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APPROACHES TO SAMPLING AND SAMPLE PRETREATMENTS FOR METAL SPECIATION IN SOILS AND SEDIMENTS

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The main aspects of sampling and sample pretreatment in metal speciation studies of soils and sediments are discussed. The risks of sample contamination by the use of inappropriate materials, containers and tools as well as the possibilities of losses of analyte during sample handling are pointed out. Field sampling methods are described and minimum sample weight criteria for representative sampling of dry soils are presented. Sampling by traps and continuous flow centrifugation methods for suspended sediments and of bottom sediments by grabs or corers are compared. To avoid significant changes in some metal species drying and storage temperatures may need to be controlled and preservation in an inert atmosphere or by irradiation is discussed. The difficulties of establishing definitive protocols for sampling and sample pretreatment are emphasized as well as the need for selecting the appropriate technique in each particular case.

KEY WORDS: Metal speciation, soil sampling, sediment sampling, sample pretreatment.

INTRODUCTION

There are many instances where estimates of population characteristics have to be made from the examination of a small fraction of that population.

In soil science the problem might be to estimate the fertilizer requirements of a particular field by the analysis of the existing soil fertilizer contents, or to diagnose a plant or animal deficiency or toxicity disorder by the analysis of a field soil for essential trace element or for heavy metal concentrations. Soil is inherently a heterogeneous material and large variations in its chemical and physical nature can occur in random samples taken over a small area of apparently similar land. Variations in topography, in farming operations, in

soil type, in drainage and in geological parent material or history can occur within the field under consideration. The first task is therefore to obtain a soil sample that is representative of the field or other area under consideration i.e. the topic of "Field Sampling" discussed below.

The estimation of the desired characteristic involves, in the present context, the chemical analysis of a soil sample for the determination of the concentration of a chemical constituent. This usually involves some chemical or physical treatment of the field sample and the taking of subsamples, for treatment and analysis, that are representative of the field sample which itself is representative of the whole field.

In metal speciation studies aquatic sediments provide valuable information not only on the nature and level of pollution but also on resuspension and redissolution of metals in the aquatic media when environmental conditions change. Moreover, speciation of sediment samples in depth provide information about the history of the pollution in the area studied.

Aquatic sediments are heterogeneous materials consisting of various sizes of particles, mainly silts, clays and sands although in most cases important amounts of organic matter from vegetation (as in lakes) or from anthropogenic sources can be present. Heavy metals can be incorporated in these materials by different processes such as adsorption, ion exchange or complexation. It is therefore difficult to obtain a proper sample for speciation analysis.

In many instances the difficulties in obtaining a representative sediment sample for speciation studies arises from the constant changes in the aquatic media that make it difficult to design a suitable sampling program. Moreover, the handling, storage, preservation and pretreatment must be accurately monitored to preserve the original distribution of the metal species until analysis.

The whole process from original sample to analysis is illustrated (reproduced from ref.¹ C IUPAC) in Figures 1 and 2 which also give the recommended, IUPAC sample nomenclature for analytical spectroscopy¹.

CONTAMINATION AND LOSS

At every stage of the whole sampling process there is the danger that the sample will become non-representative because it has been contaminated from an extraneous source or that some component has been wholly or partially lost.

Losses from dry soil are usually less important in the early, non-chemical stages although losses of the finer size fractions can occur during the handling of dry soil. Losses of volatile species from moist soil or of species such as organic forms of mercury or selenium formed by microbiological action can occur if soils are not stored at low temperature. Storage of soil in sealed polyethylene containers does not prevent losses of mercury or contamination by mercury in the laboratory atmosphere as polyethylene is porous to mercury vapour².

Contamination is a more severe problem. The selection of the individual soil sampling sites should avoid obvious sources of contamination. For example soil sampled close to a galvanised steel fence or telegraph pole is likely to have unrepresentative and high zinc concentrations.

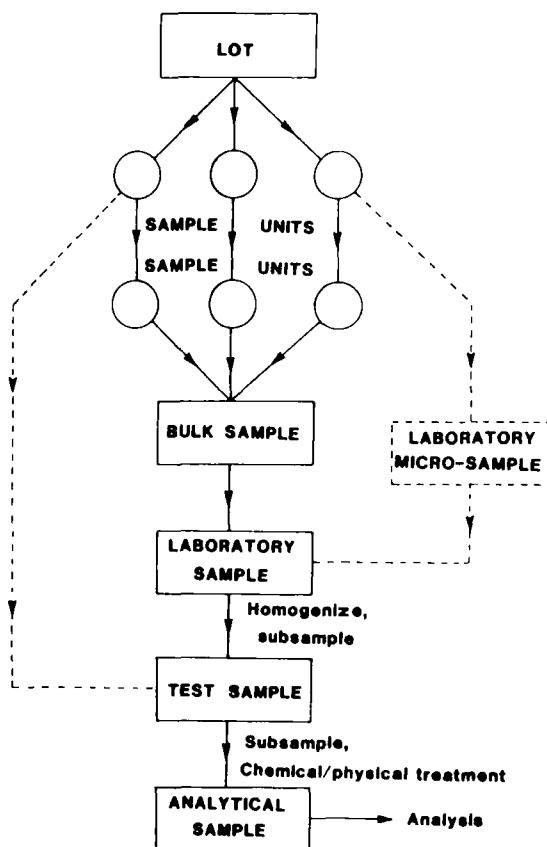


Figure 1 Schematic diagram of sampling stages and terminology. (From ref. 1 with permission).

The choice of tools and the containers used for transportation to the laboratory must be chosen to minimize contamination by elements of interest. Contact with and potential contamination by some material is unavoidable, but by the appropriate choice of material relevant contamination can be avoided or minimised.

When metals must be used the two least objectionable in general are aluminium and mild or carbon steel. These metals should be used with caution as some aluminium alloys contain copper and magnesium and sheet aluminium may have surface coatings of zinc or cadmium, while mild steel can contain lead or selenium. Stainless steels should be avoided as they can contain large (percentage) amounts of chromium, manganese, molybdenum and nickel as well as smaller amounts of cobalt, vanadium and tungsten. In general copper and its alloys are undesirable.

While the use of plastics in place of metals for tools and containers may seem the obvious solution this can be an illusion unless the proper choice of plastic is made and the selected material checked by analysis. Some plastics, including PVC, contain any of a wide range of plasticisers, fillers, stabilisers and anti-oxidants, many of which are biosignificant metal compounds, including heavy metal stearates also used as lubricants^{3,4}. In general

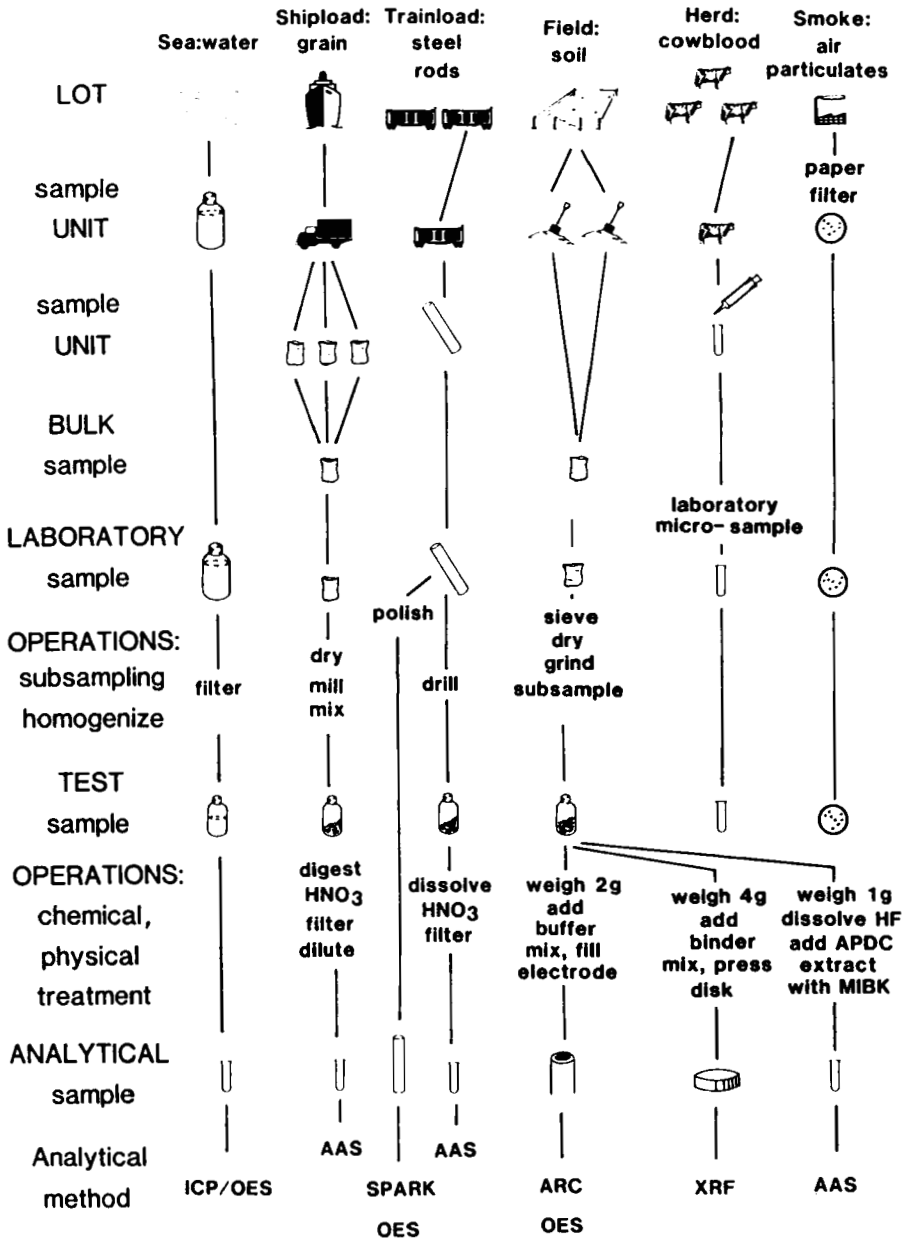


Figure 2 Examples of routes from sample to analysis illustrating the use of sampling terminology. (From ref. 1 with permission).

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polytetrafluoroethylene (PTFE), polyethylene (prepared by the high pressure process, as the high density variety may contain metal catalysts), polypropylene and silicone rubber are the preferred plastics⁴. Natural rubber contains high amounts of zinc and should be avoided.

Sample containers should be of polyethylene or glass and paper bags or boxes avoided, especially if boron is of interest, as paper is a ready source of contamination with volatile boron species^{5,6}. While it is essential that each sample should be labelled with a unique identifying number, the label should be attached outside the container and not placed inside as tapes and labels and inks may be significant sources of metal contamination⁴.

These limitations on the types of material that should be used for sampling and as containers also apply to the materials used in the construction of the laboratory and the storage of samples.

In spite of these observations, which are equally applicable to both materials, the different characteristics in composition, contamination origins, pollution levels and variability of environmental conditions suggest the convenience of dividing our recommendations into two sections: soils and sediments.

SOILS

Field sampling

It is not usually practicable to sample a field at randomly distributed points. Sampling along a diagonal is completely inadequate and sampling along two diagonals unduly weights the sample to the middle of the area. Two methods of sampling a small area of up to say 3 or 4 hectare are commonly recommended.

In the first⁷ some 25 samples are taken for each 4 hectares along a W shaped track. In the second⁸ a similar number, 24, of samples is taken along a zig-zag track, taking one sample from each sampling unit, as shown in Figure 3. Samples of arable land should be taken by auger to plough depth (say 20 cm) and to a lesser depth (say 10 cm) in permanent pasture.

For many purposes a bulked sample, made up by combining the individual sampling units, of 1-2 kg moist soil, i.e. sufficient to provide about 0.5 kg air-dry soil is the minimum required. The samples should be stored in polyethylene bags, and externally labelled with an identifying number for transport to the laboratory for drying and further treatment.

Subsampling of air-dry soil

For most analytical purposes soils will be air-dried at < 30°C, gently rolled to break up soil aggregates and sieved through sieves with round holes of 2 mm diameter to remove stones, large roots etc. This air-dry, material will generally require to be subsampled to obtain a small representative sample for

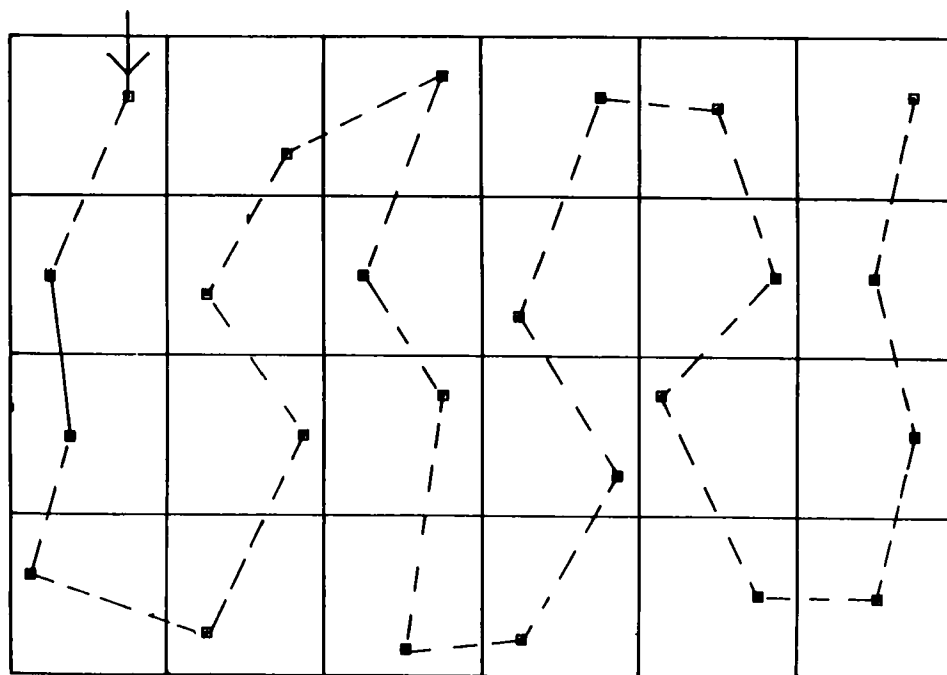


Figure 3 Field sampling along a zig zag track.

- a) grinding to $<100\ \mu\text{m}$ for the determination of the total contents or
- b) for extraction by a suitable reagent to provide a solution for the determination of extractable contents.

The problem for the analyst is to choose the minimum sample size that, taken in a representative manner, will have the same composition and in particular the same concentration of the element or elements of interest as the original bulk sample. The method of obtaining such a sample weight in a representative manner is part of the same problem.

The practical solution is to adopt the approach outlined by Jackson⁹ in which the minimum representative sample weight is that weight that contains at least 1000 sample grains. The optimum weight is some 3 to 4 times greater than this minimum. Table 1, adapted

Table 1 Relation of minimum and optimum sample weight to mesh size. (adapted from Jackson⁹).

Sieve opening (mm)	Minimum Weight	Optimum Weight (4 × Min. Wt.)
0.1	0.68 mg	2.72 say 2.5 mg
0.16	2.7 mg	10.8 say 11 mg
1	0.68 g	2.72 say 2.5 g
2	5.3 g	21.2 say 20 g
4	44 g	176 say 150 g

(Assuming a bulk density of $1.3\ \text{g}/\text{cm}^3$).

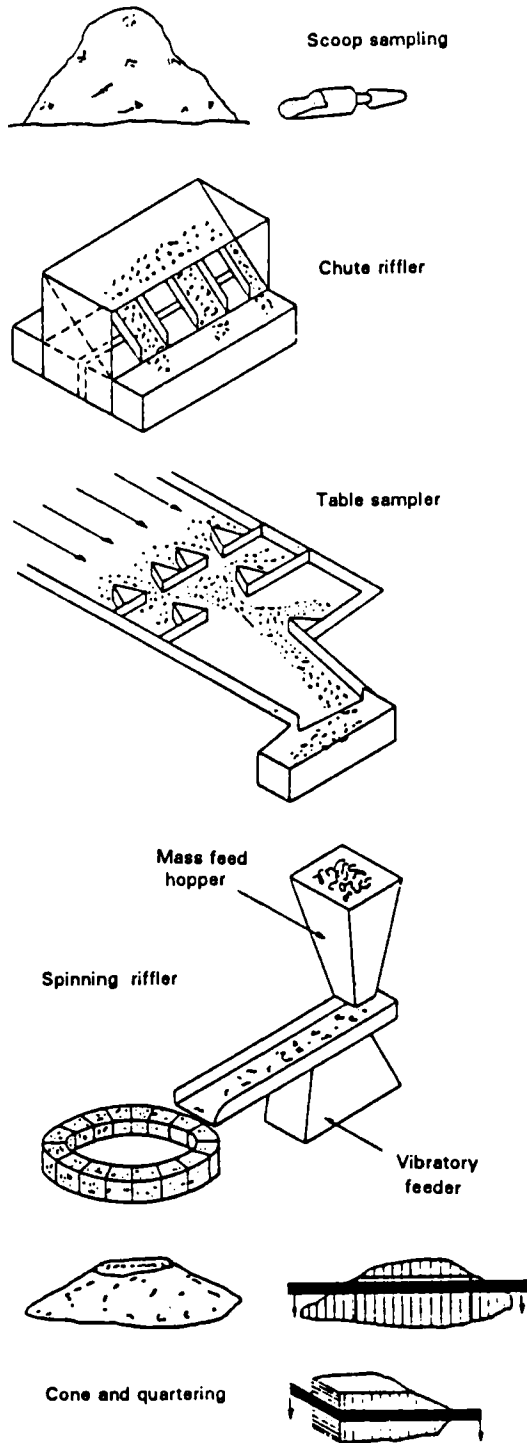


Figure 4 Sampling techniques. (From T. Allen and A. A. Khan. *The Chemical Engineer*, 109, 1970).

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from ref. 9 gives some examples of minimum and optimum sample weights for some different sieve mesh sizes. These examples assume a bulk soil density of 1.3 g/cm^2 .

The final sample of dry soil required for the analysis can be obtained by representative subsampling the bulk material in a number of different ways illustrated in Figure. 4. Mechanical riffles may not always be suitable for trace element analysis as the materials of construction can introduce contamination. Coning and quartering requires little apparatus and is adaptable to any bulk sample size. In the coning and quartering procedure the bulk material is thoroughly mixed and this is poured on to a clean sheet of polythene to form a cone. The cone is divided into 4 quarters, using a cross made of sheet aluminium, and the 2 opposite quarters combined and mixed to form a subsample of approximately half the original weight. This half sample is again coned and quartered and the process repeated until a subsample of a little over the desired analytical sample weight is obtained.

SEDIMENTS

Location of sampling points

The location of the sampling point as well as the frequency of sampling must be established taking into account the natural characteristics of each aquatic environment, knowledge of the pollution sources in the area and the nature of the waste inputs.

In lakes and basins, where the sedimentation rates are fairly uniform, the sampling points can be established by planning an appropriate grid design, as can see in Figure 5¹⁰. In coastal zones and estuaries, the different inputs such as rivers and urban waste discharges, as well as changes in salinity at the river water-sea water interface, tidal cycles and bottom streams make it difficult to obtain representative samples at the bottom. In these cases sampling must be done in selected zones, as far removed as possible from the turbulence. A knowledge of tidal seasons and bottom currents should be available¹¹.

In large, high flow rivers the samples can be collected at the bottom at different distances from the bank for each sampling point, and the sampling map can be projected along the river, as shown in Figure 5, in such a way that the final results from the analyses could reflect the major influences of the inputs received. In rivers with low and irregular flow which receive many urban and industrial effluents, such as most of the Mediterranean rivers, the most representative samples must be collected at the bank, where the water appears less turbulent, and the flow is lower. In this case sampling must be performed frequently.

Kinds of sample and sampling apparatus

Suspended sediments. The finest particles in the sediments adsorb the highest amount of pollutants and determine their transport and deposition. In rivers, metal species adsorbed on particles can be rapidly transported, whereas in estuaries, lakes and marine environments the settlement of these particles leads to the accumulation of the pollutants on the bottom.

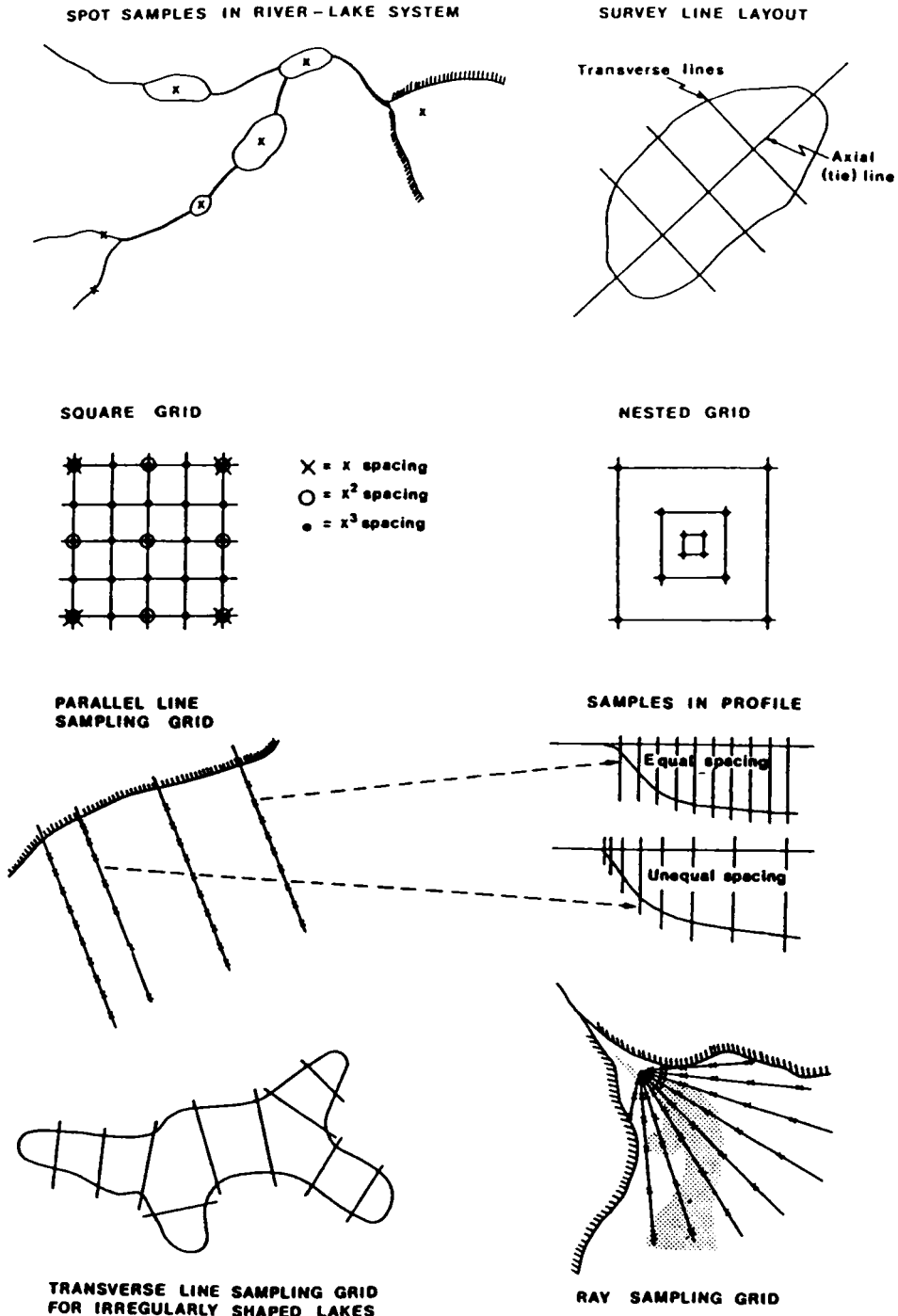


Figure 5 Examples of different types of grid design (From H. L. Golterman, P. G. Sly and R. L. Thomas, 1983, Tech. Papers in Hydrology No 26, 231 pp, UNESCO, Paris. In ref. 10, with permission).

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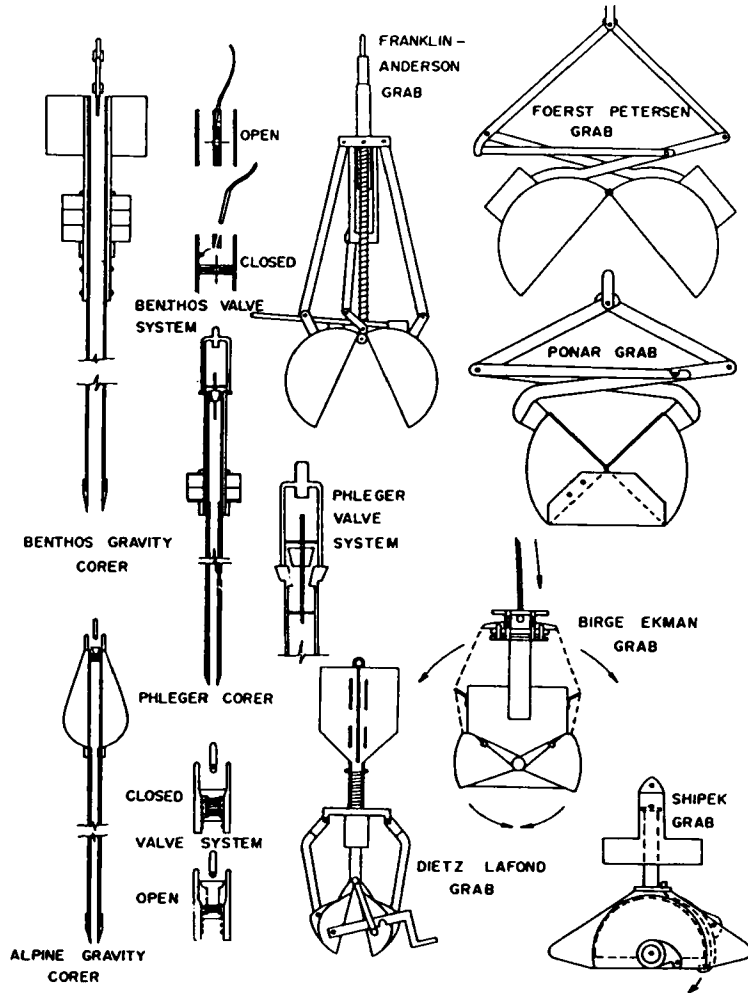


Figure 6 Corers and bottom samplers. (From P. G. Sly, 1969, Internat. Assoc. Great Lakes. Res. Proc, 12th Conf. Great Lakes Research 230–239. In ref. 10, with permission).

Sampling of suspended sediments is carried out with bottom sediment traps, which are available in different volumes and designs (Figure 6). Continuous flow centrifugation “in situ” or filtration through $0.45\ \mu\text{m}$ or better $0.1\ \mu\text{m}$ membrane filters are used to separate suspended particles from the water. Although both procedures are used, there is no agreement in the characteristics and composition of the solid phase obtained after separation: centrifugation can cause significant changes in the metal content bioaccumulated in microorganisms, and filtration gives different recoveries depending on the method used to separate the solid from the membrane. Moreover, bearing in mind that it is sometimes necessary to collect large volumes of sample in order to obtain sufficient quantities of sediment, it is not always possible to effect the separation as soon as would be desirable.

Bottom sediments. Sampling of the sediments can be carried out with a grab, the most suitable types are those from Van Veen and from Ekman-Birge, for sampling at 15–20 cm in depth. When these devices are used, there is a risk of the finest particles being lost. Moreover, this sampling method often causes undesirable disturbances to the surface sediment. A large variety of designs are shown in Figure 6.

Prior sampling of the 1–3 cm surface layer is recommended¹², since this oxic layer does not reflect the pollution characteristics of the deeper sediment and should thus be analyzed separately. Subsamples taken from the center of the grab is suggested¹³, to eliminate possible contamination by the material of the container.

After collection, the sample is placed in sealed plastic bags or containers for transport to the laboratory.

In aquatic environments where sedimentation rates are more uniform than in rivers, corers are most suitable since they provide valuable information on the different levels of pollution in the stratified layers. There are a wide variety of designs that give sediment columns varying from 30–50 cm to several meters in length. The materials of the corers must be selected carefully to avoid contamination of the sample. The corer can be inserted manually into the sediment in shallow zones, whereas in deeper zones the use of gravity corers is necessary, and in this case a continuous-flow adaptor to avoid disturbance between sediment and the overlaying water is recommended¹⁴.

After collection, corers may be sealed with a plastic sheet and kept at low temperature, or even frozen, for transport to the laboratory.

In marine environments larger samples can be collected with box corers, with a large cross-section (30 × 40 cm) or (30 × 20 cm)¹⁵.

Interstitial water. The analysis of interstitial water should be regarded as a part of sediment analysis, since the composition of the pore water determines the mobilization and equilibria of metal species between the two phases: the changes in CO₂ content and in pH are the major drawbacks in pore water sampling and representativeness is not achieved in most cases. Sampling is usually performed using dialyzers consisting of large membrane bags filled with distilled water and inserted in the sediment for some weeks. This technique was proposed to be used “in situ”¹⁶ to obtain the best results, and different approaches have been developed later¹⁷. When dialyzers are not available, pore water can be recovered using centrifugation, but significant changes in water composition may occur.

Measurements in situ

Some parameters, such as pH and E_h provide information about the nature of the sediment and its oxic or anoxic character. The measurement of these parameters in sediments and in interstitial waters must be performed “in situ” for maximum accuracy. In our experience,¹⁸ redox-potential measurement in natural media is sometimes difficult and in most cases a considerable period of time is necessary to obtain stable values, so accurate measurements of this parameter is not always possible during sampling. Redox potential and pH in sediments should be measured by inserting the corresponding electrodes directly into the wet sediment^{19,20}. If this is not possible, the best approximation is to perform the

measurement in the laboratory but inserting the electrodes into the core. This method gives much better results than those performed in a prepared aqueous suspension of the sediment in the laboratory.

Pretreatment and storage of the sample

Sample handling and storage conditions should be most rigorously established for anoxic sediment samples, since the main parameters such as pH, redox potential, sulphides and organic matter content, are liable to suffer important changes in adsorption-desorption processes, precipitation-redissolution, or complexation equilibria. With a suitable storage method, microbial activity in the sample could be totally inhibited or minimized, otherwise, the changes in some chemical metal species could be significant.

When sediment has been sampled with a grab or a dredge, and a large amount of sample is available, the solid is allowed to settle in the receiving container and the liquid is poured off. It may be advisable to centrifuge or to extrude the sample, if possible "in situ". In the case of extrusion the use of an inert gas is highly recommended to prevent contact with oxygen.

To dry the sample, it can be extended in a thin layer over a plastic sheet, in the open air for up to 2–3 weeks. During this period it is convenient to tread the sediment some times a day to avoid agglomeration. Some workers dry the sample in an oven at 60–70 °C or even at 105 °C, while freeze-drying is also proposed by others as the best way to assure minimum changes in the metal fractions in the sample. In any case no storage method guarantees the permanence of the sample speciation.

When sampling is performed with corers it is widely recommended to store samples at low temperature, the temperatures should be 4 °C or in some cases freezing is recommended (-20 °C to -30 °C). In any case the cold conditions should be started "in situ" and maintained until drying has begun. Cores can be extruded using gas pressure to eliminate the water content, and the appropriate subsampling is carried out by fractionation in sections (some cm each), the content of each fraction is kept in a sealed plastic bag. These pretreatments should be carried out in an oxygen free atmosphere to avoid irreversible changes in metal species distribution¹⁹. To perform these operations we have designed a manual teflon press, of appropriate size that allowed us to extrude anoxic marine sediment cores into a glove box, under N₂ atmosphere¹⁵. Dry samples can be homogenized using the methods of coning and quartering previously described for soils.

Preservation of the sample by irradiation is recommended in cases where bacterial activity may occur during storage²¹.

After drying, the sample should be sieved to select the finest particles using a nylon sieve mesh, 63 μm^{19, 22}. Wet sieving is recommended in some cases to avoid agglomerations during drying. After sieving, samples are stored at low temperature or even frozen, until analysis. It is convenient to keep the sample in a well sealed plastic bag and under inert conditions. As an overall recommendation long storage periods before analysis should be avoided, even for oxic sediments.

Sampling and pretreatment methods used in metal speciation on sediments is a subject of permanent discussion^{23, 24}. It is difficult to establish definite protocols since these will

depend on the local environmental conditions and the purpose of the analysis. It is, therefore usual for different opinions to be expressed in the literature on handling and storage conditions. A discussion on the main factors that influence the integrity of the sample, the selection of the techniques to use in pretreatment steps and their validity would be of great interest.

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