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Quality assurance of sediment sampling and the distribution of trace elements in the Baltic Sea sediments

Matti Perttilä

Finnish Institute of Marine Research
PO Box 33, FIN-00931 Helsinki Finland

Horst Albrecht

Bundesamt für Seeschiffahrt und Hydrographie
Bernhard Nocht Strasse 78
D-2000 Hamburg 36 Germany

Abstract

The Sediment Baseline Study was planned and organized by a special group within the ICES Working Group on Baltic Marine Environment as an outcome of the attempt to review the multitude of pollution studies of the Baltic Sea Sediments. In this contribution, we report the general conduct of the study, review the experiences gained with respect to quality assurance, give a tentative list of procedures necessary for selecting sedimentation sites suitable for monitoring work, together with a preliminary characterization of the trace element distribution in the surface sediments.The most important elements which must be considered and/or included and also well documented in a comprehensive quality assurance plan for sediment sampling to ensure that the data generated has the appropriate quality include the description of the project including the objectives and the data quality needed, site selection criteria, sampling period frequency, sampling procedures for each major measurement including subsampling, storage procedures and sample treatment, and a plan for laboratory quality control checks. Each step of the procedures should be duly documented in order to provide a possibility for tracing the results both in time and in quality.

The ICES/HELCOM Baltic Sea Sediment Baseline Study served as an example where the quality aspects of sampling and analysis were tested and elaborated.

Introduction

Marine sediments provide a possibility to assess in a consistent manner the changes in the environment. Not only the present-day distribution of contaminants can be exposed, but also at the same time the history of the sampling site, providing certain hydrochemical and biological conditions are met. The use of biota as a pollution indicator in the Baltic Sea suffers from the drawback that only very few, if any, species are represented in all the subareas in sufficiently large quantities.

In order to assess the use of sediments as environmental indicator medium, the pollutant studies in the Baltic Sea sediments were reviewed recently (Perttilä and Brügmann, 1992). One of the conclusions was that while a large amount of work has been invested in the sediment studies, both sampling and analysis methods, as well as the positions of the sampling sites, have been selected using varying criteria. For these reasons the reported concentrations are seldom comparable. A suggestion was made to carry out a baseline study covering all the important net sedimentation areas of the Baltic Sea (Fig. 1).

The Sediment Baseline Study was planned and organized within the ICES Working Group on Baltic Marine Environment. In this contribution, we report the general conduct of the study, give a list of the selected sedimentation sites, together with a preliminary characterization of the sites and approximate sedimentation rates, and trace element distribution in the surface sediments to the extent they are available at present.

During the process of the Sediment Baseline Study, several new contributions have been published in other connections on the distribution of pollutant concentrations in the Baltic Sea sediments, not listed in the aforementioned Review. These include the Gulf of Bothnia (Leivuori and Niemistö, 1994), the Gdansk Bay together with the south-eastern Baltic Proper (Szczepanska and Uscinowicz, 1994), and preliminary reports on the Riga Bay project of the Nordic Council of Ministers.

Quality aspects of the sediment sampling have been recently reviewed by Perttilä and Pedersen (1996). Their recommendations are largely based on the experiences of the Sediment Baseline Study.

Aspects of quality assurance in sediment work

Quality assurance is the total system of activities required to guarantee the appropriate quality of the product and is therefore an integrated part of all sampling programs. The sample to be analyzed has to be been taken adequately, otherwise all efforts in the laboratory for good quality control are futile, since the obtained analytical result, however accurate, does not represent the concentration at the sampling site.

A relevant quality assurance procedure is highly dependent on the future use of the data. In consequence, the objectives of the project should be well defined and clearly stated. In principle the user of the data also should define the necessary data quality parameters like precision, comparability, and accuracy.

Monitoring of the geographical distribution and time trends of element/compound concentrations in the sediments is often the aim of the study. The sediments provide an excellent archive in which to study the past and present of environmental pollution. However, especially in this case the sampling site selection is of crucial importance. The site should be representative of the sea area and it should have peaceful sedimentation conditions. Because of internal currents and other varying hydrographic effects, the net sedimentation rate may change significantly from site to site. For monitoring purposes it is essential to repeat the sampling at pre-defined intervals at exactly the same sedimentation sites. The first selection of a position for pollution monitoring sampling should thus be carried out with care. The following aspects should be considered:

- Hydrography (currents, vertical structure of water mass)
- Structure of the sedimentation basin
- Benthic communities (bioturbation)
- Rate of sedimentation
- Sediment structure (overall topography and the fine structure of the sediment surface

In highly polluted areas (eg. in regions where dumping of military wastes is known to have occurred), special precautions must be taken for clean-up procedures in cases of accidental lifting of hazardous materials on deck.

Chemicals are carried to the sediments mainly via sedimentation, that is, via the sedimenting particles, which "scavenge" the water column of pollutants, as well as feed pellets and inorganic detrital particles. The main part of the sedimenting particles are composed of aggregates of dead plankton, in or on which the pollutants have accumulated or adsorbed. Evidently, in the absence of strong currents, the strongest pollution signals are found in the vicinity of the pollution source, and the signal weakens with an increasing distance from the source.

However, very seldom the primary sedimentation site is the final sink for materials. More often, macroscale current system lifts (resuspends) the material from the sediment surface and transports it gradually to the final sink. E.g. in the Baltic Sea, where the bottom topography is very irregular, there are nevertheless only a very few final sedimentation basins in each sea area. Also the general hydrography should be considered. The structuring of the water column may prevent the vertical cycling of the water mass and the penetration of atmospheric oxygen to the bottom and anoxic and oxic conditions may vary. A continuous monitoring in such areas will usually not be meaningful as,

- precipitation/dissolution properties vary with the redox potential for certain compounds (eg. iron and phosphate)

-the benthic communities may change as a consequence of the oxygen availability which in turn will affect the bioturbation of the sediment surface and disturb the analytical signal

-the diagenetic processes within the sediment vary with the redox potential e.g. through the varying solubility

These aspects should be studied and considered before a decision is taken on the site selection for e.g. long-term environmental monitoring.

The bottom topography is very seldom monotonous in coastal and estuarine areas where sediments may have their most significant pollution signals. Rather, the overall basin is often divided into smaller sedimentation "holes", separated by sharp edges. The whole area should therefore be scanned by echo-sounding before the sampling position is selected. The navigation system of many ships usually allows the coupling of navigation data with the echogram data, so that the bottom topography can be described visually in a three-dimensional picture (Fig. 3). The most promising areas can be selected from such an echogram data. However, the bottom sediment bed cannot be deduced only from the topography. The scanning of the area should also be carried out using a low-frequency (<10kHz) sounding, which, while giving a signal of the sediment surface, also penetrates the surface and gives signal of other, deeper-lying reflector surfaces. Thus the depth of the soft-sediment layer can be measured and used for the selection of the most suitable position. To a certain extent, also some other qualities of the sediment bed can be deduced from a low-frequency echogram; e.g. the occurrence of gas, which probably has mixed up the sediment layer or will mix the sample when taken it on board.

In shallow areas (<200m), the possibility of mechanical disturbance of the bottom should also be checked before sampling, e.g. from the bottom trawling for fishery purposes. The most powerful method for the detection of the fine-structure of the sediment surface is the side-scan sonar (SSS). An experienced SSS user can easily detect e.g. the signs of bottom trawling in the echograms. Again, in order to avoid mixed-up areas it is essential to be able to track down the positions of the SSS pictures by means of coupling to the ship's navigation data.

All three above mentioned methods should be applied when selecting a suitable position for a representative sediment sampling. The two first sources of information can nowadays be obtained commercially in a single computerized instrument, but, as described above, they can relatively easily be obtained combining the echo-sounding data with the ship's navigation data. Using e.g. any surface contouring program, a three-dimensional picture of the bottom can be constructed.

In spite of all mapping techniques, the final test for selection of a position is provided by the visual inspection of a test core. The sediment core description should be documentated for future for comparisons. Changes in the sediment structure and the sedimentation conditions do occur under exceptional conditions, and it is worth while to visually make sure that no changes have taken place.

One of the prerequisites of quality is the documented repeatability of the procedures. In the earlier days of marine research, we were happy if we could be confident of reaching the sampling position to within a couple of cables. Using the decca navigation network, anything more accurate would indeed have been to ask for too much and we could in no way be certain of having sampled at exactly the same position as earlier especially when taking the difficulties of keeping the ship on position in rough weather in account.

The present-day global positioning system using satellite signals allows for positioning to better that +/- 20m. While in open-sea water sampling a precision to this degree is perhaps not needed, is indeed mandatory in pollution monitoring in sediments especially in areas with a complicated bottom topography as e.g. in the Baltic Sea, where apparently similar sedimentation basins are separated by sharp underwater mountains. As the near-bottom current system may be totally different from one basin to another, also the sedimentation rates may vary strongly because of the different horizontal transportation of the sedimenting particles. Another aspect calling for exact positioning is the fact that the benthic communities are ordinarily very stable. A benthic community may have a profound effect on the sediment surface by bioturbation which as mentioned earlier, will effect the concentrations measured.

Computer-aided navigation of today enables the ship to stay exactly on position for prolonged periods of time. This can be even improved by means of taut-wire technique. In this technique, a weight is lowered to the bottom and the wire is kept tight via an automatic tension compensating unit. Small deviations in the angle of the wire with respect to the vertical line are sensed by a circular sensor. The sensor signals are passed to the navigation computer which then gives orders to the propulsion mechanism for corrective measures. In depths less than 400m this techniques enables the ship to keep the position within a radius of a few meters.

Sampling devices

The most common sediment samplers are the box corer and the gravity corer. The box corer has the advantage that, due to its large surface area, the sampler has to be operated only once, and the resulting sample can then be subsampled several times on deck. The best results are obtained on very soft bottoms, and especially when only the sediment surface, i.e. the most recently deposited layers, need to be studied. On the other hand, the gravity corer (Niemistö, 1974) penetrates sufficiently deep even if the bottom consistency is somewhat harder.

The ordinary gravity corer has the disadvantage that due to its inherent asymmetry it often hits the sediment surface at an angle. To overcome this drawback, a double corer has been developed (Fig. 2).

In very sandy and hard bottoms, neither box corer nor gravity corer gives satisfactory results. In such a case, a drilling corer might prove useful. The sampling vehicle is first lowered carefully on the sediment surface. With the sampler lying on the surface, the corer tube is then pressed slowly into the sediment by means of hydraulic pressure. Mechanical back and forth turning of the corer tube can also be applied to ease the penetration. However, it should be noted that hard bottoms are usually dispersive bottoms and consequently not suitable with respect to monitoring.

Sampling procedure

The actual sampling procedure in sediment work is considerably more demanding than in case of water chemistry. It needs a lot of experience to "feel" the correct rate of lowering of the sampler, and to raise the sampler out of the sediment without losing the information contained in the sampler (more specifically, without dropping the sediment and without disturbing the surface layer). Therefore, only an designated person should be allowed to handle the winch.

Whatever sampling method is used, the first step on deck should always be the visual inspection of the sediment. Any irregularities in the outlook of the sample should lead to the rejection of the core. The most common disturbances can be seen in the core surface, caused by the improper hitting of the sampler into the sediment, or irregularities during the lifting of the sample. Also, it can be seen if the sampler has hit the surface at an upright position. If not, the sample should be discarded. Strong bubble formation - due to the pressure difference - may also lead to the rejection of the sample and the sampling site.

A sediment core as a whole is seldom of interest for pollution studies. It must be subsampled. The core is cut down to suitably thin slices which are each stored in separate containers. In routine monitoring, only the sediment surface is often used for the analyses, but even in such cases a subsample is often taken from the deeper sediment core to provide "background" concentrations.

The subsampling is the procedure during which the sample is most exposed to contamination. However, the danger of contamination is not comparable to that when sea water samples are handled, because of the much higher natural concentrations of elements and substances in the sediments. The equipment naturally has to be cleaned thoroughly. The cutting instruments should be of neutral materials. For the most purposes, polyethylene and polystyrene plastics provide the most practical materials, which are easy to handle and easy to keep clean. In most cases, the cutting of the sediment sample is started from the top of the core presenting the most recent pollution levels - ordinarily the highest in the core, also due to diagenetic effects. As the slicing is then proceeded down towards diminishing concentrations, the greatest danger to contamination are the previous subsamples. In part this contamination can be avoided by rigorous and regular washing of the equipment between the cuttings. The best solution for the washing is the sea water. In some cases the partial mixing of subsamples cannot be avoided, since the usually very soft sediment surface layer, containing over 90% of water, easily slides down the inside of the core tube. If this sliding is considerable, there is no other way than to discard the sample.

The cutting instrument was calibrated, in order to ensure the regular thickness of the subsamples.

The ICES/HELCOM Baltic Sea Sediment Baseline Study

In view of the rather discouraging results on the comparability of analytical data from different laboratories (see, eg. Brügmann and Niemistö, 1987, Perttilä and Brügmann, 1993), one of the prerequisites set on the Sediment Baseline Study was to ensure a proper quality control for the work. The traceability of the work was controlled by means of rigorous documentation of sampling and pretreatment. Trace element analyses were carried out in two laboratories, the Bundesamt für Seeschiffahrt und Hydrographie (Hamburg, Germany), and the Finnish Institute of Marine Research (Helsinki). Analytical quality control was maintained by means of quality system in both laboratories. Moreover, both laboratories were at the same period participating in a major international quality assurance programme, the EU-QUASIMEME programme.

General aspects on the sedimentation in the Baltic Sea

In the bathymetric map of the Baltic Sea (Winterhalter 1981), several large basins are clearly discerned. In the bathymetric large scale map, however, the isobaths are drawn with 20 m intervals which makes it impossible to evaluate the small scale variations within a large basin. The small scale variations are either a result of differences in the basic topography, rocks, ridges etc. or some of them may be a result of the differences in the sedimentation.

The prevailing opinion has been that in the Baltic Sea there are basins in which the sediments form a final sink for many elements and substances. When benthic fauna is absent, the sediments in these basins are often laminated and seasonal changes layer by layer can be recognized. Many of the best examples of such sediments are found in the nearshore basins where shallow ridges and islands effectively shelter the local basin from any disturbances and erosion (eg. Morris &al. 1988).

Recently laminated sediments ranging from a few to some 30 - 35 laminae on the top of homogenous looking, older sediments have been found in the open Baltic Proper (Jonsson & al. 1990). An explanation for this change of facies has been assumed to be the long lasting stagnation and thereby the increased area of anoxic conditions with no bioturbation caused by benthic macrofauna. Former dynamic bottom areas populated with benthic animals have been changed to tranquil sedimentation bottom areas where seasonally influenced laminae are formed.

The Cs-137 activity can be followed down in the sediment core. At most of the stations of the Sediment Baselinew Study, the topmost sediment layers showed high activity, with a peak at the depth of 3-10 cm. In sediment layers below the peak, the Cs-137 activity decreased rapidly to background values. It can be assumed (Perttilä and Niemistö, 1993) that the sediment layer with the activity peak corresponds to the immediate Chernobyl fallout, giving thus a rough estimate of the net sedimentation rate.

The preliminary measurements of gamma emitting nuclides at least indicate, that the sediments chosen are sedimentation basins. This is confirmed at least partly by the depth to which the Chernobyl fallout of 137 Cs now seems to be buried. The clear echo sounding records of dune like formations and in some cases the direct video images of the sediment surface indicate that in some areas our understanding of the sedimentation process has to be reconsidered.

Bioturbation and relatively strong bottom-near currents (15 - 20 cm/s) near bottom current detach particles and aggregates from the sediment surface in several basins. Particles are then transported along the sediment surface. In some cases, the sediment surface seem to be rolled off by the current like miniature carpets. On some other sampling stations the macroscopic benthic animals were seen to dig into the sediment surface, and even a very faint water movement was transporting clouds of material away. All this influences the depth of the Chernobyl maximun fall out of 137 Cs and any other deposition characteristics of the sediments.

In addition to bioturbation and deep-water currents, also the presence of Fe/Mn-micronodules in surface sediments of many basins of the Baltic Sea obscures the interpretation of heavy metal contamination. Often, linear relations between Fe- and/or Mn-normalized ratios of heavy metal concentrations are used as contamination indicators. However, the drastic increase of those metals (e.g., Cu, Ni, Zn) in scarcely visible micronodules (less than about 2 mm) must be taken into account. Additionally, these relations are influenced by the diameter of the nodules (redox regime) which show, up to 2 mm, relatively high trace metal concentrations.

It appears that in most of the shallower basins with depths around 60 m or less, independent of the area of the Baltic Sea (Arkona and Mecklenburg basin in the South, the Gulf of Finland and the Gulf of Bothnia in the North), sedimentation is not permanent. The above described visually observed reworking of the sediment surface makes the vertical timescales uncertain and uncontinuous. This kind of sediments are probably less suitable for even low frequency monitoring.

The deeper basins often show massive sedimentary packages of soft sediments of recent character, as observed by echo soundings. In these basins, stagnant dead bottom periods alternate with nonstagnant periods characterized by a recolonisation of benthic fauna and thus a return of water movement. This alternation may govern the vertical sedimentary record, rendering age determination meaningless. Only the deepest parts of the Baltic Sea seem to act as final sinks for particles to form continuous packages of layers.

The distribution of many elements and compounds is to a certain extent determined by authigenic enrichment in anoxic sediments as sulphides. This seems to be especially the process by which occurs the precipitation of the elements Cd, Cu, Ni and Zn.

In many other shelf areas, e.g. in the North Sea, the surficial sediments are oxic. The thickness of the oxic layer varies, depending on the rate of sedimentation, and the availability of oxygen through physical water mixing, extending up to several centimeters. This oxic layer acts as an effective barrier, depending on the thickness and porosity, against the diffusion of dissolved metals from the overlying water to the underlying anoxic sediment. In the Baltic Sea, however, the prolonged periods of oxygen depletion in the central deep basins reduces, or even depletes the surficial oxic layer. Anoxic conditions are also occasionally observed even in the shallow parts of the Belt Sea below in late summer/early autumn. Under these conditions the sediment surface layer provides for a huge pool of elements with soluble oxidation forms, such as Fe(II) and Mn(II) compounds.

Increase of dissolved oxygen in the near-sediment water layer as a consequence of the salt water influxes into the Baltic Sea causes the oxidation of a great part of the dissolved Mn(II) and Fe(II) compounds and settling of the resulting hydroxides on the bottom. The resulting complexes bind an appreciable trace metal fraction (Moenke-Blankenburg et al., 1989).

Large-scale distribution of trace metals in the Baltic Sea sediments

The large-scale distribution of trace elements in the surficial sediments of the Baltic Sea are displayed in Fig. 4a-k.

Some trace elements, including Cd, Cu, Zn, Ni, As and V, tend to be enriched in sediments accumulating under anoxic or suboxic (Cd) waters, also in uncontaminated areas. Basins with frequently occurring anoxic conditions in the bottom water are those of the Baltic Proper (locations 180, 176, 171, 169, 167). The western Gotland Deep (location 178) also suffered from formation of H2S in the past. Suboxic or anoxic conditions were also observed earlier in some areas of the Gulf of Finland. The Gulf of Bothnia, however, is well ventilated. Trace element enrichment in this area cannot be explained by poor oxygen conditions.Trace element enrichment may be expressed in terms of enrichment factors (ef) or as excess concentrations (cxs) over background values. Maximum enrichment factors and excess concentrations detected during SBS are as follows (core number given in brackets):

max ef	**max cxs**

Cd:	100 (171)	12 μ/g (178)
Hg:	31 (193)	0.46 μg/g (193)
Pb:	12 (160)	185 μg/g (160)
Zn:	16 (171)	960 μg/g (180)
Cu:	13 (171)	180 μg/g (180)
Ni:	6.7 (180)	95 μg/g (180)
As:	31 (193)	240 μg/g (193)

Both, enrichment factors and excess concentrations, may be misleading in the case of strongly varying rates of sediment accumulation. If high rates of sediment accumulation are due to sedimentation of near by eroded old material, any anthropogenic signal will be diminished by dilution. In such cases the down core inventory (sum of excess concentration times mass per slide) may be more conclusive. In several SBS-cores background concentrations were not attained. The cores were to short to reach pre industrial layers. These are: all cores from the Gulf of Finland except GF1 (181), northern Baltic Proper (180) and Gdansk Deep (169). The inventory in these cores is underestimated to an unknown degree. Figs. 5a-e show the inventory of excess metals for Cd, Hg, Pb, Cu and Zn. Fig. 6 shows the inventory of total As.

Cadmium shows the highest enrichment factors and the highest inventory in the central basins (171, 178, 180) the inventory being even underestimated for 180. Concentrations and inventory of Cd in the Lübeck Bight are known to be affected by anthropogenic activities, as industrial wasted had been dumped into this area in the past. Anthropogenic influences are also expected to affect the Cd concentrations in other areas. They are, however, not easily deduced from measured concentrations. In some areas, e.g. at the deep water station 182 in the Gulf of Finland, the down core profiles of Cd seem to tell more about the history of the oxygen conditions in the bottom water than about inputs of Cd into these areas. In the well ventilated Gulf of Bothnia, however, observed higher concentrations and higher inventories (cores 192, 193) should be related to massive discharges of Cd into the Gulf.

In terms of enrichment factors Mercury is the second most enriched trace metal in Baltic sediments. (Arsenic will be discussed separately.) Highest Hg/Al ratios were detected in the Gulf of Bothnia (193), followed by the central basins (171, 180). In contrast to Cd, the inventory of Hgxs is small in the central basins and also in the Bornholm Deep (167), indicating absence of long range transport of Hg. By far the highest inventory was found in the eastern Gulf of Finland (185) and in the Kattegat (156), both inventories being even underestimated. Highest concentrations of Hg in the Gulf of Finland and in the Gulf of Bothnia were detected in subsurface sediments, indicating a strong reduction of load. According to datings performed by A. Jensen and according to the depth of the Cs-137 maximum, the load appears to have decreased since the 1970s.

The highest enrichment factors and excess concentrations of Lead were detected in the Lübeck Bight (160). Concentrations are also high in the central basins and in the Bothnian Bay (193). The inventories in the central basins, however, are low. Pb is expected to enter the marine environment mainly via the atmosphere. The low inventories in the central basins indicate that land-based discharges are also of importance.

Zinc is also an element which tends to be enriched in sediments underlying anoxic waters. Consequently, by far the highest enrichment factors and excess concentrations were detected in the central basins (171, 180). The inventory in the Lübeck Bight (160), originating mainly form past dumping of industrial wastes, is higher than in the Gotland Deep (171) but lower than in the northern Baltic Proper (180). In addition to location 180, high inventories were also detected in the Gdansk Deep (169) and in the eastern Gulf of Finland (185), all three of them being even underestimated. In contrast to the Bothnian Sea (190, 192), showing moderate inventories, the load of Zn to the Bothnian Bay seems to be low.

Cu again has highest enrichment factors in the central basins (171, 178, 180). As there is some uncertainty regarding background values of Cu, there are some indications that background Cu/Al ratios may vary within the Baltic Sea, the calculated inventory of Cuxs may also be uncertain to some degree. Nonetheless, the inventories are high in the Gdansk Deep (169), the northern Baltic Proper (180) and in the eastern Gulf of Finland (185), all three inventories being even underestimates.

Nickel is almost exclusively enriched in the central basins. There are very minor indications only of enrichment in other areas (Gulf of Bothnia, Kiel Bight).

Chromium-Aluminium ratios vary little only throughout the Baltic. Slightly higher ratios were detected at the "Lithuania" position (170). In contrast anomalously low ratios were detected in the southern Gulf of Finland (183). The SBS cores show little evidence of accumulation of excess Chromium, although other studies revealed very high local concentration maxima in the Bothnian Bay and in the Bothnian Sea, and the highest individual values in the eastern Gulf of Finland.

Arsenic enrichment factors and inventories area very high in the Bothnian Bay (195, 193) and the northern Bothnian Sea (192). This is almost certainly due to very high industrial discharges which took place there fore some decades until the early

Summarizing, the present data indicates that the lateral distribution of elements like Cd, Cr, Cu and Ni are affected by an effective transport to the central basin, possibly being sedimented also effectively due to the often anoxic conditions. Mn and Fe are governed by the redox conditions. In addition, As, Cd, Pb and possibly Hg seem to be representative of local pollution. The share of atmospheric input is still at present only roughly estimated, but represents probably a determining source for metals found in the sediments of the Baltic Proper.

Leivuori and Niemistö have reported the results of cores taken during the Baseline Study and the Year of the Gulf of Bothnia (Leivuori and Niemistö, 1994). They note that in the Gulf of Bothnia, the rapid land uplift exposes former accumulated sediments to erosion and the mixed material flow towards the deepest basins of the Gulf. Close to the outlets of the industrial areas, high concentrations of mercury, arsenic and cadmium are detected. In areas shallower than 60m, the net accumulation is practically nonexistent, and accordingly there is a continuous net flow to the central basins. Therefore no simple change in concentration vs. distance from outlet cannot be found in the sediments. The determining factor controlling the trace element concentratiuons seems to be the depth of the station area; the deeper the basin, the more permanently the elements are trapped in the sediments.

Compared to the Bothnian Sea, the Bothnian Bay sediments contain relatively high concentrations of arsenic, cadmium, lead and mercury (Leivuori and Niemistö, 1994, present results). For most other elements, the concentrations are roughly the same in the two areas. A budget calculation shows that practically all the discharged lead is sedimented in the respective basins, while for mercury, cadmium, copper and zinc the input is not in balance with the estimated sedimentation.

Oradovski et al. (unpublished results) have covered the eastern end and the southern side of the Gulf of Finland, as well as the eastern Baltic Proper at a relatively dense station grid. They report a very variable character of the trace element concentrations in the surface sediments, finding the highest concentrations of all metals in the vicinity of the Sant Petersburg and Vyborg. In the Gulf of Finland, high concentrations were also found in the central parts as well as in the northern Baltic Proper. Low values were found in the Narva Bay area. Oradovski et al. note that the explanation for the high trace element concentrations found in the northern Baltic Proper station (Teili1) is possibly due to the fact that this station is the deepest one in its area, and thus acts as a permanent trap for sedimenting material.

It appears that in several cases, especially in the northern parts of the Baltic Sea, the stations covered during the Baseline Study yielded excellent dating by means of ^{210}Pb. However, is the central areas, notably at the eastern and western Gotland Deep areas, a very poor ^{210}Pb distribution was obtained. As especially the eastern Gotland Deep serves as an inofficial reference station for many sediment studies carried out in the Baltic Sea, the dating results are somewhat disappointing. It would appear that in the central Baltic Sea area, a drastic sediment movement may have taken place, changing the sediment structure down to the depth of some 5 cm.

The differences and drawbacks of the different dating methods used during the Baseline Study are still under debate. The ^{137}Cs method, especially in the Gulf of Finland and the Gulf of Bothnia, appears to yield a very distinct signal of the "Chernobyl level", the level formed during 1986, the year of the nuclear catastrophy in White Russia. Lamination of the undisturbed sediments has been in certain cases proved to provide a useful method for determining the linear accumulation rate, but controversial have also been expressed. A these methods were all in use during the Baseline Study, it was considered worthwhile to carry a comparative study of the three methods, but the results are still under debate.

Conclusions

Cd and Hg are the two most enriched metals in the sediments. Gradients of decreasing metal concentrations with increasing core depths and from the land-based sources in an offshore direction are revealed in at least the Gulf of Bothnia, where results from the detailed programme of the Year of the Gulf of Bothnia are considered together with the Baseline Study results. In most of the areas now considered as contaminated the situation did not change until 1980.

The Gotland Deep, however, shows striking differences in the depth, thickness and structure of varves. The samples were of a totally different character than expected. On the top of the samples there was a 10 cm thick fluffy homogenous looking layer of very watery, loose grayish sediment. In 1992, a similar, but thinner layer had already been observed (Niemistö 1992).

In the Gulf of Finland, the recent changes development has been the opposite. The halocline so characteristic at the depth of some 50 m in the western Gulf and at 30 m in the East has been degrading slowly as a consequence of the decreasing salinity (Perttilä & al. 1995). The recent inflows of high-salinity sea water into the Baltic Sea have now ended this development at least temporarily. Several seasonal turnovers of the whole water body have obviously taken place resulting in oxidizing conditions at the sediments surfaces down to 80 - 85m depth. The benthic fauna has recolonized these areas (Andersin & Sandler 1991). The topmost laminae of the sediments have disappeared probably as a result of bioturbation. The sedimentation basins in the Gulf of Finland are numerous and a mosaic of small basins is characteristic of the Finnish side where the crystalline Pre Cambrian bedrock dominates with rugged forms. On the Estonian side the Cambrian and Ordovician basement has smoothened the ruggy forms and some larger sedimentation basins are found.

In the Gulf of Bothnia the dominant feature is the almost constant erosion of the older sediments in the less than 60 - 70 m deep coastal areas as a result of land upheaval which continuously rises former sedimentation bottoms up to the hydrodynamically active zone. The eroded material is transported towards the deeps. The present sedimentation contains a mixture of material of very old and present autochtonous origin.

In the Danish marine area, extended investigations of mud accumulation rates and trace metal concentrations in sediments have been carried out in recent years (Pheiffer-Madsen and Larsen, 1986). Only 25 % of the cores showed a mixing depth of less than 2.5 cm and a mixing coefficient of less than 0.5 $cm^2 yr^{-1}$. This means that most cores are rather heavily disturbed in the surface layers.

The problem of distinguishing between anthropogenic and diagenetic influences on the observed vertical trace-metal profiles and their horizontal distribution patterns cannot be solved completely.

Large amounts of potentially toxic metals (Cd, Hg, Pb, Zn) are stored in the sediments in remobilizable binding forms.

Picture legends

Fig. 1. The Baltic Sea Sediment Baseline Study cruise map

Fig. 2. Gemini sampler

Fig. 3. Example of bottom topography mapping (Bruun, 1996)

Fig. 4 Large scale distribution of trace elements in the surficial sediments of the Baltic Sea. Sources: Sediment Baseline Study (Leivuori 1996), The Year of the Gulf of Bothnia 1991 (Leivuori and Niemistö 1995), and Nordic Council of Ministers-Riga Bay Project (Leivuori and Niemistö, unpublished results) (Figures prepared with the Data Assimilation System (DAS) which is under development at the Department of Systems Ecology, Stockholm University). a)cadmium, b)lead, c)mercury, d)zinc, e)copper, f)chromium, g)arsene, h)nickel, i)iron, j)aluminium, k)lithium

Fig 5. Excess concentrations for a)Cd, b)Hg, c)Pb, d)Cu and e)Zn

Fig.6. Inventory for total As

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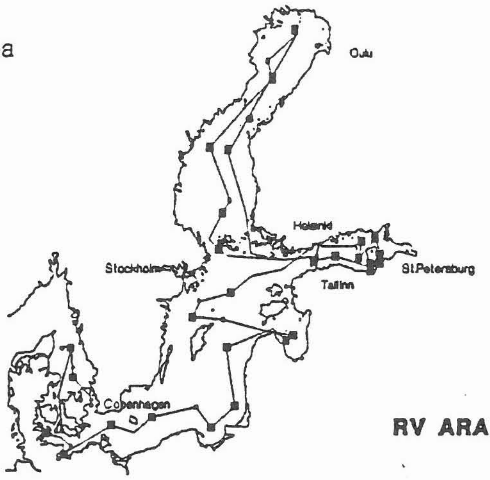
Fig. 1. Cruise itinerary of the 1993 ICES/Helcom Sediment Baseline Study

13.6. - 9.7.1993

Baltic Sea



RV ARANDA

Finnish Institute of Marine Research

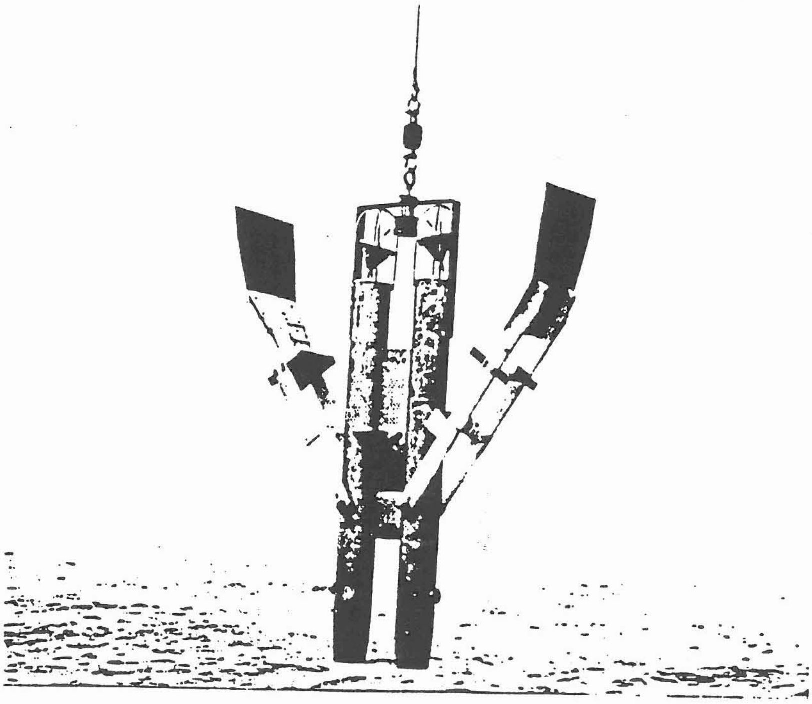
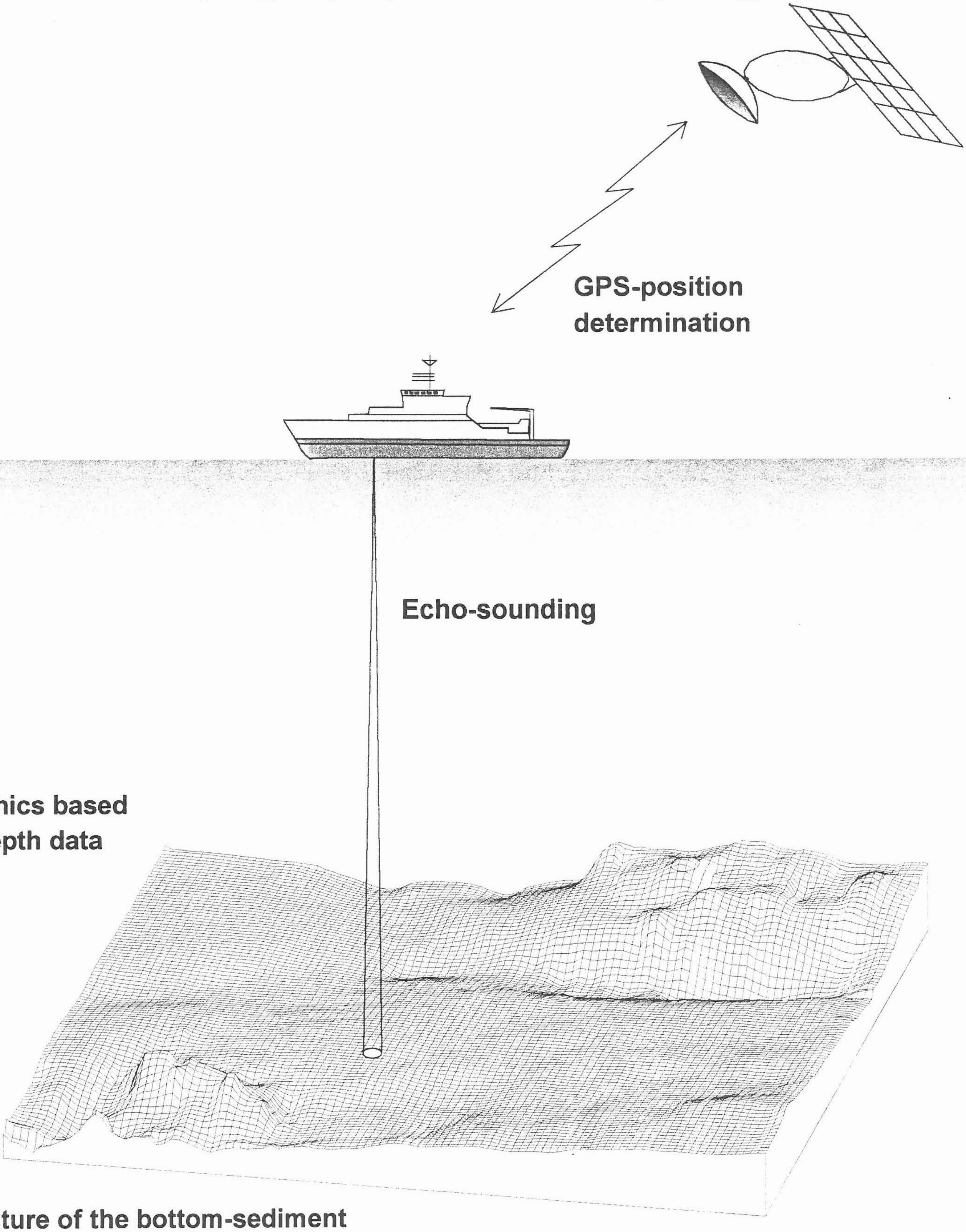


Fig. 2 . GEMINI double sediment sampler ready to descend

Bottom-topography of the sampling areas



GPS-position
determination

Echo-sounding

Graphics based
on depth data

Structure of the bottom-sediment

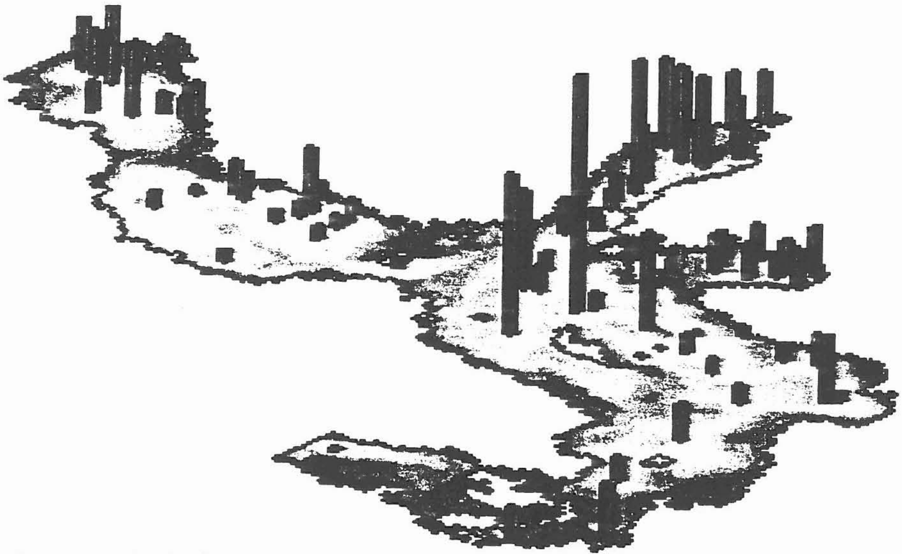


Fig. 4a. Cadmium

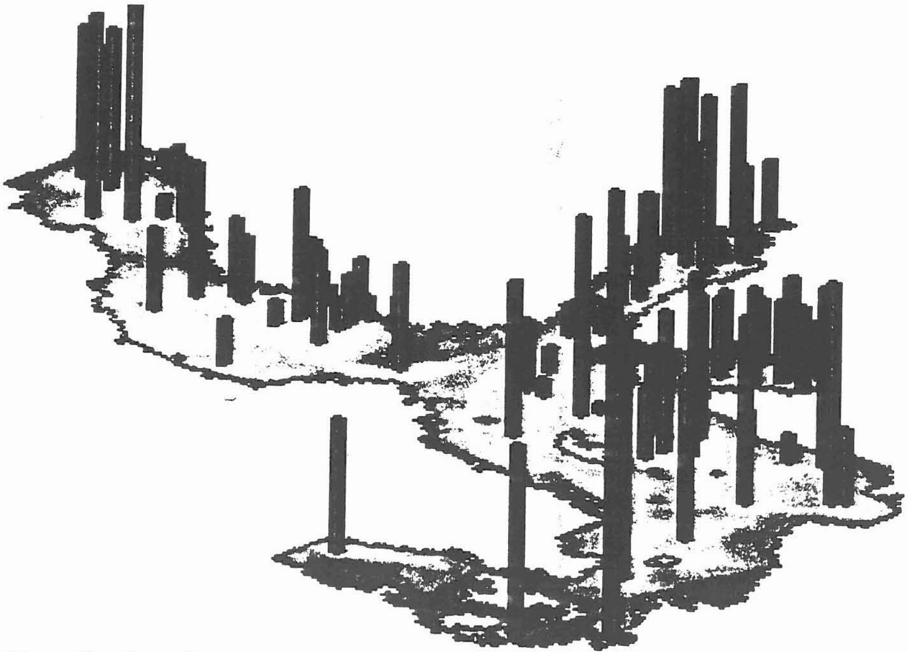


Fig. 4b. Lead

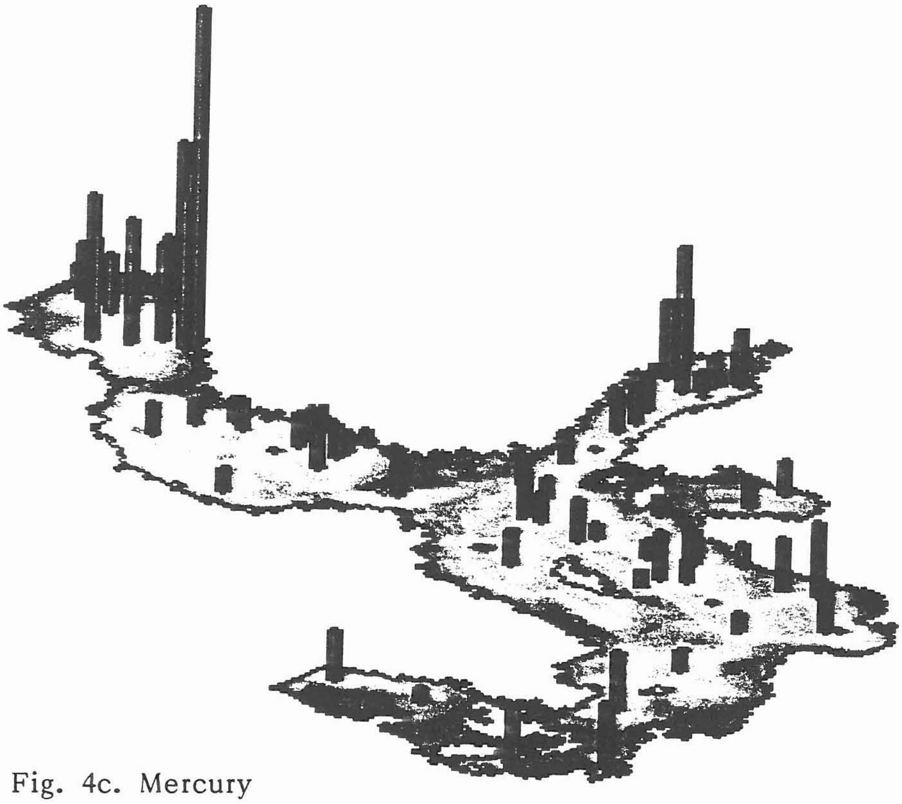
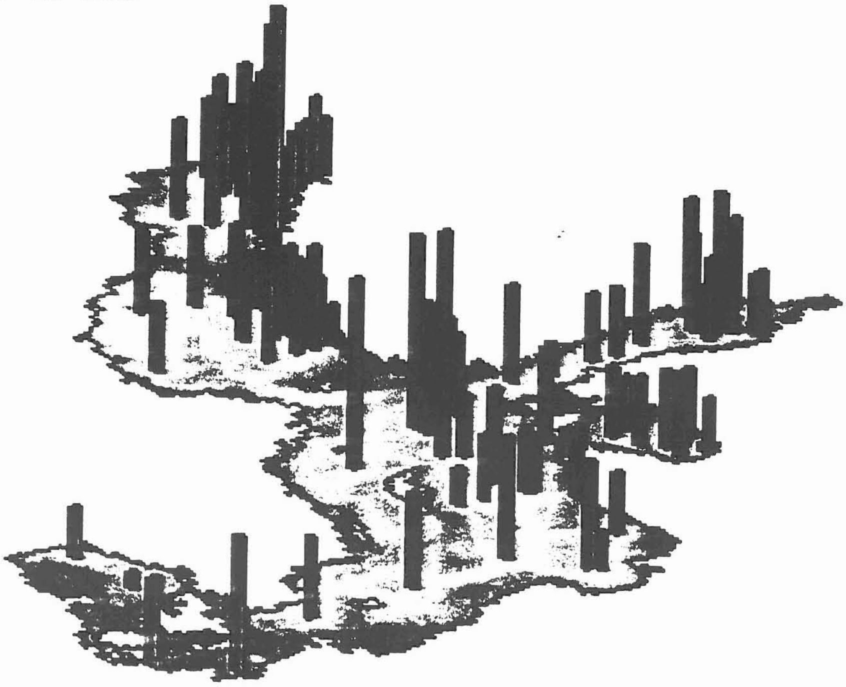


Fig. 4c. Mercury

Fig. 4d. Zinc



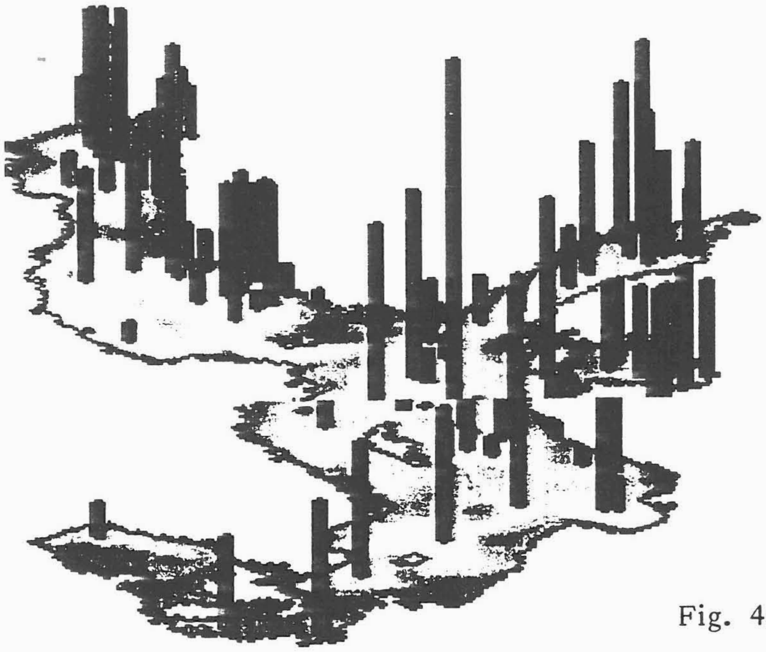


Fig. 4e. Copper

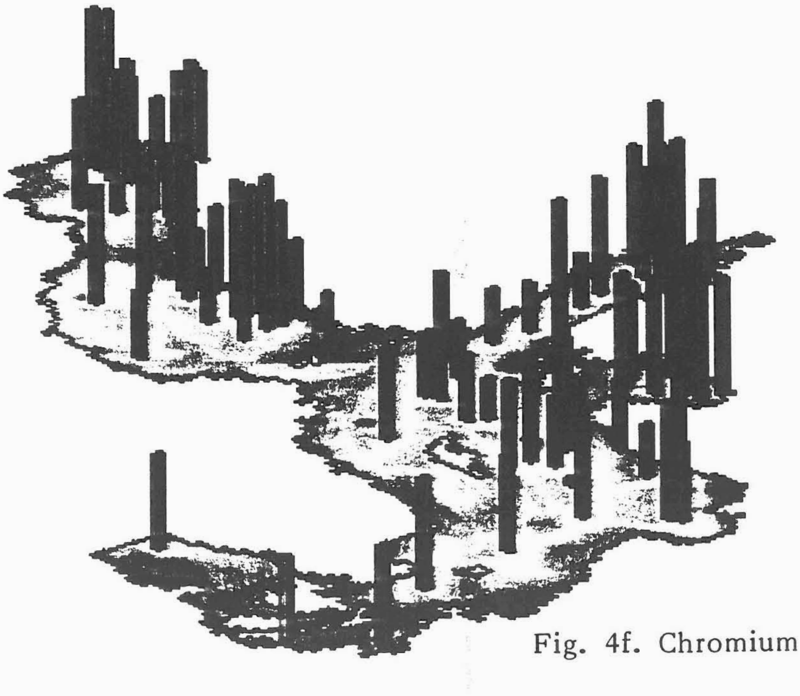


Fig. 4f. Chromium

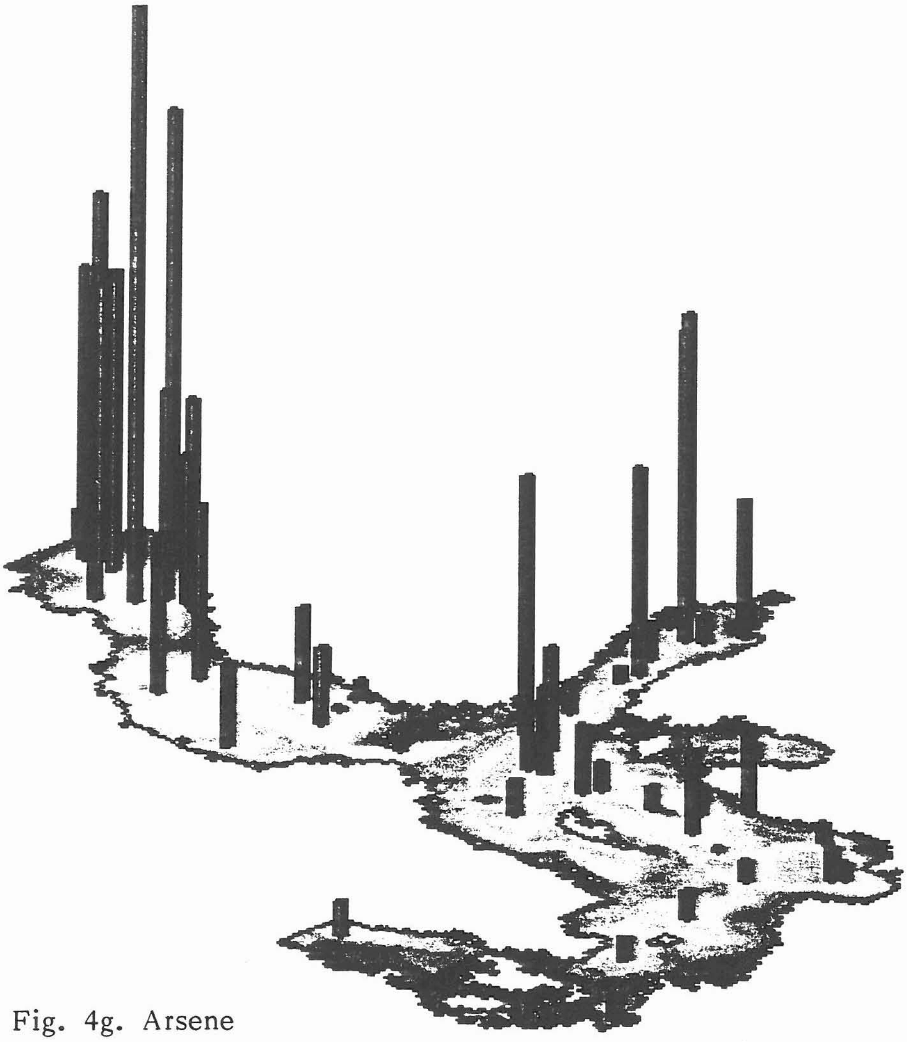
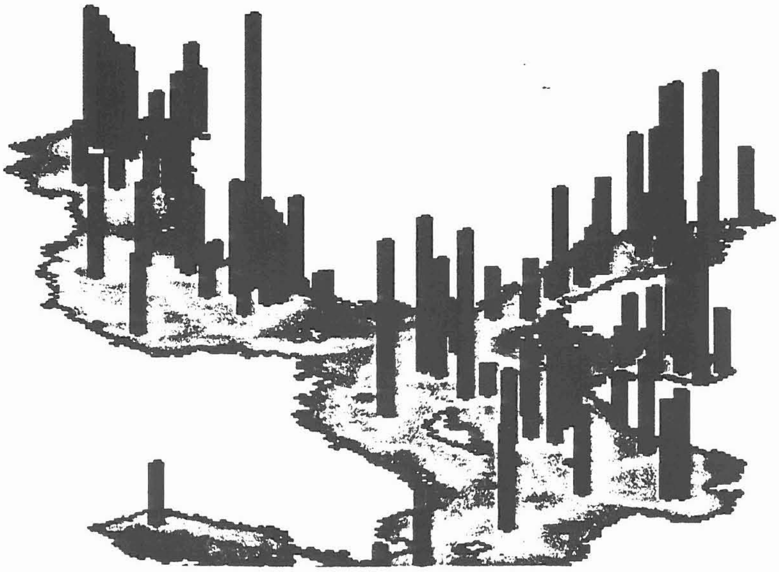


Fig. 4g. Arsene

Fig. 4h. Nickel



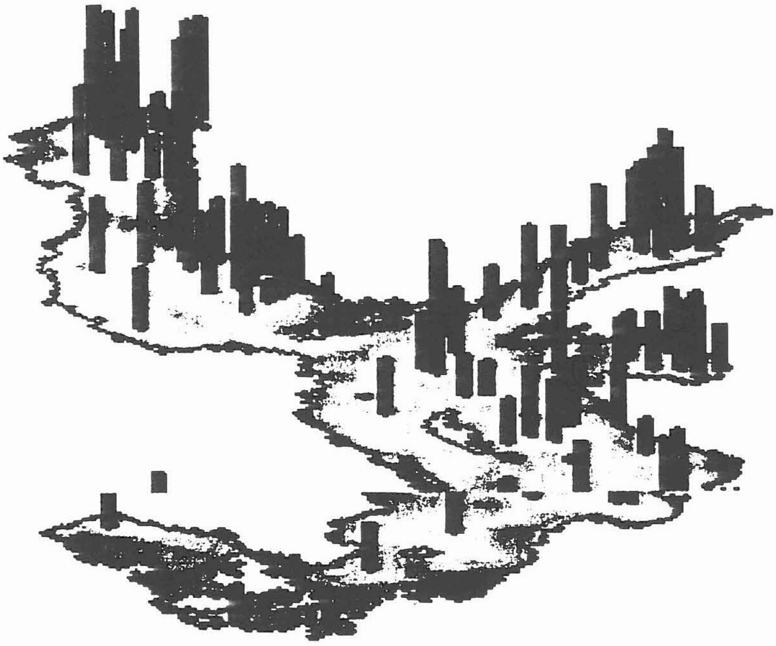
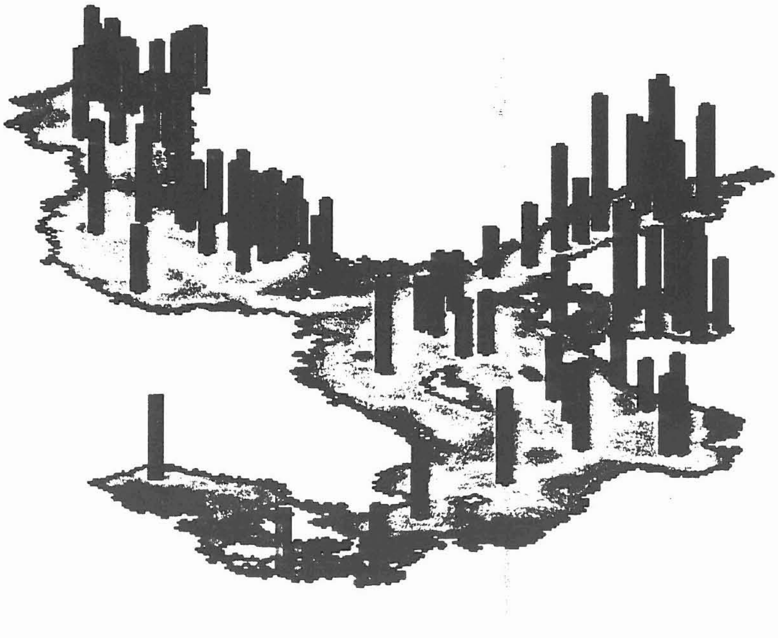


Fig. 4i. Iron

Fig. 4j. Aluminium



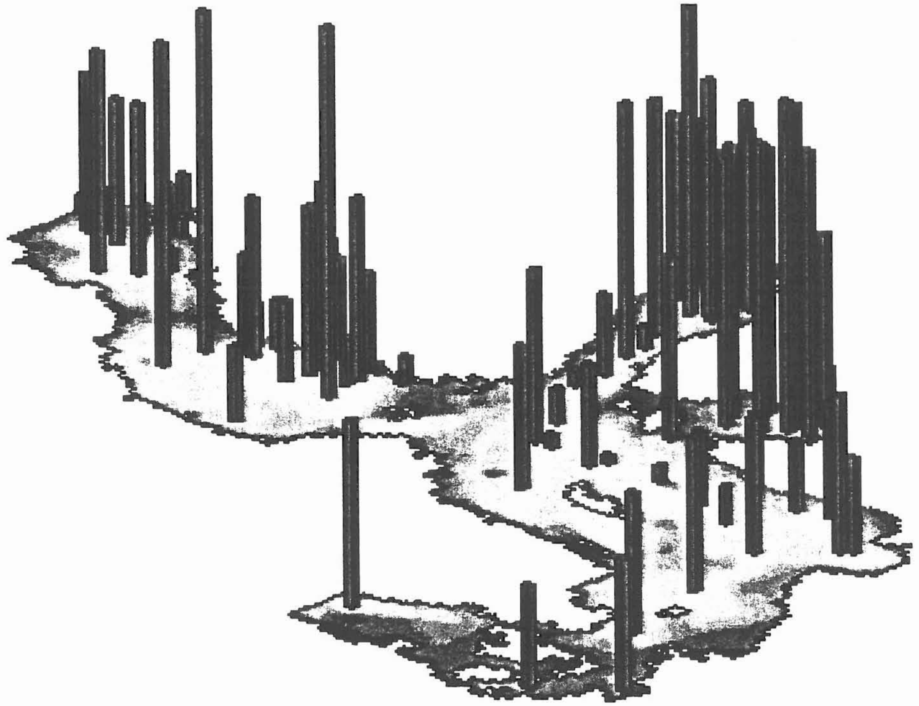


Fig. 4k. Lithium

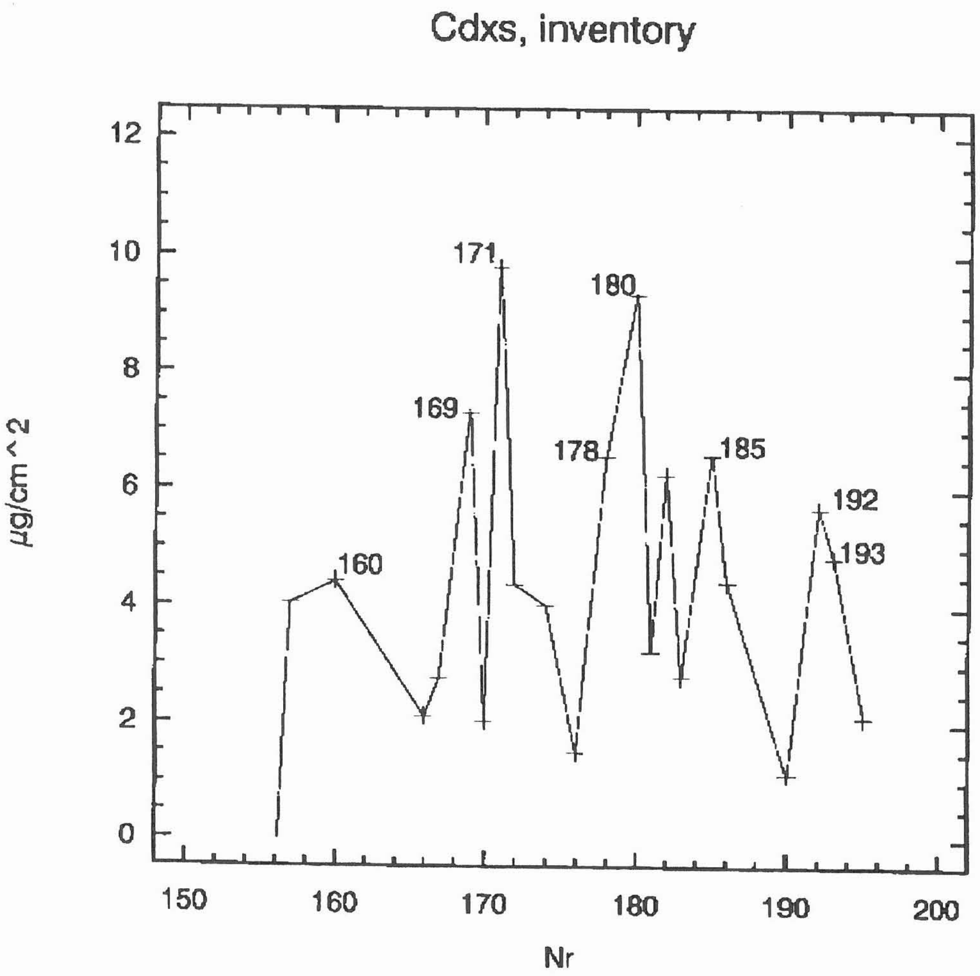


Fig. 5a. Cadmium

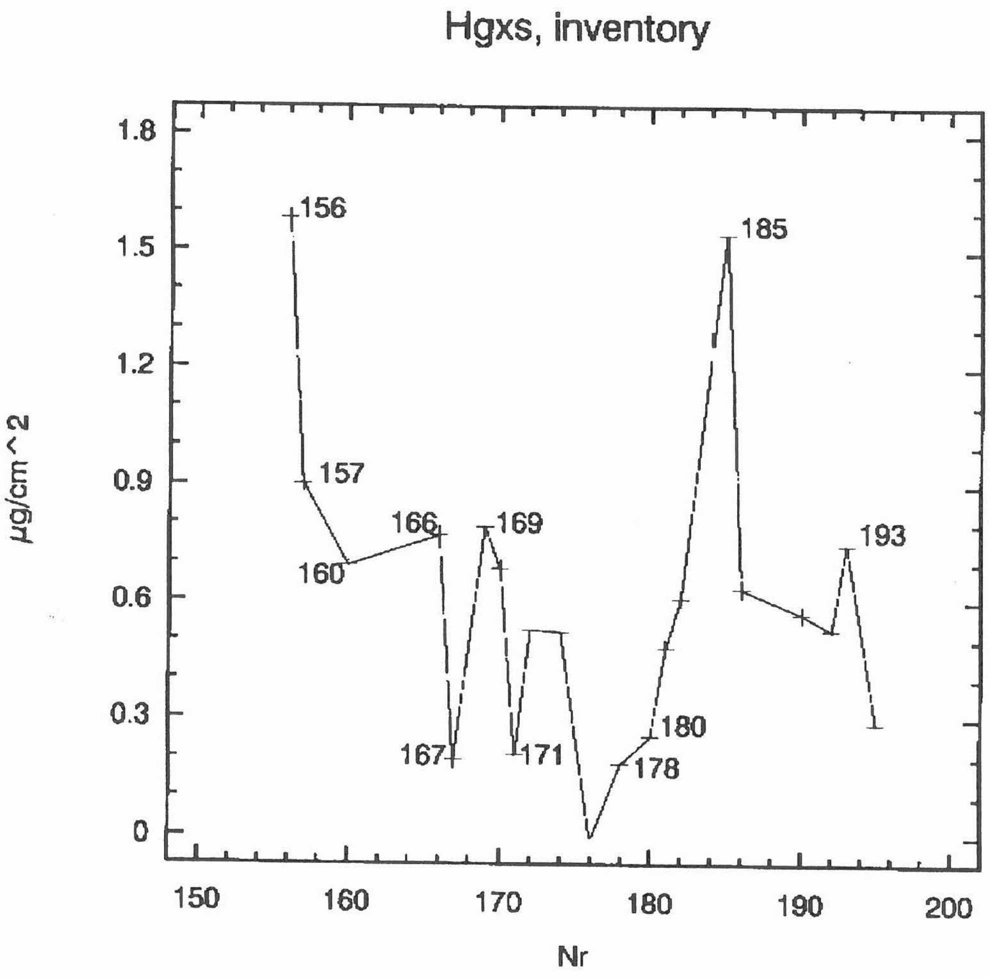


Fig. 5b. Mercury

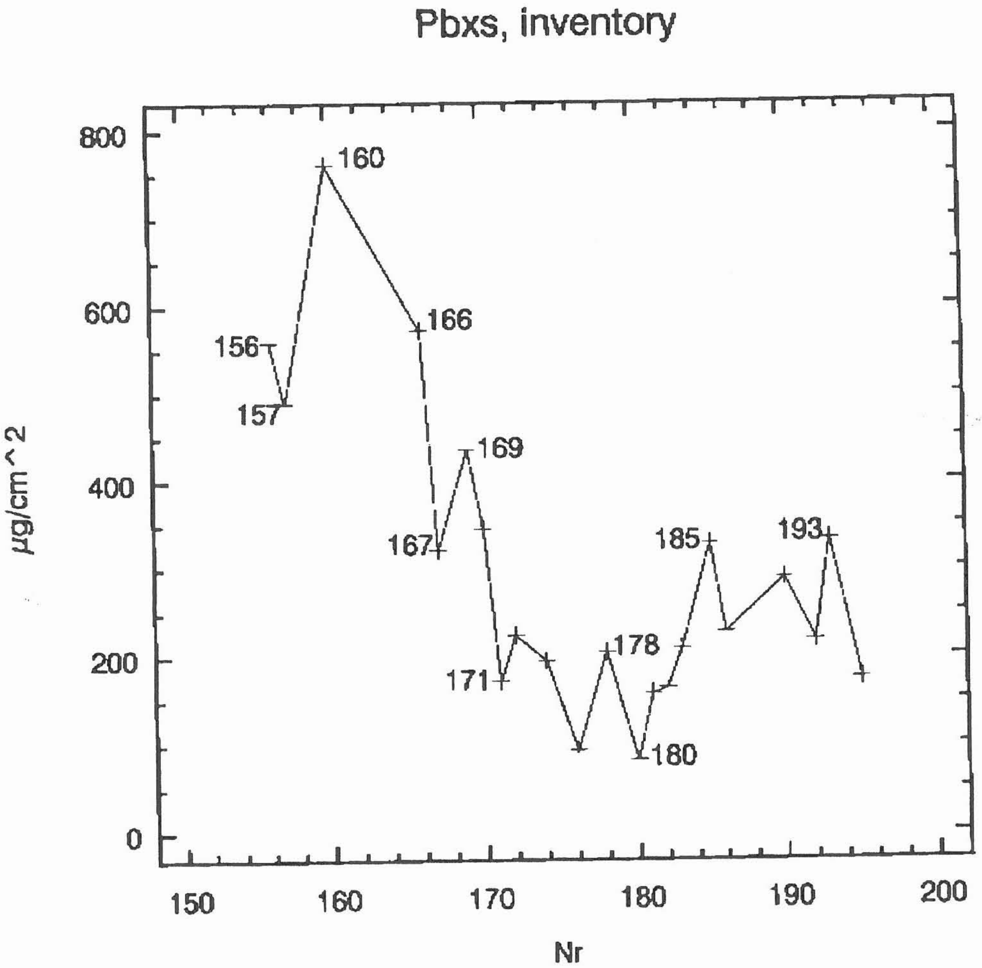

Pbxs, inventory
µg/cm^2
800
600
400
200
0
150
160
170
180
190
200
Nr
160
166
156
157
169
167
185
193
178
171
180

Fig. 5c. Lead

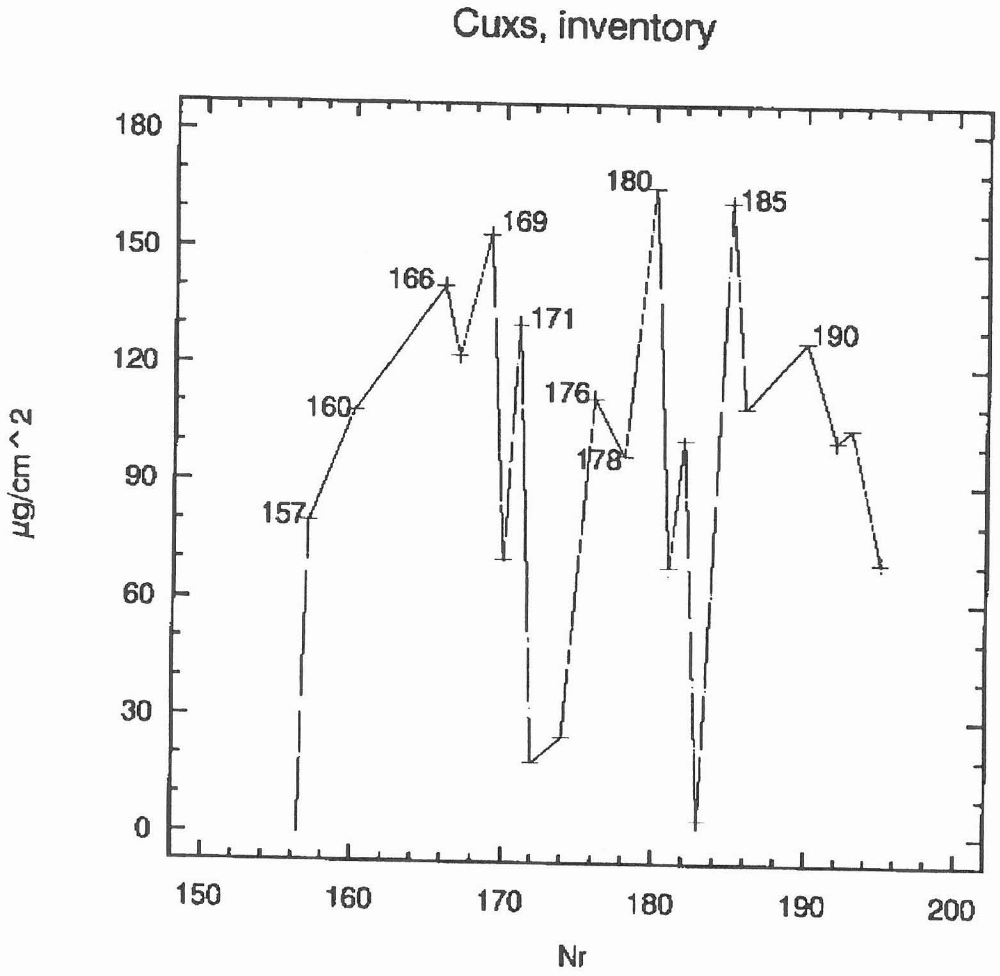


Fig. 5d. Copper

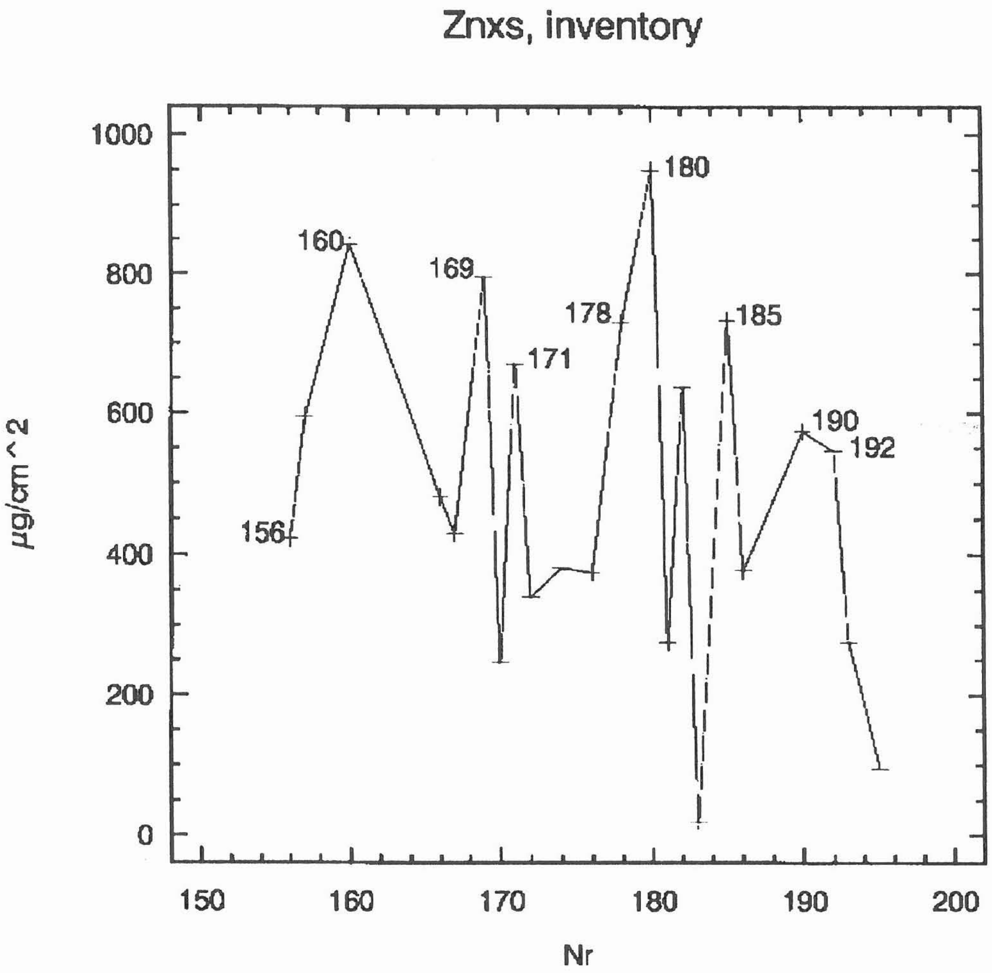

Znxs, inventory
µg/cm^2
1000
800
600
400
200
0
150
160
170
180
190
200
Nr
156
160
169
171
178
180
185
190
192

Fig. 5e. Zinc

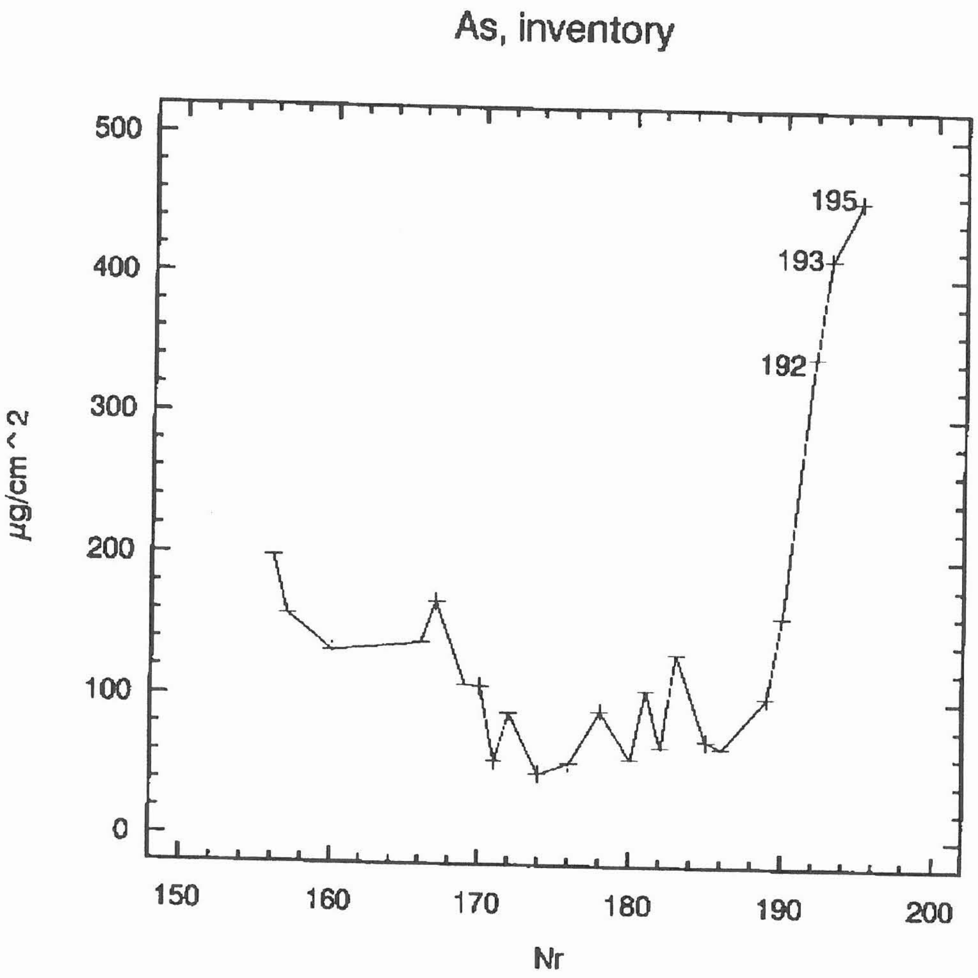

As, inventory
µg/cm ^ 2
500
400
300
200
100
0
150
160
170
180
190
200
Nr
195
193
192

Fig. 6. Arsene