Standardization of methods of analysis for heavy metals in sediments

A. J. de Groot[1], K. H. Zschuppe[1] & W. Salomons[2]
[1] *Institute for Soil Fertility, P.O. Box 30003, 9750 RA Haren (Gr.), The Netherlands*
[2] *Delft Hydraulics Laboratory, c/o Institute for Soil Fertility, P.O. Box 30003, 9750 RA Haren (Gr.), The Netherlands*

Keywords: standardization, heavy metals, sediments, base-line levels, chemical partition

Abstract

In studies of heavy metals in sediments, there is a need for standardization of the procedures for sample collection and preservation, chemical analyses and presentation of results. The method and depth of sampling depend on the aim of the investigation and on local sediment conditions, such as consistency of the sediment, rate of sedimentation, diagnetic processes and bioturbation. Therefore no general recommendations can be given in this respect. During collection and preservation, contamination and loss of constituents must be avoided. In sediments, the best means for estimating total contents of metals is digestion with HF, in combination with strong acids. Other methods include X-ray fluorescence and neutron activation analyses. The use of HF is considered objectionable by some laboratories. A reasonable alternative is aqua regia. Because variations in granular composition affect metal contents, it is advisable to use the fraction $< 63\ \mu m$ for the analysis.

Chemical partition of sediments provides an insight into the source of metallic constituents, and their pathways to deposition areas. A three-step extraction procedure, in the sequence 0.1 M hydroxylamine-HCl, H_2O_2 30% and HF, is proposed.

Finally, attention is paid to the anthropogenic enrichment of metals in sediments. The establishment of base-line levels is discussed.

Introduction

Numerous investigations have been carried out to establish environmental changes in sediments of rivers, estuaries and nearby coastal areas. Under natural conditions the concentration of heavy metals in sediments reflects the occurrence and abundance of these metals, in rocks or mineralized deposits, in the catchment area of the relevant rivers. At present, however, and in many cases, the anthropogenic contribution to the heavy metal burden of the rivers equals or exceeds the amount released by weathering. A large fraction of the discharged metals becomes part of the suspended matter, and therefore contributes to the metal contents of the sediments. As these sediments are an integral part of a river system and may be influenced by pollution over long periods and over a widespread area, they are very suitable for monitoring purposes. International comparisons of heavy metal pollution of sediments, however, are very difficult, because there are no standards for collection, preservation and analyses of the samples, nor for the presentation of the analytical results.

In this communication, a number of suggestions for standardization of the analysis for heavy metals in sediments is given. Since sample collection is a rather complicated matter (because the aim of investigations and local conditions of the sediment determine how the deposits have to be sampled) directions will be given for only selected aims and conditions. The samples should be preserved in

Hydrobiologia 92, 689–695 (1982). 0018-8158/82/0923-0689/$01.40.

such a way that contamination with metals and loss of constituents are avoided. The analyses of sediments require the use of more or less drastic procedures for solubilization of the metals and these will be discussed. Also, the distinction of metals associated with different chemical phases in the sediments will be considered. One of the greatest problems in making comparisons of the results of various studies on heavy metal levels is caused by the effect of grain size. In sediments, the relationship between metal contents and grain size composition is often overlooked. Therefore grain size has to be taken into account when the heavy metal contents of sediments are presented.

Finally, some attention is given to the extent of pollution of sediments with respect to the 'base-line levels'. These levels can be determined in samples which are representative of the conditions existing before the industrial revolution.

Sample collection and preservation

Sample collection

To study the most recently deposited layers of sediments in the aquatic environment, it is often sufficient to take the uppermost centimeters of sediments with a grab sampler. There are different principles on which most types of grab samplers work:

1) A pair of weighted semi-cylindrical jaws press into the sediment by their own weight while they are open. When the device is lifted, the two jaws close by their own weight or by a tension spring.
2) An open sampling box cuts into the sediment and is closed from below, by a mechanism, when it is raised.

The important difference between the two methods is that, with the box type, sediments can be taken in their original and nearly undisturbed state. The simple excavator type, however, is better suited for coarser sediments and is superior to the sampling box types for that material, because the complicated closing mechanism of the latter is often jammed by gravel grains. Different types of the excavator type include the Van Veen grab, the Smith-McIntyre grab, the Ponar grab, the Shipek grab, the Franklin-Anderson grab, the Dietz-La Fond grab and the Petersen grab.

Although the grabs of the excavator type are designed for sampling the uppermost centimeters of bottom sediments, it is also possible to collect the uppermost skins of these sediments. For that purpose the grab is opened carefully, aboard ship, and then the top layer of the contents is subsampled. Box corers, however, are better suited for taking almost completely undisturbed samples of the top layer. Moreover, the contents of the box can be divided into different layers. Different types of box corers which may be used include the Reineck box corer, the Birge-Ekman dredge, the Auerbach-Wippermann grab and the Soutar-Gamble corer. A disadvantage of subsampling different sediment layers from box corers is that it must be done by removing successive slices downwards from the top side of the sample, within the box. In this respect, a better recovery may be had by the use of the Jenkin mud sampler. This sampler consists of an open perspex tube provided with lids at each end, which are closed mechanically after the tube has been thrust into the mud. By introducing a piston into the lower part of the tube, after it has been hauled up, the mud column can be lifted upward and can easily be divided into several slices. We have successfully used the Jenkin mud sampler in collecting sediment profiles to a depth of about 60 cm. Word (1976) compared the efficiency of seven grab samplers; most successful were the Van Veen grab and a box corer. Based on the findings of Word, and on our experiences, we recommend the Van Veen grab for sampling the upper layers of soft and firm sediment. For deeper layers of soft silt the Jenkin mud sampler or a box corer of, for instance, the Reineck type are reliable. For deeper layers of firm material core samplers are needed. However, no gravity or piston corer will penetrate more than about a meter into pure sands. Some workers had considerable success with vibrating corers. Finally the Shipek grab is a good alternative for sampling the upper layers of sandy sediments, especially for sediments far below water level (Sly 1969, 1981).

Sample preservation

Before being subsampled for physical and chemical analysis, it was found necessary to place samples into cold storage to halt biological activity and to prevent any chemical transformation in the sediments. Before further treatment, sediment samples are often dried. For drying sediments, different temperatures can be used: room temperature, oven-dried at temperatures ranging form 30 °C up to 110 °C, or freeze-dried. In a few cases, metal analyses are carried out on moist samples, especially when exchangeable metals are to be determined. Soil chemists prefer drying at a temperature of about 40 °C.

For the determination of non-volatile metals, all drying procedures are acceptable. At temperatures higher than 40 °C, however, significant losses of mercury may occur. Therefore, drying at 40 °C is proposed. In any event, samples should be kept in such a way as to avoid contamination by metals and to prevent loss of constituents before analysis.

Total-metal determination

The chemical analysis of a sediment usually consists of a digestion procedure and a determination of the extracted metals. To estimate the total metal contents of sediments, a rigorous digestion with strong acids, or combinations of strong acids, is generally used. Sediment analyses may be carried out, also, by other reliable methods such as X-ray fluorescence, neutron activation analysis and emission spectrographic techniques. Digestion procedures, prior to an estimation of total amounts of metals in sediments, involve the use of HF, in most cases in combination with strong acids, e.g. aqua regia. However, in many laboratories HF is considered objectionable. Although using a teflon-bomb for the digestion procedure somewhat diminishes the disadvantage of the use of HF, the method remains rather laborious. Partly for this reason other methods, involving strong acids, are used in many laboratories. Although it is not yet known to what extent HF can be replaced by other digestion techniques, it is well known that different, 'strong attack' leaching procedures do not always dissolve equal amounts of metals.

Diversity, both in sediments and in digestion procedures, gives rise to different amounts of extracted metals. In this connection, diversity in sediments refers to differences in the relative abundances of heavy metals in the crystal lattices of the individual minerals. Diversity in digestion procedures refers to their greater or lesser capability for destroying metalliferous minerals in the sediment.

In view of these considerations, it is advisable to study digestion procedures for heavy metals in sediments, from different origins. Selection of an extraction method on the basis of a minimal difference from the HF-method is one of the possibilities. Another possibility is to make a differentiation on the basis of the extent of destruction of metalliferous minerals in sediments. Such an evaluation of an extraction method, however, involves an intensive mineralogical analysis of the sediment before and after the extraction procedure.

According to our present knowledge, the best extraction technique, for estimating the total contents of metals in sediments, is digestion by HF in combination with strong acids. Where the use of HF is considered objectionable, from a laboratory-technical point of view, aqua regia is a reasonable alternative.

Grain size and metal concentration in sediments

Although naturally metal-rich heavy minerals occur in the fine sand fractions, the highest concentrations of both natural and contaminant metals are usually found in the very fine grained muddy sediments. This non-uniform distribution of trace metals over the range of grain size fractions causes variations in the metal contents of sediment samples, even from within the same area. To compare the metal concentrations in sediments from different areas, and to determine the course of heavy metal pollution in time, corrections have to be made for differences in grain size composition. Different methods have been compiled by De Groot, Salomons & Allersma (1976), Förstner & Wittmann (1979) and Förstner & Salomons (1980). A summary is given below:

A. *Separation of grain size fractions*
204 μm —— 175 μm —— 63 μm ——2 μm;

B. *Extrapolation from regression curves*
% < 16 μm —— % < 20 μm —— % < 63 μm —— specific surface area;

C. *Comparison with 'conservative' elements*
Ratio element/aluminum.

The generally linear relationship between metal contents and a grain size fraction (B), may be used as a suitable basis for the standardized presentation of heavy-metal contents in most sediments. An ex-

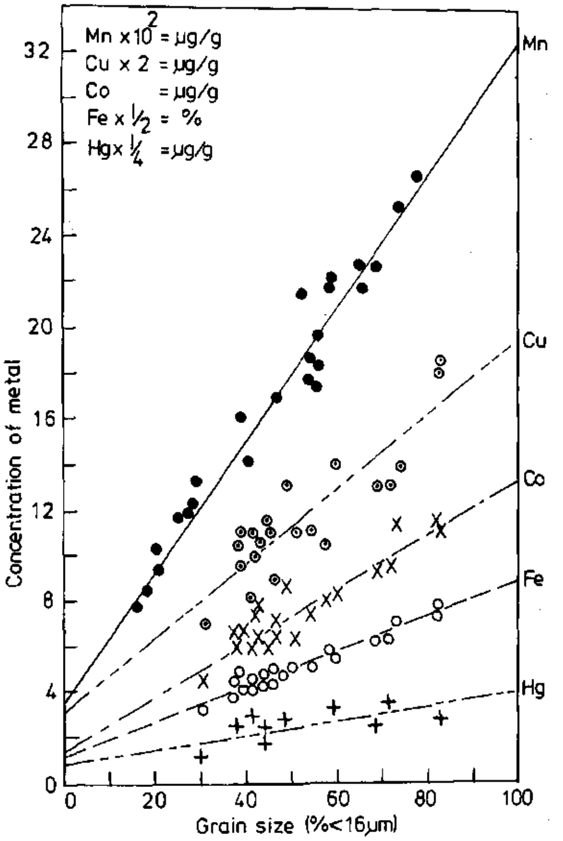

Fig. 1. Relationship between the metal composition and the grain size distribution for samples from the river Ems.

ample of such a relationship using the fraction < 16 µm in samples from the same location is given in Fig. 1.

To characterize such a group of co-genetic sediments, the linear relationships can be extrapolated to 100% or 50% of the fraction < 16 µm. Also, the fractions < 20 and < 63 µm, and the specific surface areas, have been used in correlation studies of heavy metals in different sediment fractions (Lichtfuss & Brümmer 1977; Smith *et al.* 1973). The calculation of a regression line, however, requires a large number (10–15) of samples from one location. Moreover, it is often impossible to determine a regression line, due to the limited range in grain size of the sediment at a certain location.

Another way to treat grain size corrections is to isolate a certain granular fraction, and analyze the metals within such a fraction (A). Separation of grain sizes is advantageous, because only a few samples from a particular location are needed. However, the separation of the fractions less than 2, 16 or 20 µm is time-consuming; moreover the method requires resuspension in (distilled) water, which may cause remobilization of metals. On the other hand, separation of the fraction less than, for instance, 204 or 175 µm by sieving has the disadvantage that the separated fractions contain considerable amounts of large grains, which are usually low in trace metals (Förstner & Salomons 1980). It has therefore been proposed to use the < 63 µm fraction for comparisons of metal contents (Förstner and Salomons, 1980). The advantages are:

1) Trace metals have been found to be present mainly in the clay/silt particles;
2) This fraction is nearly equivalent to the material carried in suspension;
3) Sieving does not alter metal concentrations by remobilization;
4) Numerous studies on metals have been performed on the < 63 µm fraction;
5) Comparisons among the metal concentrations in muddy sediments and in coarser sediments (e.g. those from the sea floor) are possible.

Separations of the fractions < 63 µm are performed either by dry- or by wet-sieving. Dry-sieving is possible only if the sample has been freeze-dried. The use of disposable nylon sieves, a method developed by the Rouen Municipal Laboratory (France), is recommended by the Centre Océanologique de Bretagne (France). Care should be taken to sieve just enough sediment, with a minimum of water. The combined water and sieved sediment should be oven-dried at 40 °C.

Another way (C) to eliminate grain size is to normalize the metal concentrations to the amount of 'conservative' elements such as aluminum. This method has the disadvantage of giving ratio values instead of real concentrations but, at present, there is insufficient data to determine the difference between the concentrations derived by the use of methods (B) and (C). If only small quantities of sediment sample are available, e.g. in the case of suspended matter, metal/Al ratios may be a good alternative, because the Al contents can be determined on small amounts of material and often in the same extracts as those for the heavy-metal determinations.

Chemical partition

To assess the impact of contaminated sediments on the environment, information on total concentrations, alone, are not sufficient. Only a part of the metals present may take part in short-time geochemical processes or may be bio-available. For this reason, a series of different extraction procedures have been devised to gain a more or less detailed insight into the distribution of metals within the various chemical compounds and minerals. A summary of several methods is given in Table 1.

Various single leaching steps are combined into leaching schemes to determine trace metals in sediments, e.g. differentiation of trace metals into a reducible, an oxidizable and a resistant fraction; a distinction between exchangeable metals, metals present in metal hydroxide coatings, organic solids, and the crystal phase; determination of metal contents in interstitial water and in exchangeable, easily reducible, moderately reducible, organic and residual fractions.

It should be pointed out that the extraction procedures are not as selective as is sometimes stated. Re-adsorption of metals may take place and the results are influenced by the duration of the experiment, the temperature and the ratio of solid matter to volume of extraction solution.

Unfortunately there is a proliferation of extraction schemes, which also make it difficult to compare the results of analyses. Therefore a 'standard extraction scheme' has been prepared by Salomons & De Groot (1978) and summarized as follows:

1) An extraction with 0.1 M hydroxylamine-HCl. This step includes the extraction of exchangeable cations and of carbonate-bound metals;
2) An extraction with acidified peroxide (30%). This extraction should be followed by an extraction with ammonium acetate to remove any reabsorbed metal ions;
3) Dissolution of the remaining sample with HF to estimate the metals left in the residual fraction.

The rather important 'exchangeable phase' (representing very loosely bound trace metals which regulate or reflect the composition of surface waters) is not included in this scheme. To determine the amount of exchangeable metal ions, an extractant is used which contains cations that are more strongly bound, than metals, to the exchange sites ($BaCl_2$, $MgCl_2$ and NH_4OAc). Although the ion-exchangeable fraction of trace metals is ill-defined, ammonium acetate is a generally accepted agent.

Table 1. Summary of common methods for the extraction of metals associated with different chemical phases in sediments (Salomons & Förstner 1980).

Adsorption and cation exchange

Extractions with: $BaCl_2$, $MgCl_2$, NH_4OAc.

Detrital/non detrital; authogeneous/lithogeneous fractions

Extractions with: EDTA, 0.1 M HCl, 0.3 M HCl, 0.5 M HCl, 0.1 M HNO_3

Manganese and iron phases; reducible, easily and moderately reducible phases

Extractions with (in approximate order of release of iron): Acidified hydroxylamine, ammonium oxalate, hydroxylamine-acetic acid, dithionite-citrate.

Carbonate phases

Extractions with: CO_2 treatment, acidic cation exchange, NaOAc/HOAc (pH 5).

Organic phases; humic and fulvic acids, solid organic material

Extractions with: H_2O_2, H_2O_2-NH_4OAc, H_2O_2-HNO_3, organic solvents, 0.5 N NaOH, 0.1 N NaOH/H_2SO_4, Na hypochlorite-dithionite/citrate

Salomons & Förstner (1980) used the above mentioned 'standard extraction scheme' (including an estimation of the ion-exchangeable fraction) in an analysis of 18 different river sediments and a summary of their results is given in Fig. 2.

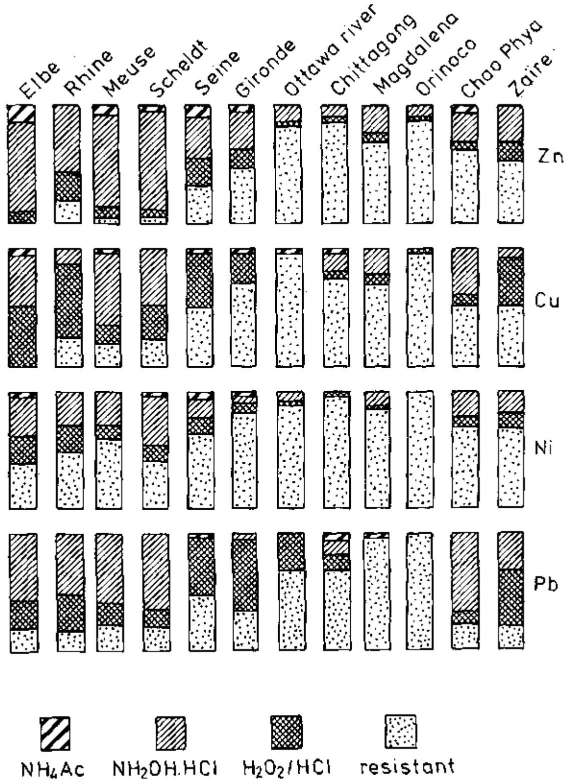

Fig. 2. Chemical partition of trace metals in some river sediments.

Anthropogenic enrichment of sediments with metals

To determine the 'extent of pollution' of sediments by metals, the natural levels (base-line levels) of these substances must be established and then substracted from the measured values of metal concentrations. In this way the total enrichment caused by anthropogenic factors can be found. However, it is difficult to make an ideal comparative basis for natural levels. Since no observations exist which record the presence of heavy metals during the preindustrial period, sediments deposited at that time must be used as proxy data. These are now buried beneath later deposits and have been subject to a wide variety of geochemical processes. As a result, they may have lost or increased part of their heavy metal content. Such data usually represent minimum values. Another way of defining background levels is to use the heavy metal contents of the average shale, deep-sea clay, or near-shore sediment. However, these data represent averages, whereas in river sediments local mineralizations in their catchment areas may result in naturally high concentrations of some metals. In addition, the mineralogical composition of the sediment may differ from that of the average shale or deep-sea clay. For instance, organic matter, which is an excellent scavenger for a number of metals, is more abundant in some river deposits than in many marine sediments.

In Table 2, heavy metal contents of Rhine river sediments, from different years, are compared with

Table 2. Mean heavy metal contents in $\mu g/g$ (values at 50% $<$ 16 μm) in sediments from the Rhine river, compared with those of uncontaminated sediments (base-line levels).

		Zn	Cu	Cr	Pb	Cd	Ni	Hg	As
Rhine sediments sampled in:									
1958		2420	294	642	533	14	54	10.5	198
1970		1855	323	789	447	27	62	14.5	136
1975		1905	325	820	399	31	81	10.1	54
Base-line levels:									
Rhine deposits from the 15th and 16th century		93	21	77	31	0.5	33	0.14	12.2
Nearshore sediments	1)	95	48	100	20	–	55	–	–
Clays and shales	2)	80	57	100	20	0.3	95	0.4	6.6
Shales	3)	95	45	90	20	0.3	68	0.4	13
Deep-sea clays	3)	195	250	90	80	0.4	225	–	13

Sources of data: 1) Wedepohl (1960); 2) Vinogradov (1962); 3) Turekian & Wedepohl (1961) a number of base-line levels. With respect to the base-line levels, it is obvious that the values of Zn, Cu and Ni are higher in deep-sea clays than in the average shale. This is probably caused by the addition of these elements during transport and after deposition in the oceans. In our opinion, the metal concentrations in sediment samples deposited at a time shortly before the recent industrial expansion, e.g. in 1920, will constitute the best values, against which changes in metal concentrations can be evaluated. Radiometric dating techniques may be very helpful in establishing the location of such sediments.

A very useful method for expressing the anthropogenic metal burden has been developed by Müller (1979). Müller proposed the 'Index of Geoaccumulation (Geo-Index)', defined by $I_{geo} = {}^{2}\log \frac{C_n}{1.5\,B_n}$, in which:

$C_n =$ measured concentration of an element 'n' in the fraction $< 2\ \mu m$,

$B_n =$ natural base-line value of the relevant element in the fraction $< 2\ \mu m$. The correction factor 1.5 is used in connection with the lithologic deviations from the base-line level.

$I_{geo} = 0$ means an unpolluted sediment, and

$I_{geo} = 6$ expresses a 64-fold enrichment of the sediment in comparison to the base-line level.

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Received and accepted 28 October 1981.