 30, 33) Cs-137 data were available. Only six Pb-210
data sets from the eight were included in the compilation (18,
22, 23, 30, 33, 35). Cores 22 and 33 were analyzed by the same
laboratory. Of the five Cs-137 profiles, only four were con-
sidered (18, 29, 30, 33).

## Results and discussion

From the unsupported Pb-210 profiles, the sedimentological par-
ameters have been estimated according to the following mathema-
tical model:

$$\frac{dA}{dt} = D\frac{d^2A}{dz^2} - \omega\frac{dA}{dz} - \lambda A$$

where

$A$ = Pb-210 activity ($mBq \cdot g^{-1}$)

$D$ = mixing coefficient ($cm^2 \cdot y^{-1}$)

$z$ = depth (cm)

$\omega$ = linear accumulation rate ($cm \cdot y^{-1}$)

$\lambda$ = decay constant for Pb-210 ($y^{-1}$)

$t$ = time

In this model a mixing depth ($z_m$) is defined, where $D > 0$ for $z \leqslant$
$z_m$ and $D = 0$ for $z > z_m$. Using the steady state solution of this
equation, $z_m$, $D$, $\omega$, and $F$ (Pb-210 input in $mBq \cdot cm^{-2} \cdot y^{-1}$) can be
estimated. The $average$ linear accumulation rates ($\omega$) have been
calculated from the estimated mass accumulation rates
$R$ ($mg \cdot cm^{-2} \cdot y^{-1}$). In Table 23, the estimated parameters and some of
the analytical results are outlined.

In order to check the validity of the estimates of parameters,
the unsupported Pb-210 profiles (Table 24) have been re-calcu-
lated according to the model given above. The results are rep-
resented by the full lines shown in Figure 18. The analytical
(unsupported) Pb-210 values are shown therein by crosses. In some
figures, the Cs-137 activities were also added. In most cases, a
reasonable agreement was obtained between the calculated profiles
and measurements of unsupported Pb-210 activities. The Cs-137

measurements, carried out on several cores, confirmed the concept of substantial mixing. The radionuclide Cs-137 has been artificially released into the environment since 1954. However, in the investigated cores it was found down to depths far before that time if they would be undisturbed. Mixing depths of about 16 cm which can be derived from some Cs-137 profiles are well in accordance with those $z_m$ values taken from the Pb-210 profiles.

The reliability of the analytical data is elucidated in the last two lines of Table 23. Results on the total Pb-210 activity and the loss on ignition ($550^0$C) are shown for the surface sediment layer (0 - 1 cm). The mean value of the Pb-210 activity for these samples is $228 \pm 27$ mBq·g$^{-1}$ ($\pm$ 12%). As indicated for example by the differences in the loss on ignition values, in addition to analytical artefacts arising during the radionuclide measurements, the observed variations are probably partly due to differences in the general sediment characteristics of the six cores. These different sediment characteristics could be caused by both sampling problems (reproducible dissection of the first slices of mud sediments with a very high water content) and a real "sediment patchiness". Such a patchy distribution would be mainly due to the activity of benthic biota (bioturbation; feeding behaviour of animals at the water/sediment interface. In addition, anthropogenic influences (dredging, fishing activities, morrings, etc.) cannot be excluded for that area.

Three of the participating laboratories have also analysed the samples ABSS and MBSS, distributed during the first step of the intercalibration exercise, for their Po-210/Pb-210 activities. Their results are given in the following table:

| Sample | Core No. GDR 113 | | | |
|---|---|---|---|---|
| | 18 | 30 | 35 | Mean |
| ABSS (mBq·g$^{-1}$) | $117 \pm 11$ | 82 | $127 \pm 9$ | $109 \pm 24$ |
| MBSS (mBq·g$^{-1}$) | $68 \pm 4$ | 74 | $74 \pm 5$ | $72 \pm 3$ |

The results agree fairly well, especially for MBSS, thus indicating that the Pb-210 data at least from these three laboratories are comparable within the limits of the coefficients of variation.

Conclusions

In addition to the remarks summarized in the introduction to this report, the results of the intercalibration exercise on sediment dating can be outlined as follows:

- The determination of the Pb-210 activity in sediment samples of the type studied here does not seem to cause major analytical problems.

- Difficulties raised for the proper interpretation of the measured Pb-210 profiles which were strongly influenced by a mixing of the surface layer down to 10 - 17 cm, could be partly resolved by the use of a mathematical model. The mass sediment accumulation rates, estimated from this model, agreed for the difference cores to a realtively high extent ($36 \pm 5$ mg·cm$^{-2}$·y$^{-1}$, corresponding to a linear accumulation rate of $1.3 \pm 0.2$ mm·y$^{-1}$).

## References

Häsänen, E., 1977. Dating of sediments, based on 210-Pb measurements. Radiochem. Radioanal. Letters, 31, 207-214.

Pheiffer-Madsen, P., Sørensen, J. 1979. Validation of the lead-210 dating method. J. Radioanal. Chem., 54, 39-48.

Table 23  Estimated and analyzed parameters for six dated sediment cores.

| | Core No. GDR 113 | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | 18 | 22 | 23 | 30 | 33 | 35 | Mean |
| $R(mg \cdot cm^{-2} \cdot y^{-1})$. | 33 | 45 | 32 | 34 | 36 | 35 | $36 \pm 5$ |
| R.S.D. | $\pm16\%$ | $\pm5\%$ | $\pm8\%$ | - | $\pm24\%$ | - | - |
| $\omega(mm \cdot y^{-1})$ | 1.2 | 1.6 | 1.2 | 1.3 | 1.2 | 1.2 | $1.3 \pm 0.2$ |
| $z_m$ (cm) | $15.5^1$ | 9.5 | 10.5 | $16.5^1$ | $13.5^1$ | 17.5 | $13.8 \pm 3.3$ |
| $D(cm^2 \cdot y^{-1})$ | 15 | - | 2.0 | 2.0 | - | 3.0 | - |
| $F(mBq \cdot cm^{-2} \cdot y^{-1})$ | 21.7 | 28.3 | 18.3 | 11.7 | 34.2 | 31.7 | $24.3 \pm 8.6$ |
| $A(mBq \cdot g^{-1})^2$ | 214 | 231 | 262 | 184 | 227 | 248 | $228 \pm 27$ |
| I.L. (% d.w.) | 17.7 | - | 17.7 | 13.3 | - | $15.7^3$ | - |

R     = mass accumulation rate (estimated).

$\omega$     = linear accumulation rate.

$z_m$     = mixing depth.

D     = mixing coefficient.

F     = Pb-210 input.

A     = total ("supported") Pb-210 activity.

I.L. = ignition loss ($550^0$C).

[1] confirmed by Cs-137 values.

[2] surface layer (0 - 1 cm).

[3] segment 1 - 2 cm.

Table 24    Total ("supported") Pb-210 activity in segments of six cores ($mBq \cdot g^{-1}$).

| Depth (cm) | Core No. GDR 113 | | | | | |
|---|---|---|---|---|---|---|
| | 18 | 22 | 23 | 30 | 33 | 35 |
| 0 - 1 | 214 ± 11 | 231 ± 22 | 262 ± 26 | 184 ± 6 | 227 ± 7 | 248 ± 12 |
| 1 - 2 | 241 ± 10 | | 298 ± 30 | 146 ± 8 | 229 ± 7 | 271 ± 9 |
| 2 - 3 | | 267 ± 24 | 234 ± 23 | 147 ± 5 | 212 ± 6 | 292 ± 14 |
| 3 - 4 | 129 ± 7 | | 189 ± 19 | 141 ± 7 | 256 ± 8 | 307 ± 12 |
| 4 - 5 | | 231 ± 22 | 203 ± 20 | | 258 ± 14 | 271 ± 16 |
| 5 - 6 | 144 ± 6 | | 177 ± 18 | 95 ± 5 | 234 ± 13 | 269 ± 17 |
| 6 - 7 | | 280 ± 26 | 175 ± 18 | | 257 ± 14 | 266 ± 13 |
| 7 - 8 | 127 ± 5 | | 206 ± 21 | 100 ± 8 | 252 ± 14 | 235 ± 13 |
| 8 - 9 | | 262 ± 26 | 189 ± 19 | | 220 ± 15 | 263 ± 11 |
| 9 - 10 | 137 ± 7 | | 187 ± 19 | 88 ± 8 | 224 ± 13 | 227 ± 11 |
| 10 - 11 | | 208 ± 23 | 195 ± 20 | | 246 ± 14 | 182 ± 10 |
| 11 - 12 | 199 ± 10 | | 121 ± 15 | | 269 ± 8 | 152 ± 9 |
| 12 - 13 | | 155 ± 19 | 104 ± 12 | | 280 ± 15 | 134 ± 7 |
| 13 - 14 | 200 ± 10 | | 98 ± 15 | 82 ± 3 | 261 ± 13 | 143 ± 9 |
| 14 - 15 | | 105 ± 9 | 96 ± 14 | | 140 ± 9 | 142 ± 8 |
| 15 - 16 | 149 ± 8 | | 65 ± 13 | 67 ± 3 | 145 ± 9 | 123 ± 8 |
| 16 - 17 | | 71 ± 7 | 55 ± 12 | | 91 ± 7 | 105 ± 8 |
| 17 - 18 | 105 ± 7 | | 43 ± 11 | 68 ± 4 | 91 ± 7 | 106 ± 17 |
| 18 - 19 | | 59 ± 6 | 37 ± 11 | | 92 ± 7 | 80 ± 4 |
| 19 - 20 | 54 ± 5 | | 29 ± 9 | 43 ± 5 | 82 ± 7 | 63 ± 5 |
| Mean Pb-210 | 154 ± 54 | 187 ± 83 | 148 ± 79 | 106 ± 43 | 203 ± 68 | 194 ± 79 |
| Support of Pb-210 | 22 ± 2 | 23 ± 3 | 23 ± 4 | | 23 ± 3 | 22 |
| Mean dry weight ($g \cdot cm^{-3}$) | 0.267 ±0.443 | 0.290 ±0.057 | 0.298 ±0.090 | 0.258 ±0.032 | 0.308 ±0.059 | 0.296 ±0.062 |
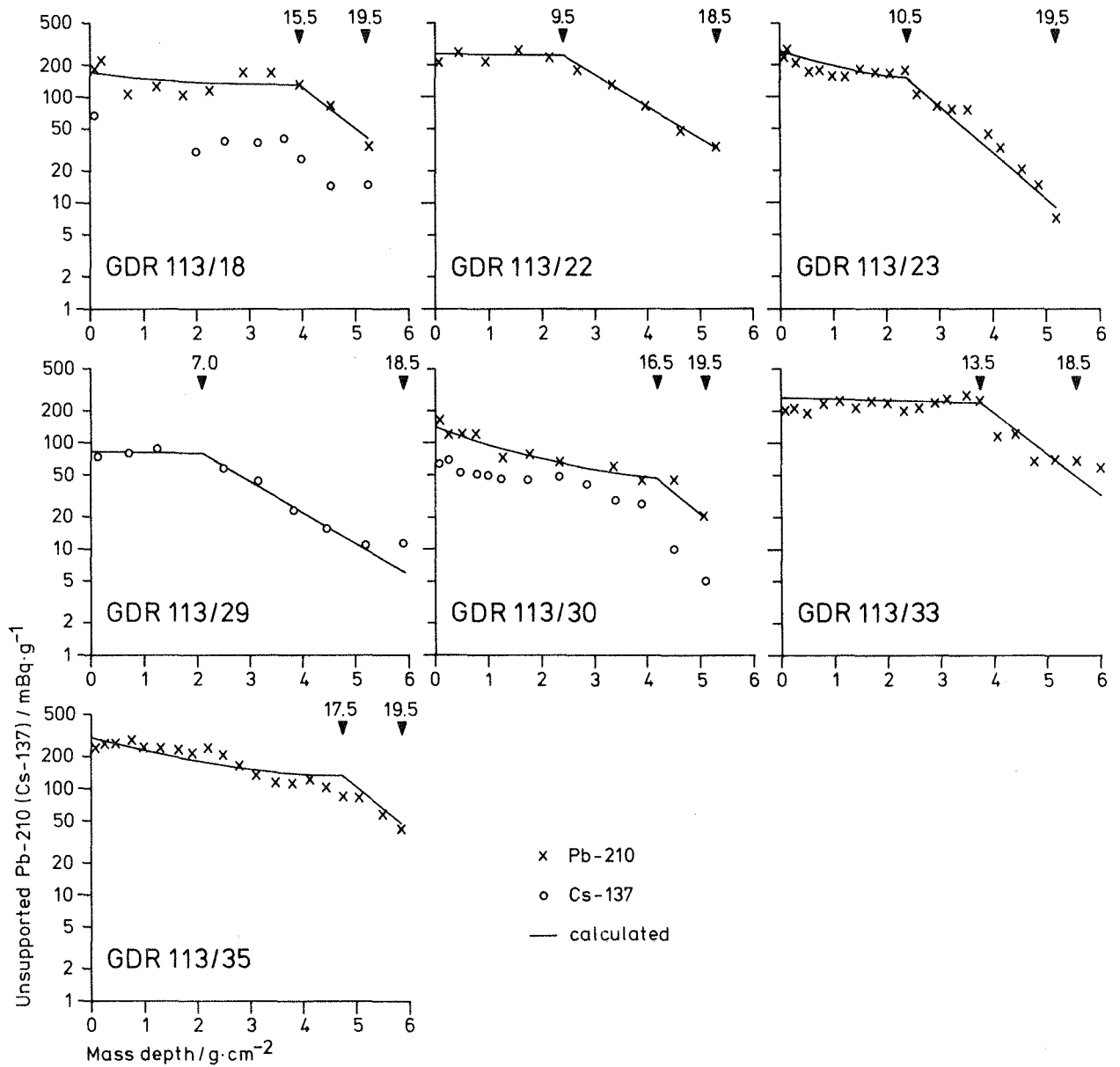
Figure 18  Measured and calculated profiles of unsupported Pb-210 and Cs-137 in
7 parallel cores from station GDR 113. (The arrows indicate different
linear core depths, given in cm.)

REPORT OF THE PREPARATORY MEETING FOR
BALTIC SEA SEDIMENT STUDIES


Rostock, 4-6 January 1984


# 1 OPENING OF THE MEETING

## 1.1

Aarno Voipio, director of the Finnish Institute for Marine
Research opened the meeting and welcomed the participants from
all the Baltic countries. Dr. Dieter Lange welcomed the par-
ticipants on behalf of the Institut für Meereskunde, Warnemünde.


## 1.2

Dr. Lauri Niemistö was appointed as Chairman. The list of par-
ticipants is attached as Annex 1.


# 2 RELATION OF SEDIMENT STUDIES TO EXISTING INTERNATIONAL ORGANISATIONS COVERING THE BALTIC SEA AREA

Dr. Lauri Niemistö reviewed the background for the work to be
discussed during the meeting. He stressed that the ICES/SCOR
Working Group expected to have a report on the Baltic Sea
sediment studies no later than 1986. The Helsinki Commission
(HELCOM) has also expressed a great interest in sediment studies
in the Baltic Sea although they themselves have not started these
studies.


# 3 REPORT ON THE ICES/SCOR INTERCALIBRATION EXERCISE FOR PILOT SEDIMENT STUDIES IN THE BALTIC SEA - STEPS 1 AND 2

Dr. Lutz Brügmann presented the report of the first step. This
preliminary report has been sent to the majority of the partici-
pants and the following conclusions from the report were accepted
by the group.

The results reported by the laboratories participating in this
exercise indicate that:


a) The distributed reference samples seem to be well homogenized
   and not remarkably contaminated during the different steps of
   their preparation. There was likewise no indication that
   single samples were contaminated during packing or shipping.
   There were several cases where laboratories reported values
   which were omitted later as "outliers", but this had to be
   done routinely for both independent samples ABSS and MBSS,
   presumably reflecting inproper treatment during the analytical
   procedures.

b) The performance of the data for most determinands (Zn, Cu, Pb, Mn, Fe, Ni, C-org., Al, Co) was relatively good. Unacceptable, however, were the deviations in the reported results for Hg, Cd, Cr and C-inorg.

c) The approach of using a simple and quick weak-leaching method, to get an idea of the potential bio-available fractions of heavy metals in organic rich fine-grained sediments could be confirmed. For elements relevant from the toxicological point of view, such as Pb, Cd and Zn, nearly the total contents present in the samples could be extracted by 1 N HCl. For metals fixed primarily in the silicate lattice, (e.g., Al, Fe, Cr, Mn), only between about 5% and 30% was released by this agent. Medium amounts (40-60%) became available for Cu, Ni and Co.

d) With the exception of the primarily lattice-bound elements Al, Fe and Mn (possibly Cr, too, but this could not be shown due to the high standard deviation), most of the oxidizing decomposition procedures used without HF addition released the investigated heavy metals entirely from both samples.

It was agreed that the results of the intercalibration were not satisfactory for Hg and Cd. A small group discussed in more detail the results from the Baltic Sea laboratories, including the analytical procedure. The Baltic Sea laboratories were neither worse nor better than the other laboratories. 9 laboratories from these countries analysed for Cd and 7 for Hg, but only 4 laboratories produced acceptable results for Hg.

It was decided that Arne Jensen should, as intersessional work, distribute solutions of samples ABSS and MBSS, a blank and a standard solution to the Baltic Sea laboratories and ask for at least triplicate determinations for cadmium. In addition, a new sediment sample should be distributed and analysed for Hg and Cd in at least triplicate. As the majority of laboratories were present at the meeting, no information was necessary in advance. In a letter some advice for improvement of methods would be given and the suggestion to analyse, e.g., the Canadian sediment reference material for checking the accuracy of the method. The deadline for returning of results is 31 January, 1985. A report can then be presented at the ICES/SCOR Working Group meeting.

It was suggested that the Baltic Sea Laboratories, when analysing sediments, should include one of the intercalibration sediments in the analysis. The results should then be sent to Lutz Brügmann who could prepare a new report within a few years. Lutz Brügmann has more samples available.

Dr. Lutz Brügmann presented a verbal preliminary report of the second step of the sediment intercalibration exercise and the data resulting from this second step were discussed. Dating was carried out by 7 laboratories. Their results showed:

- that the 20 cm cores used were too short to cover background values for e.g. 210-Pb in the sea area investigated (background values could, however, be obtained from Ra-226 measurements).

- that an increasing sedimentation could probably be observed towards the top of the cores, beginning in about the 1960s. The lower parts showed a sedimentation rate of about 1.5 mm per year. However, further interpretation of these results is necessary.

- for the proper use of 137-Cs data for dating, information on the fluctuations of inflowing 137-Cs into the Baltic originating, e.g., from Windscale/Sellafield, must be considered.

- that in principle the data from most of the different laboratories are intercomparable.

- 6 laboratories took part in the geochemical phase of the intercalibration. The results confirm the output from the first step, that good comparability is obtained for elements such as Pb, Zn and Cu and unacceptable deviations for Hg and Cd. Most laboratories were able, from an analytical point of view, to detect gradients in metal profiles which exhibited high concentrations between about 8 and 13 cm depth and which decreased towards the bottom of the cores (Ni, Cu, Zn, Pb, Cd, Hg); for Mn inverse gradients were observed.

Some laboratories have not sent results yet from the second phase. However, they are urged to do so. Results will be accepted until 31 December 1984.

A small group which included only 5 persons, all of whom have dated a core, discussed the dating results and how better agreement could be achieved. The group agreed the following conclusions:

- Useful sediment dating techniques are the Pb-210 method or that supported by the Cs-137 method, or other proper methods.

- The participants determine Pb-210 via Po-210 in essentially the same way. However, there exists some differences in the measured shape of the Pb-210 profiles (Pb-210 activity versus depth). It cannot be decided at this moment whether these differences originate from the fact that different cores are used for dating or not. The calculated sediment accumulation is probably due to the difficulties of estimating the supported Pb-210 values, and the use of different calculating methods.

- It was suggested that another core should be dated by at least one laboratory to decide upon the reason for the observed differences (natural variability or variability caused by the whole dating procedure).

- The participants decided to distribute the primary data to each other before the end of October in order to make further discussions about interpretation methods possible.

- Dr. P. Madsen agreed to prepare a report of this intersessional work to be attached later to the report of the intercalibration exercise. Deadline 31 January 1985.

## 4 NATIONAL REPORTS

National reports presenting on-going and planned studies in relation to sediments were presented by all the countries.


## 5 INTERPRETATION PROBLEMS IN RELATION TO POST-DEPOSITIONAL REDISTRIBUTION AND GEOCHEMICAL EFFECTS ON DETERMINANDS

Dr. Rolf Hallberg presented an introductory paper on this topic. A long discussion followed and it was agreed that the best areas for studying the pollution history of the Baltic Sea sediments are the deep basins with stagnant reduced waters.


## 6 DISCUSSION ON THE PARAMETERS AND METHODS FOR WHICH A READINESS FOR JOINT STUDIES EXIST

Under the presentation of the national reports, it was realized that a great amount of work already has been done in the Baltic Sea concerning sediments. All the countries have dated or are going to date cores as shown in the following:

| | | |
|---|---|---|
| Denmark | – | about 20 cores in the Southern Baltic Sea |
| | – | about 50 cores in the Danish Belts and Kattegat |
| Sweden | – | about 6 cores |
| Finland | – | about 15 cores |
| German Democratic Republic | – | about 10 cores |
| Federal Republic of Germany | – | about 5 cores |
| Poland | – | a few cores from 1975-1976 and same next year |
| USSR | – | about 25 cores |

The group decided that information on the extent of accumulation areas and all determinations of recent accumulation rates should be compiled on a map in the scale of approximately 1:2 mill.

Information on the Bothnian Sea, Bothnian Bay and the Gulf of Finland is to be compiled by L. Niemistö, and on the Baltic south of the Åland Islands by B. Larsen.

In order to achieve this, the members of this group are requested to send the following information:

- the results and positions of dated cores from the Baltic Sea containing information on recent accumulation rates.

- information on investigations carried out on the dated cores such as content of heavy metals, nutrients, sediment parameters and radionuclides.

- if it is found necessary copies of the sediment map by Winterhalter et al. (in Voipio (ed) : The Baltic Sea) will be distributed with some explanatory remarks to the appropriate people of this group. They are requested to assist in the necessary modifications of the map for the present purpose.

The information should be sent to Birger Larsen or Lauri Neimistö before the 31 December 1984. Birger Larsen and Lauri Niemistö will then on the basis of the received information prepare a report before the 1 April 1985. This report can be presented at ICES/SCOR meeting in May.

On the basis of the intercalibrations carried out and other information given at the meeting on the present knowledge, there was a consensus that a critical review on the contamination record in sediments, for use in mass balances for the Baltic Sea, can be made for the following determinands:

1) Organic carbon, total N and P.

2) Heavy metals considered, e.g., by the Helsinki Commission to be of highest priority. Adequate abilities to obtain inter-comparable results for Pb, Zn and Cu are available. With regard to the determination of Hg and Cd, further research is continuing in order to improve the analytical procedures.

The Group noted that no intercalibration has taken place on organochlorines and hydrocarbons. However, information on the content of these substances in the sediments is essential to a proper review of the contamination of the Baltic Sea. It is recommended that available information concerning these sub-stances should be compiled and evaluated. Intercalibration of the content of these substances in sediments is highly recommended.

It was a general understanding that basic sedimentological as well as physico-chemical data are necessary for proper inter-pretation of the contaminants mentioned above. Such information includes preferably: dry weight, grain size distribution, content and type of clay minerals, pH, Eh, Fe, Mn and alkalinity. For interpretation of analytical results it is necessary to date the sediment samples with a proper method (e.g. 210Pb, 137Cs).

Study of man-made radionuclides can greatly enhance the understanding of the circulation and the evaluation of the mass balances of the other contaminants dealt with above.


## 7 COOPERATIVE ACTIVITIES

The Meeting considered the need and possibilities to organize a pilot study reflected in the report of ICES/SCOR Working Group. The Meeting felt that there might not at the moment be an urgent need to organize such a pilot study in the sense of starting with sediment sampling covering most of the representative net sedi-mentation areas of the Baltic Sea, and/or to work out and improve methodologics for a later proper sediment monitoring. On the other hand there seems to be a large amount of experimental material of satisfactory quality which would permit the preparat-ion of a critical review concerning the contamination of sedi-ments as already indicated above.

The Meeting noted that there are several activities going within the framework of ICES and the Helsinki Commission to study

further the possibilities to facilitate oceanographic research, especially sediment sampling, in the various parts of the Baltic Sea area. On the other hand, the Meeting was informed by several participants of the possibilities of obtaining sediment cores to be taken during the cruises organized by their countries. The Meeting recommended the use of such possibilities to obtain sediment samples from the sea areas of the greatest interest.


## 8 REPORT

The report was reviewed and approved by the Group and the Meeting closed with many thanks to the hosts of the meeting, and the representatives of the Institute of Marine Research, Helsinki, for their excellent arrangements.

## ANNEX 1

## THE PREPARATORY MEETING FOR BALTIC SEA SEDIMENT STUDIES

Rostock, 4-6 January 1984

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## Indication of spine colours

Reports of the Advisory Committee
on Fishery Management ......................... Red

Reports of the Advisory Committee on
Marine Pollution ............................. Yellow

Fish Assessment Reports ....................... Grey

Pollution Studies ............................. Green

Others ........................................ Black

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