

***Collection and preparation of
bottom sediment samples for
analysis of radionuclides and
trace elements***



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COLLECTION AND PREPARATION OF BOTTOM SEDIMENT SAMPLES FOR
ANALYSIS OF RADIONUCLIDES AND TRACE ELEMENTS

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FOREWORD

The IAEA has been providing support to developing Member States in the use of nuclear and nuclear related techniques for various applications, with special reference to environmental studies. With a view to helping to develop analytical facilities and capabilities in order to achieve scientific progress and social development, the IAEA has been promoting the growth of science in Member States over several years by disseminating information in the form of TECDOCs on focussed themes. The present publication is the first in a series of TECDOCs on sampling and sample handling as part of the IAEA support to improve reliability of nuclear analytical techniques (NATs) in Member State laboratories.

One of the major global concerns since the 1960s has been the monitoring of environmental changes to understand the implications of various anthropogenic activities in the post-industrial era. Important compartments of the environment are air, water, vegetation, particulate matter, soil, biological organisms and sediments. A large number of advanced techniques have been developed to monitor the environment; however, the measured analytical data are crucially based on the sampling and sample preparation of the chosen matrix, e.g. sediments. Changes in contamination, biological status and physical characteristics of lakes, rivers and coastal marine systems during the past have often led to significant changes in the composition of accumulating sediments. Sediments are the sinks for elemental cycles in aquatic systems and are recognized as one of the largest sources of in-place pollutants. Therefore sediments are the host for pollutants and provide information on the various processes such as sedimentation, water dynamics, sediment contaminant interaction, sediment–organism interaction and historical indicators. Thus, the analysis of sediments can aid in reconstructing the history of changes, understanding human impact on the ecosystem, and suggesting possible remedial strategies. In order to arrive at the best possible practices that could be adopted by the Member States, a consultants meeting was organized on “Collection and preparation of bottom sediment samples for analysis of radionuclides and trace elements” from 10 to 14 January 2000 in Vienna. The subject of the meeting was confined to bottom sediments with a focus on collection and sample preparation as a crucial step in the entire analytical process. Although there are many approaches and methods available for sediment analysis, the scope of this report is limited to sample preparation for (1) analysis of radionuclides, including sediment dating using radionuclides such as ^{210}Pb and ^{137}Cs and (2) analysis of trace, minor and major elements using nuclear and related analytical techniques such as neutron activation analysis, X ray fluorescence and particle induced X ray emission.

The purpose of this TECDOC is to provide information on the methods for collecting sediments, the equipment used, and the sample preparation techniques for radionuclide and elemental analysis. The TECDOC is intended to be a comprehensive manual for the collection and preparation of bottom sediments as a prerequisite to obtain representative and meaningful results using NATs. Quality assurance and quality control (QA/QC) is emphasized as an important aspect to ensure proper collection, transportation, preservation, and analysis since it forms the basis for interpretation and legislation. The report consists of the summary of the theme and discussions, followed by conclusions and texts of the presentations by the experts during the meeting. The IAEA is grateful to the experts for their contribution to this report.

From the IAEA, B. Smodiš, Division of Human Health and V.R.R. Annareddy and M. Rossbach of the Division of Physical and Chemical Sciences, were responsible for preparing this TECDOC.

EDITORIAL NOTE

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1. INTRODUCTION

1.1. Scientific and technical background

Bottom sediments consist of particles that have been transported by water, air or glaciers from the sites of their origin in a terrestrial environment and have been deposited on the floor of a river, lake, or ocean. In addition to these particles, bottom sediments will contain materials precipitated from chemical and biological processes. Natural processes responsible for the formation of bottom sediments can be altered by anthropogenic activities. Many man-made materials have entered bodies of water through atmospheric deposition, runoff from land, or direct discharge into the water. Most hydrophobic organic contaminants, metal compounds, and nutrients, which enter the water become associated with particulate matter. This particulate matter then settles and accumulates in the bottom sediments. Under certain conditions the contaminants in the bottom sediments may be released back into water or enter the food chain. Consequently, bottom sediments are a sink as well as a source of contaminants in the aquatic environment. These contaminants may pose a high risk to the environment on a large scale and hence need to be monitored at regular intervals. Environmental monitoring includes sampling and analyses of the sediments.

Extensive surveillance, monitoring, and research activities are required to assess the extent and severity of sediment contamination, to evaluate the effects of contaminated sediments on freshwater and marine environment, and to prepare a plan for appropriate remedial action. In field studies, monitoring is carried out to determine the variation in the concentrations of different contaminants as a function of time and depth. In many reports on the investigations of sediments, a detailed description of sampling techniques is often overlooked. Sampling procedures often vary depending on the objectives of the monitoring, method of analysis and the need of the analyst. However, in order to compare the results of the studies carried out at sites with different environmental conditions and contaminants, harmonized sampling techniques must be used. Processing a non-representative or incorrectly collected or stored sample may lead to erroneous conclusions and the waste of resources. Without adequate care QA/QC measures, sampling could become the weakest link in the entire process of sediment analysis. Therefore, it is of paramount importance to harmonize guidelines for sampling and sample preparation that will meet the requirements of the various methods of analysis.

Analysis of sediments provides environmentally significant information. Their chemical characterization is needed to understand the natural and anthropogenic influence on the bodies of water. Sample preparation includes separation of coarse material, homogenization and drying, and it is the first crucial step of sediment analysis. Nuclear and related analytical techniques such as gamma ray spectrometry is used for radionuclides determination while neutron activation analysis (NAA) and X ray fluorescence spectrometry (XRF) are used for elemental characterization. Although these are non-destructive techniques, they require proper sample preparation prior to the.

1.2. Scope of the report

This report aims to provide information on the (i) existing methodologies and procedures for the collection of bottom sediments and (ii) preparation of samples for analysis by nuclear and related analytical techniques. The most appropriate procedures for defining the strategies and criteria for selecting sampling locations, for sample storage and transportation are given in this report. Elements of QA/QC and documentation needs for sampling and sediment analysis are discussed.

Collection and preparation of stream and river bottom sediments, lake bottom sediments, estuary bottom sediments, and marine (shallow) bottom sediments are covered. Although there are many approaches and methods available for sediment analyses, the scope of the report is limited to sample preparation for (1) analysis of radionuclides (including sediment dating using radionuclides such as Pb-210 and Cs-137) and (2) analysis of trace, minor and major elements using nuclear and related analytical techniques such as NAA, XRF and PIXE.

2. GENERAL SAMPLING STRATEGY

2.1. Selecting sampling sites

Sampling sites are most efficiently selected when there is a priori information about the regional geology and the processes that influence the existing sediment distribution. The selection of sediment sampling stations should be based on a knowledge of the bottom dynamics of the study area. The three processes which most completely characterize the bottom dynamics are erosion, transportation and accumulation. Obtaining information about these processes through review of the previous work is the first step towards designing an efficient sampling strategy. Data sources such as bathymetric and topographic maps, aerial photographs, and land-use maps should be carefully examined to infer these processes and related bottom characteristics. Sidescan sonar, seismic reflection and swath bathymetry techniques (Fig. 1) [1, 2] are a significant aid in the design of a new bottom sediment sampling programme since they provide continuous coverage of the seafloor. Synthesis maps in Massachusetts Bay and on the Continental Shelf off New York based on these modern techniques are used to identify the location and extent of fine-grained sediment deposits where contaminants are likely to accumulate and areas of coarse-grained sediments or outcropping bedrock where erosion is common [3]. Such maps help in the design of an efficient sampling programme because fewer samples can be selected to represent larger areas. This can reduce the number of samples required as well as the ship time, number of analyses, and the overall project costs. Knowing locations of coarse sediments or bedrock prevents unproductive sampling efforts in areas where the risk of damage to sampling equipment is high.

On a much smaller spatial scale, bottom video and photography have been a tremendous aid in characterising the sea floor prior to sampling. Video cameras on the sampling tools make it possible to view and select the specific sampling site and to assess disturbance and other measures of quality as the sample is being collected.

2.2. Navigation

It is critical to know where samples are taken within a geographical grid. Thus the first step in designing a sampling programme is to plot desired sampling locations on a navigation chart or other suitable map having a latitude and longitude base. Selection of the navigation method should be made at the planning stage of the programme. The selection is based on the spatial scale of the study, the presence of fixed objects in the study area (such as islands, or bridges), and the navigational tools available.

The most modern navigation tool is the differential global positioning system (DGPS) that can provide precision to within 3 meters. It is available worldwide and is accessible with a hand-held receiver at a cost of US \$700. This system can be a significant aid in long term studies where repeated sampling is envisioned at the same location or in sampling specific targets

identified by other surveying tools. For example, sampling near barrels of industrial and/or radioactive wastes in Massachusetts Bay identified using sidescan sonar techniques [4] has been possible because of the precision of DGPS navigation used in both the sidescan and sampling surveys.

Good precision is also obtainable with optical instruments such as a sextant capable of reading double horizontal angles simultaneously. This is a common and versatile method for use at distances of 200 m to 5 km from identifiable objects on shore that also appear on the navigation chart or topographic map.

Electronic positioning systems are often required when surveys are carried out beyond the sight of objects on land because of distance or poor visibility related to weather. Examples include Loran C, Mini Ranger, Trisponder, or Radar. Radio methods include “line-of-sight” microwave electromagnetic position fixing (EPF) systems. Loran C is one of the microwave EPF systems with a range up to 2800 km. The accuracy obtained with Loran C is variable, but an accuracy of 20–40 m can be achieved using the best calibration techniques.

2.3. Sampling approaches

The first step in planning a sampling strategy is to clearly define the objective. The objectives of a sampling programme can broadly be divided into monitoring and assessment goals. Surveillance and assessment are intended to provide preliminary information about the site on the material to be analyzed while monitoring is planned to obtain information on temporal and spatial variations of the analyte within a specific geographic area for both regulatory and non-regulatory purposes.

The overall sampling protocol must include the sampling locations and all of the equipment and information needed for the samples such as: the types, numbers, sizes of containers, labels, field logs, types of sampling devices, number and the type of blanks, sample splits and spikes, the sample volume, any composite sample specifics, preservation instruments, transport plans, on field preparations (filtration, pH adjustments), field measurements (pH, Eh, etc.), report format and environmental conditions during the sample collection.

Generally three different approaches have been adopted for sample collection: judgemental, systematic and random. There are also further variations that can be found among the three approaches and combinations among them. For example, the systematic grid may be square or triangular and samples may be taken from the nodes of the grid, at the centre of space defined by the grid or randomly within the spaces defined by the grid. In Table I, the differences among the primary approaches are summarised. The judgmental approach utilises earlier knowledge on the site details and employs the smallest number of samples leading relatively to the largest uncertainty. Samples collected may make use of prior knowledge about the site in order to obtain useful data, however samples for monitoring require absolute random samples to exclude personal bias. The advantage of random sampling lies in its simplicity of assumptions, but the disadvantage is that it is more expensive. Since the masses of analytes are variant both in space and time, some kind of stratified random sampling is most efficient. Often a combination of judgmental, systematic and random sampling is the most practical approach.

Stratified sampling permits the division of heterogeneous population into more homogeneous sub-populations that are less variable than the original population. A sampling independent of

different portions of the population is advisable. This sampling technique is also useful for areas that have already been mapped and consist of well-defined zones with different sediment types such as gravel, sand, silt and clay. Locations with fine grained sediments and high organic contents which have a greater affinity for contaminants should be sampled in greater detail, for example, at 100%, than the locations with sand and gravel, sampled at 50% and 10% respectively. Once the stratification population is established, the sampling of the subsets is then undertaken in random cases in each subset.

In certain zones of rivers and lakes where there are rapids and falls, it is not advisable to take bottom sediment samples because erosion is such that fine-grained sediments do not remain long and are quickly transported downstream. Consequently, sampling upstream of rapids and falls before reaching the eddies is the recommended approach.

TABLE I. SUMMARY OF THE SAMPLING APPROACHES [5]

Approach	Relative number of samples	Relative systematic bias	Basis of selecting sample sites
Judgmental	Smallest	Largest	Prior history, visual judgement
Systematic	Larger	Smaller	Consistent grids or pattern
Random	Largest	Smallest	Simple random selection

2.3.1. Sampling size

The basic criteria for sample size, that is, the number of samples, should include consideration of the representativeness of the system as well as the amount required for measurement. In a reconnaissance survey of river or lake for sediments, sampling is carried out on a grid with a density of one to several samples per square kilometer. This sampling density provides a satisfactory picture of the geological and geo-chemical background. The density of the sampling and station spacing is usually 1 km but sometimes 750 m or 500 m apart, as determined before starting the survey in accordance with the geology of the region. If it is decided a sector is to be examined in great detail, a grid with shorter spacing should be used. The density of the grids is dictated by the local conditions and accuracy desired. In the cases, where there is fine-grained sediment, two sediment samples are taken 10 to 20 m apart. In contrast, gravel sites are ignored, but when gravel is to be sampled, it is poured into a 5mm sieve placed above a bucket and screened until a sufficient amount of material containing sand and fine-grained material is obtained (from 100 g to several kilograms).

Consider the example of a proposed dredging project to remove contaminated sediments. The selected size of the grid represents a compromise between the volume and size of the area. It is assumed that the contaminants are randomly distributed within the area and the sampling station is defined at the centre point of each grid. The dimensions of the sampling grid can be calculated using 1000 m^3 as a management unit and the thickness of sediment planned for the removal. For example if the thickness of the sediment to be dredged is 0.2 m, the area of the sampling grid is 5000 m^2 , which corresponds approximately to a dimension of $71 \text{ m} \times 71 \text{ m}$. The number of grids can be evaluated by dividing the study area by the dimensions of one grid. If no historical information is available for either sediment particle size or contaminant distribution at the study area, about 60% of the grids is sampled on the basis of random selection and sampling sites are designated at the centre of each grid. If data on sediment particle sizes are available, then grids can be designated as containing gravel, sand or fine-grained sediments on the basis of median particle sizes. Again, 60% of the total number of

grids is to be sampled, but the same proportions of gravel, sand and fine-grained sediments must be maintained in the study area. These sediment types have to be sampled at a minimum of one per sampling station. For example, the study area contains 52 grids, out of which 49% have fine-grained silt and clay, 40% sand, and 11% gravel. On the basis of 60% sampling criteria, about 32 samples consisting of 16, 13, and 3, respectively, from fine-grained, sand and gravel zones have to be collected.

2.3.2. Representativeness of the sample

The variation in the composition of surface sediments results from the inherent heterogeneity of the matrix. This would reflect in the representativeness of the sample result. The sampling plan together with the size of samples could overcome the heterogeneity problem. Furthermore the amount of sample used to determine the average contaminant concentration is an important factor to obtain the representative result. It is preferable to use a large size test sample and number of aliquots. When digestion is the sample-processing step, the large size of the sample could overcome in homogeneity problems to a greater extent since the digested extract is expected to be more homogeneous. In addition, the use of composite samples can overcome the heterogeneity.

2.4. Quality assurance and quality control during sampling

A sampling programme design must consider the quality of data that is needed, i.e. the degree to which total error must be controlled to achieve the required level of confidence. This should include consideration for the type and number of samples necessary to control and minimize the bias (systematic error) and maximize the precision of sampling effort. The data collection planning process should provide a logical objective and quantitative balance between resources available for collecting data and the quality of data with its intended use. The focus for the sampling QA/QC should be to identify, measure and control the errors during complete sequence of sample collection, preservation, storage and shipment to the laboratory prior to analysis. In order to include sampling in a quality assurance and quality control programme, the samplers have to be trained and instructed in special sample handling procedures according to the field standard operation procedure (FSOP) [6]. The variance in the sampling procedure has to be estimated by two identical sampling procedures at the same sites (duplicate sampling) from a minimum of 3% of all sample points [7].

To minimize the sampling error and to assure standardized sampling despite different individuals collecting sediments, a sampling record card has to be completed for each sample (standard sheet similar to DIN 38 414 S11 [7a] and an example is given in Annex I). Transport conditions have to be documented and the arrival at the laboratory has to be confirmed by the laboratory personnel [8]. Field blanks made up of analyte free water and appropriate standards must be used to calibrate field instrumentation (pH, Eh, conductivity etc.).

3. COLLECTION OF SEDIMENT SAMPLES

Sediments and suspended matter in surface waters are frequently heterogeneous due to small-scale changes in hydrological regime and geomorphologic changes in the catchment area. This variability is minimized by taking several sub-samples (minimum 5), which are mixed together in a composite sample [7]. If the interest is mainly in the fine sediment fractions (<0.063 mm), a sample mass of only 1 kg (dry weight) is sufficient in most of the cases. If

larger sediment fractions are of interest then the sample size has to be increased for homogeneity reasons. If possible the acceptable level of heterogeneity should be tested with multiple sampling at a particular sampling area [9]. As a rule of thumb, the sample weight should increase with the cube of the largest expected grain size (see Table. II).

TABLE II. EMPIRICAL SAMPLE WEIGHTS DEPENDING ON THE LARGEST GRAIN-SIZE IN SEDIMENTS AND LOOSE SAMPLES [10]

Estimated largest grain size in sediments and loose samples (mm)	Sample weight (kg)
0.125	0.003
0.252	0.025
0.5)	0.129
1	1
2	5
3	20
5	80
10	300
15	600
25	1,250

River sediments

Frequently during monitoring only the recent sediments (accumulated over the last 0–6 months) are of interest. For practical reasons, at each sampling area (approximately 50–100 m on both river banks) the surface sediment (0–3 cm depth) is collected [11, 5] with a flat hand shovel as sub-samples from several points with low current velocities, in order to obtain the finest-grained sediment. Sediments settled during low and medium discharge are sampled. Sediments deposited during or after floods are normally too coarse-grained and are diluted by freshly eroded unpolluted sediments from mountainous areas. To collect samples from deeper waters or from deeper in the sediment column for investigation of historical inputs, grab samplers or corers can be used (see Sections 3.2 and 3.3).

In order to estimate the potential to mobilise pollutants from the sediment to the adjacent water, in the case of re-suspension or deposition on land, the main factors influencing mobilisation, such as pH, Eh and temperature, were measured potentiometrically in the wet sediments. In practice the *in situ* measurement of these variables at each sampling spot is very time consuming. These three variables, were quickly measured in the collected composite sample, which allow an approximate categorisation of the pH and redox conditions in the sediment at a sampling area. These measurements made in running water, including electrical conductivity, characterise the general situation in the body of water at the time of sampling.

Lake sediments

Lakes are classified as shallow ($H < 7$ m) and deep ($H > 7$ m). This classification is relevant in terms of thermal stratification. The stratification in a lake has profound consequences on the physical, chemical and biological phenomena. For example, aeration occurs in the epilimnion, while in the hypolimnion, anerobic conditions may occur. The vertical component of water

transport is of great interest in the understanding of mass flux and mass balance. Traditionally vertical transport is expressed by Ficks' law with a vertical turbulent diffusion coefficient, and field data on temperature and chemical processes are commonly used to determine this parameter [11a]. In addition, lake sediments provide a basis of reconstructing history of man's impact on the lake environment and in such studies the establishing of accurate chronologies of sedimentation is of vital importance not only for dating events but also for sediment accumulation rates.

Marine sediments

In estuarine or coastal waters, grab samplers or corers are most commonly used to collect recently deposited sediments. Sampling equipment is discussed in chapters 3.2 and 3.3. For pollution monitoring, a sampler that collects material at the water-sediment interface without loss or disturbance should be selected. The upper section of the sample (0–1 or 0–3 cm) should be carefully taken in order to assess the most recent contributions of contaminants to the surface.

3.1. Sediment environment: Variability with respect to different water bodies

There have been attempts to classify sedimentary environments, and the geological literature is full of such classifications. In this report we have focused only on sampling in fluvial, lake and marine sedimentary environments. For interpreting environmental geochemistry data, we want to know the erosion area, the condition and timing of sedimentation, and as the sediment composition at the sampling site. One has not to be a full trained sedimentologist to do this, however, some basic training in sedimentology and the main sedimentological principles should be considered. For further reading we refer to sedimentological textbooks [12,13].

Fluvial sedimentation

Generally, we distinguish between (1) **active stream sediments** in the river channel or slopes of river banks and bars and (2) **overbank sediments** in the natural levees, crevasse – splay, flood basin and flood plains of river systems. Active stream sediments are deposited more or less continuously in shallow or deeper river waters. Under relatively low flow conditions, thin laminated silt deposits (<2 cm) can accumulate as surface cover above sandy river bars [14] particularly downstream of natural barriers. These silt deposits are eroded during the next flood, preventing major sequences of fine-grained sediments. Active stream sediments are sometimes difficult to find in mountainous braided rivers and creeks as well as in bounded river channels in industrial and urbanized areas. Overbank sediments are deposited normally during high floods. The velocity of the stream is reduced by overtopping the banks, causing deposition of much of the suspended fine sediment on the river banks with decreasing grain size away from the channel. These sedimentary deposits from one flood event may be a few centimeters to several decimeters thick [12]. Overbank sediments and in particular flood basin deposits (lowest lying part of a river flood plain) represent the long continued accumulation of fine-grained suspended sediment. This allows for reconstruction of sediment composition backwards into pre-industrial times. However, flood-sedimentation is not directly comparable to sedimentation during low or medium water levels.

The ratio of dissolved pollutants to total suspended matter in the water column is also important. The amount of pollutants adsorbed per gram of sediment is relatively low during floods because of dilution. During normal and low water discharge, the suspended matter is

considerably less concentrated and of a finer grain-size, which means it has a high capacity per gram for pollutant adsorption. For that reason, sampling of fine-grained sediments after flood events should not be overemphasized in the sampling schedule. Similarly, sediment sampling during the rainy season in tropical or subtropical regions can cause sediment matrices of dominating quartz without sufficient adsorption capacities [15]. For sampling active stream sediments, which are regarded as representative samples of the drainage basin upstream of the sample site, coarse (>0.06 mm) and fine (<0.06 mm) sediment fractions have been collected. In recent years coarser fractions have been advocated in the form of overbank sediments as a sampling medium for regional geochemical mapping [16]. Sampling widely spaced sections of overbank sediments therefore have the potential to provide a sampling medium for geochemical surveys which can yield both spatial (drainage basins 60–600 km²) and temporal data, and also be used as a tool for detailed studies of mining and industrial contamination [8].

Lake sediments

The concentration dynamics of inert soluble matter is a general property of the lake, being determined by the flow, mixing pattern and residence time distribution in the lake. The concentration dynamics of a specific non-conservative component is obtained by superimposing its kinetics of loss (or accumulation) on the concentration dynamics of inert soluble matter. Lake sediments provide a basis for establishing kinetic aspects of specific non-conservative components. Furthermore, sedimentation rates based on paleynological or stratigraphy methods often provide historical averages involving many meters of the sediment layer. Such measures may not adequately reflect the rates within the upper 20 cm or so of sediment where significant sediment-water exchanges are occurring at the present time [17] and application of radiometric methodology to sedimentary geochronology has enjoyed considerable success.

Textural properties of lake sediments (e.g., porosity, water content) can serve as tools for evolving and assessing the possible effects of sediment focussing, slumping and inhomogeneity in the sediment composition. Sediment focussing is a process whereby water turbulence moves sedimented material from shallower to deeper zones of a lake. According to Hakenson's scheme [18], 50% water content of surfacial sediments in a lake sediment core marks the transition between zone of erosion and transportation and 75% water content of surfacial sediments marks the transition between zone of transportation and accumulation.

Marine sediments

Collecting representative samples in a marine area requires prior knowledge about the sea bed. Initially, some guidance can be obtained from bathymetric maps, knowledge of tidal currents, and information about the likely exposure to high energy current forces such as waves from major storms. In areas with heavy use of bottom-trawls for fishing, e.g. south of Iceland and in the North Sea, surface sediments are frequently disturbed. As discussed by Bothner (Annex no: this volume), a great deal of information about bottom morphology and regional patterns of sediment texture can be obtained by using bottom imaging techniques such as side scan sonar. This preliminary survey tool, if used before the sampling plan is designed, can be extremely useful in selecting sampling locations that will efficiently characterize a new study area.

3.2. Grab sediment samples

3.2.1. Objective of collection

The lateral variations in the chemical composition of grab sediments act as a guide to local pollution centres. Tracing pollution by means of water analysis frequently gives rise to difficulty, which may be usually associated with sampling procedures and physico-chemical conditions pertaining to the species rather than to accuracy and precision of analytical techniques. Some of the trace metals as well as radionuclides get rapidly scavenged by the particulate matter in the water body which eventually settles down to the bottom sediment. The distribution coefficients (K_d) for many elements (isotopes) are significantly high and hence the determination of these elements in sediments can play a key role in detecting the sources of pollution. Although sediment analysis does not represent the extent of intoxication, they may be employed on a semi-quantitative basis in comparative studies to trace the sources of pollution such as surreptitious discharges from the nearby industries. Since many of the toxic pollutants affect sediment-dwelling organisms and in turn may get transferred through the food chain to humans, attempts have been made to set up guidelines for pollutant contents in aquatic sediments in order to protect environmental health.

3.2.2. Types of sampling devices

The purpose of sampling is to collect a representative, undisturbed sample of the sediment to be investigated. There are many factors, which need to be considered in the selection of suitable equipment. These factors include the sampling plans, the type of available sampling platform (vessel, ice etc.), location and access to the sampling site, physical character of the sediments, the number of sites to be sampled, weather and number and experience of the personnel who will carry out the sampling. Because of these factors, the standardization of sampling technique is difficult. Generally the aim is such that the selected sampling equipment should recover undisturbed sediment samples.

Bottom sediment deposits can be sampled by grab samplers or dredges, which are designed to recover sediment material from the top few centimeters of the lake/river bed. Grab samplers consist of either a set of jaws which are lowered to the surface of the bottom sediment or contain a bucket which rotates into the sediment upon reaching the bottom. The dredges usually have bevelled lips to scrap upper layers of the sediments. For special purposes, the dredges may have teeth to plough the bottom and stir out burrowing molluscs, worms etc. The fine-grained bottom sediments are collected with Van Veen type of the sediment sampler. This device consists of two bowl-clamp shaped sections which are held open by a catch. When the sampler touches the sediment, the catch is released and the bowl shape sections close together, trapping sediment from a penetration depth of about 20 cm.

There are some requisite properties needed for the grab samplers for their general operational suitability. These are the stability and capability to prevent sample loss from washout. In addition, sample volume also needs to be considered when choosing a surface sediment sampler. Several comprehensive reviews are available on bottom sediment sampling devices. These reviews have described a wide variety of bottom sediment samplers designed for biological and geological studies mainly in marine environment, but they can be used in pollution studies in the marine and freshwater environment [19–21]. The theoretical and practical aspects and advantages and disadvantages of various types of sediment samplers are also discussed in these reviews [11, 22]. The information given on the different devices in the

following section should be used as a guide and not be construed as an endorsement for any particular sampler.

3.2.2.1. Birge-Ekman grab sampler

This is a light weighted equipment (5–10 kg) with a sampling area of about 15 cm × 15 cm. It can collect a sample 3L in volume. It is designed to collect soft sediments manually in the absence of strong currents. The lack of sample disturbance, square cross section and moderate penetration make it suitable for collection of 2 to 3 cm of bottom sediments. Because of its lightweight and easy handling, it is well-suited for small boat operations. The modified Ekman samplers are available in different sizes and may require winch or crane to hoist.

3.2.2.2. Ponar grab sampler

This equipment (about 23 kg) has a sampling area of 23 cm × 23 cm with a collection volume capacity of 7.3 L. It consists of a pair of weighted, tapered jaws held open by a catch bar across the top of the sampler. The jaws of the sampler overlap to minimise washout during descent of the equipment. A special messenger of Ponar grab sampler prevents accidental closing during handling or transport. This grab sampler is useful for most of the sediment types from soft, fine grained to firm sandy material with the exception of clay both in freshwater and marine environment. The equipment produces little or no disturbance during the collection of samples.

3.2.2.3. Shipek grab sampler

This heavy weight sampler (about 50 kg) is designed to collect a volume of 3L sample from a sampling area of about 20 cm × 20 cm. It is useful to collect soft, fine grained to sandy material from any depth with even a sloping bottom. Despite the large size of the sampler, its weight ensures a near perfect descent to the bottom. The double Shipek sampler consists of two single Shipek samplers and is useful for collecting duplicate samples from the same site. The Mini- Shipek sampler (about 5 kg) should prove adequate for the recovery of small amounts of material from 3 cm of the surface sediments. Because of its weight, it is suitable for hand-line operation from different sampling platforms. Under some conditions the stratigraphic order of the top 3 cm can be flipped by 180° as the sample is collected.

3.2.2.4. Peterson grab sampler

This is a heavy weight sampler with a wide base line (when jaws are open). It maintains a near vertical descent to the bottom under all conditions and it is suitable for samples of hard bottom material such as gravel and firm clay. When the sampler is used in very coarse or Shelly sediment, large sediment grains and pebbles may be trapped between the jaws preventing their closure and causing severe sample loss. The Teflon coated lead weights provide improved penetration depth. The equipment requires a lifting capacity of about 150–250 kg.

3.2.2.5. Van Veen grab sampler

This heavy weight sampler has a sampling capacity of about 18L. The increased opening at the bucket top provides less oscillatory shock waves. The addition of Teflon coated lead weights to the upper edges (similar to Petersen sampler) improved their penetration into firm sediments [23]. The instrument requires a lifting capacity of about 100–400 kg. The Van Veen

grab is suitable for obtaining bulk samples ranging from soft and fine-grained to sandy material for biological, hydrological and environmental studies in deep water and strong currents.

3.2.2.6. Smith-McIntyre grab sampler

This heavy weight sampler (about 90 kg) can collect samples of about 10–20 L in fine-grained and sandy sediments. However, it requires a lifting capacity of about 200–300 kg. A free-fall from about 10 m above the lake or ocean floor is sufficient to collect a sample even from firm sediments. The rubber flaps fastened to screen frames cover the brass screen during retrieval operation and prevent the entrance of water which might wash out any trapped material. Safety pull-pins are provided to prevent any premature closure or accidental release of the cocked assembly.

3.2.3. *Advantages and disadvantages of different systems*

The samples collected through grab samplers should resemble the original material as closely as possible without loss of a particle size or geo-chemical fraction. Disturbance or sample alteration could occur through sediment compaction, mixing or fractional loss. These disturbances can be caused by a pressure wave in advance of the lowered sampler, frictional resistance during sediment penetration, tilted penetration of the sampler, and wash out or other losses during retrieval. The advantages and disadvantages of different grab sampling devices are summarized in Table III. They are evaluated by their triggering system, design, protection from wash out, and stability.

3.3. Sediment cores

3.3.1. *Objective of collection*

Sediment cores are collected for many reasons. Core samples serve as an excellent tool for establishing the sedimentation rate, the history of contaminant additions to the water system, and the inventories of pollutants. These determinations are possible since suspended particles and bottom sediments adsorb pollutants dissolved in the water system and control their transport and ultimate deposition. In areas where sediment accumulation is constant and there is minimal sediment mixing by biological or physical processes, the age of the sediments increases systematically with the depth of the core. In the absence of chemical mobility within the sediments, the changes in contaminant concentrations with the depth of the core can be converted to a record of history of contaminant inputs.

3.3.2. *Types of coring devices*

A large number of devices have been developed to collect sediment cores. We will describe gravity corers, multiple gravity corers, hydraulically damped corers, box corers, piston corers, freeze corers, vibro corers, and drilling, and discuss their advantages and disadvantages. A valuable text which describes well-established coring equipment is Murdoch and MacKnight, 1991[25].

When taking a sediment core, it is important to collect the original layers of the sediment without disturbance and to avoid losing important parts of the core, especially the surface layer of high water content which may hold the most recent pollutants.

TABLE III SUMMARY OF VARIOUS SAMPLERS [11, 124]

Grab sampler	Trigger system	Design	Protection from wash out	Stability
Ekman	Good and consistent, can be affected on soft bottoms	Excellent, jaw shape follows arc of cut, no sample displacement	Good, except when used for very coarse or Shelly sediment	Fair (less stable), wide open base gives good stability, but light weight would lead to operational problems under poor sampling conditions, inadequate or incomplete sediment penetration.
Ponar	Good, tends to be over -sensitive on gravel bottom	Excellent, jaw shape follows arc of cut, no sample displacement	Good, in addition to overlap jaws, a pair of metal plates mounted close to moving side faces of jaws further reduce possibility of wash out.	Very good, heavy weight sampler with wide base line (when jaws are open), maintains a near vertical descent, stable stance on the bottom in most waters with relatively weak currents (lakes)
Shipek	Good, though slight settlement may occur before triggering on soft materials	Excellent, cutting action is very clean producing minimal disturbances particularly in soft places such as mud, silt and sand.	Excellent, bucket closes with its separation plane aligned in horizontally rather than vertically. When bucket is properly rotated wash out is completely avoided.	Excellent, its weight ensures a near vertical descent and stable stance on the bottom in most waters even under rapid drift conditions
Peterson	Good, tends to be over- sensitive on hard gravel bottoms	Poor, jaw is semi-cylindrical in shape, sample displacement occurs under maximum capacity.	Good, except when used for very coarse or shelley sediment	Good, like Ponar maintains a near vertical descent, however after sampling tends to fall over (unless on a soft bottom)
Van Veen	Good, improved release mechanism made sampling easier in unsheltered waters.	Weighted jaws made of stainless steel with large surface area ideal for rough sea conditions.	7–20% variation in measuring volume of sediment *, addition of rubber flaps over screened opening aimed to prevent washout.	Excellent, weighted jaws, the chain suspension and doors and screen allow vertical descent to bottom even when strong underwater currents exist.
Smith-McIntyre	Good, safety pull-pins provided to prevent premature or accidental closure.	Externally mounted side and bottom plates on the jaws prevent jamming and improper closure.	Rubber flaps fastened to the screen frames cover the brass screen during retrieval and prevent washout.	Stable, two-jaw buckets mounted on weighted steel frame allows sampler to rest squarely on the bottom, a free fall of 10 m above the lake or ocean floor is adequate to collect samples from firm sediment cover.

Note: Reader should take note of observations and make selection on the basis of requirement.

The tube diameter should be as large as is practical in order to provide sufficient material for analysis, to minimize the impact of smearing along the core edge, and to minimize the possibility of core compression. If the top layer of sediment contains significantly higher concentrations of the analyte of interest, it may be necessary to eliminate a potential smearing problem by discarding the outer rim of material in contact with the barrel. Obtaining the wet weight of the discarded material in contact with the core barrel will make it possible to estimate the bulk density of each slice with increasing sediment depth. In practice, a tube diameter of about 5 cm and 12 cm is commonly used. Problems associated with friction of the sediment along the inner wall of the barrel are more pronounced in the smaller barrels but are also dependent on the sediment type. Fine-grained sediments are most problematic.

3.3.2.1. Simple gravity corers

In principle, a gravity corer is an open tube fitted with a weight so that gravity can force it sufficiently deep into the sediment to isolate a sediment sample. A large number of gravity corers have been developed which vary in complexity from simple tubes to heavy and sophisticated instruments. The simplest possible corer is a piece of plastic tubing. In very shallow aquatic environments, e.g. shallow streams or tidal flats, such a tube can be pushed into the sediment, sealed at the top and retrieved. A simple tube may also be operated by a scuba diver, or it may be used for sub-sampling from a large box corer on deck. An obvious advantage of this approach is that it is simple and inexpensive. It is also an advantage that the sampling can be carried out under visual inspection – it is not going on “in the blind”. However, the use of this approach is limited to the cases where the operator can get direct access. In most situations, this is not possible.

To be able to operate a corer on a wire from a boat wagging above the sediments to be sampled, several modifications have to be added to the simple tube design:

- The tube is fitted with a suitable metal load to add weight for more efficient penetration;
- A mechanism is added to seal the top of the tube after penetration in order to form a vacuum on retraction of the core;

For sampling at shallow depths from small boats, several light weight hand-held corers are available with tube diameters as large as 8 cm. The benefits are the fact that it is simple, low-priced and does not require a winch – thus they may be applied with a very low level of logistic support, and they may be preferred in shallow environments where there is no access for heavy boats. A disadvantage is the limitation in weight and thus the limitation in depth penetration. Also, this type is normally not suitable in sand or in watery mud.

Some typical examples of manually deployed corers are the Phlegar Corer (weight: 8–15 kg depending on the number of lead weights; core tube: 3.5 cm i.d) and the Kajak Brinkhurst Corer (weight: 9 kg; core tube: 5 cm i.d) and their modifications [25]. These instruments are capable of collecting cores of about 70 cm long from soft, fine-grained sediments. A disadvantage of the small diameter core barrel (3.5 cm) is the smaller quantity of material per unit core length and the possibility of higher friction-related compaction as the sample is collected.

Limitations encountered with a simple gravity corer may be overcome by adding further features to the sampler, such as a mechanism for sealing the bottom of the core after retraction

from the sediment bed in order to avoid loss of the core. This is particularly necessary with large tube diameters. If significant weight is added to the gravity corer, a boat and winch may be required to operate the sampler. The benefit of increasing complexity is the ability to work in deeper environments such as estuaries and on the continental shelf and to obtain longer cores of larger diameter. A disadvantage is the high cost of the coring devices and the extra logistical support required for their operation. Other problems with corers that are used in deep water include the difficulty of choosing a specific sampling site within a heterogeneous bottom and viewing the corer behaviour as the sample is collected. Some problems, like double penetration or the corer falling over, can be solved with greater complexity in the corer design if necessary.

Benthos Gravity Corer (weight: 175 kg; core tube: 6.6 cm i.d) and Alpine Gravity Corer (weight: 1100 kg; core tube: 3.5–4.1 cm i.d) are examples of winch or crane deployed gravity corers. Benthos Gravity corers are designed to recover up to 3 m long cores from soft, fine-grained sediments. The Alpine Gravity Corers have an inter-changeable steel barrel in lengths of 0.6, 1.2 and 1.8 m. In all of these corers, a sealing valve is located at the top of the core liner to help retain the sediment in the barrel during pullout and transit to the sea surface.

Multiple corers typically consist of several core barrels mounted on a single fin and weight system. They have been developed for multiple sampling at one site, comparative studies, evaluation of sediment sampling precision and the determination of sediment heterogeneity.

3.3.2.2. Hydraulically damped corers

A few hydraulically damped corers have been designed specifically to collect short (<0.7 m) cores with minimal disturbance loss of material at the water-sediment interface [26–28]. The unique operating feature of these instruments is a water filled piston that provides a slow and selectable rate of core-barrel penetration after the coring apparatus is set on the bottom (Fig.1).

This mechanism minimizes the “bow wave” which is known to occur in corers that free-fall into the bottom at a high rate. The frame provides an advantage over a simple tube gravity corer by maintaining the core tube in a vertical position even if the penetration is low. The frame also permits installation of a mechanism that seals the bottom of the core tube immediately after the tube is extracted from the sediment. A bottom core seal improves the success of capturing sandy sediment in the core tube without an internal core catcher. The seal at the top of the core can be either a check valve activated at the time of penetration or a piston that is held in position relative to the sediment surface.

Because the core is sealed at both the ends at the moment sampling is complete, this instrument provides samples suitable for analysis of contaminants in interstitial water and bottom water in contact with the sediment.

3.3.2.3. Box corers

Box corers are used to collect large volumes of surface material having a surface area of up to 50 x 50 cm and a maximum depth of about 50 cm. The instrument is lowered to the bottom at a rate controlled by the speed of the ship’s winch (plus the uncontrolled speed of the ship’s motion).



Fig 1. Hydraulically damped corer sampler.

The box penetrates the sea floor under the weight of lead (or ideally stainless steel if lead contamination is a concern) added above the box. As the winch begins to retrieve the core after full penetration, a single spade (Reineck design) or two opposing jaws (Ekman design) with rubber sealing surfaces are pulled through the sediment to a position in contact with the cutting edges of the box, ideally making a tight seal [29]. In practice, this instrument takes an excellent sample in muddy sediments. There is minimal compaction of the sediment during coring with this instrument because of the relatively large ratio of surface area to wall contact area (compared to a small tube corer). Once on the deck, the box core sample is often sub-sampled by pushing clean core tubes into the mud for a variety of special studies. In sands, box corers are seldom successful. The nature of the sealing spade is not sufficiently tight to

trap water, which runs through a sandy sample and past the seal. This flow typically erodes material from the box before sub-sampling is possible.

3.3.2.4. Piston corers

Conventional piston cores are used when long cores (3–30 m) in fine-grained unconsolidated sediments are required. Ships equipped with hydraulic cranes and winches capable of lifting 20 tons are necessary for achieving cores longer than 10 m. The coring instrument utilizes an internal piston which is held just above the water-sediment interface as the core barrel penetrates the sediments during a free-fall from a fixed height above the bottom. One of the earliest designs was in 1947 by Kullenberg. A description of its function and a comparison with other coring tools are provided by Weaver and Schultheiss, 1990 [30]. A pilot gravity core is often used as the trigger for the piston corer in part to collect a sample of the less disturbed surface sediment. The surface sediment collected by a piston corer is typically re-suspended or lost because of the high entry velocity and resulting bow wave or the high vacuum created by the piston. Disturbance of the core sample is also often related to the difficulty in maintaining the position of the piston relative to the sea floor. The winch wire can spring back in response to the sudden loss of tension as the corer free-falls into the sediment.

3.3.2.5. Freeze corers

A new device utilising a hollow wedge filled with dry ice and alcohol has been developed to collect a frozen core in soft sediment having high water content [31]. It has a hydraulic system for controlling the rate of sediment penetration. Two slabs of frozen sediment are recovered having dimensions of up to 100 cm long, 20 cm wide and 5 cm thick. Cold room facilities (-8 to -10°C) are useful for convenient post collection processing.

This instrument has successfully recovered sediments in lakes without disturbance. It weighs a total of 115 kg and can be disassembled and transported in a minibus. It can be operated from a small boat or raft and can work through the ice. A different freeze corer design has been developed and used to collect cores in gravel from a river bed [8]. The instrument uses a hollow pipe that is driven into the sediment and is then filled with liquid nitrogen. This is a major breakthrough for collecting a stratigraphic sequence in unconsolidated coarse-grained sediment.

3.3.2.6. Vibra corers and drilling

Vibra corers and drilling equipment are typically used in sediments that are resistant to the conventional methods of coring. Vibra cores utilize a motor-driven vibrator attached to the coring tube to make its function similar to a pneumatic jackhammer. Vibra coring equipment is available in a wide range of sizes including portable back-pack gasoline motors (which recover one-meter cores in sand [32]) and ship-operated systems weighing a few tons which collect cores in excess in sandy Continental Shelf sediments [33]. Vibra corers often re-suspend sediment at the water-sediment interface. They may or may not disturb the fine structure of the stratigraphy. The complexity of this coring system and the potential disturbance of the sediment structure are the major disadvantages of this coring system. The advantage is the success of recovering cores of significant length that cannot be sampled by other methods. Vibra corers are mainly used to assess geo-technical or structural properties of the sediment and have rarely been used for obtaining sediment samples for the study of environmental pollution.

Drilling rigs provide another means of collecting sub-surface sediments. Industrial applications include drill rigs for oil and water exploration for which there is an extensive literature that will not be reviewed here. Research on coral reefs has included the development of drilling tools that can be operated underwater by divers [34, 35] or on the exposed coral platform. Because of annual growth rings in corals, analysis of drilled cores have been used to establish a record of historical changes in metal concentrations in sea water adjacent to the reef [36]. Drilling is a complex process requiring mobile power generators and robust frames to hold the drilling tool but in some environments it is the only option for recovering consolidated sediment, coral or rock.

3.3.3. Extruding and slicing

Obtaining sub-samples from a retrieved core is achieved by a variety of techniques depending on the objectives of the sampling programme. Cutting cores at 1–2 cm intervals is often done for measurements of sedimentation rates and for determination of contaminant inventories over the time. Care should be taken to avoid as far as possible disturbing the original layering and smearing effects during subsampling.

An example of an extrusion mechanism is given by Bothner (proper annex no., this vol.): a frame that holds the core while a piston is pushed upward using a hydraulic jack. An extension placed on top of the tube can be used to collect and cut the core as it extends prior to transfer to a suitable container. If a very watery top sediment layer is to be retrieved, this extension should be sufficiently tight to hold water. A design suited for extruding and cutting soft and watery cores has been described by Niemistö [37]. In the case of significant differences in contaminant levels from top to bottom, the extrusion will add further smearing from the upper to deeper layers. In some cases, trimming of the edges of the core should be considered. With increasing core diameter, it becomes increasingly difficult to perform accurate thin slicing. It is therefore often necessary to decide on a medium core diameter as a compromise between a small diameter with smearing problems and a larger diameter with slicing problems. In practice 10 mm slices can normally be retrieved from cores up to around 10 cm diameter. In some cases, a core can be frozen and then successfully sliced with a cutting tool, e.g. a band saw, either in the tube or after being pushed out of the tube. One problem with this technique may be the possibility of disturbance of the sediment layering during the freezing process.

4. TRANSPORTATION AND STORAGE

The objective of any sampling programme is to deliver samples to the laboratory that are representative of the original material. After the collection of the sediments using grabs or corers at the field site, the samples must be transported to the laboratory under conditions that do not compromise the subsequent planned analysis. This may involve special steps to maintain cold temperature, to reduce potential contamination and to minimize mixing for biological, chemical, and physical analyses, respectively.

4.1. Containers for sediment samples

Containers and implements should be carefully selected for sediment handling in the field and laboratory, in order to minimize contamination. Containers should neither contaminate the sample nor promote loss of constituents through sorption effects. For example, the presence of a plasticiser in the plastic containers can be considered as a contaminant. Similarly metal

containers may contaminate samples which are analyzed for metal constituents. Many types of containers made from relatively inert materials like quartz, Teflon, polyethylene, and hard glass have attractive as well as undesirable attributes. Polyethylene, Teflon and hard glass implements are ideal for handling sediment samples which are to be analyzed for inorganic compounds. Plastic bags made of polyethylene, polypropylene and other suitable plastic can be used for the storage of wet or dry sediment samples. Sediments for biological testing can be collected, transported, and stored in plastic or glass containers.

During the sampling and handling of sediment samples, the following precautions need to be taken:

- Minimize the interaction between samples and containers/ implements,
- Minimize the interaction between samples and external environment,
- Test the material which comes in contact with samples for the analyte of interest,
- Treat the sample containers with the same precaution as that of samples,
- Wash the containers and implement with appropriate cleaning agents,
- Run appropriate analytical blanks which can be referred to every sample.

4.2. Cleaning procedures for containers

Sediment samples being tested for inorganic constituents can be collected in contaminant-free plastic or glass containers with a large lid allowing for easier filling and removal of the sample. Glass containers have the disadvantage of breaking during the transport. Selection and preparation (cleaning) of sample containers should be done by the analyzing laboratory or by technicians according to the laboratory's protocol. Data on the chemical composition of sample containers from the manufacturer, if available, will help in avoiding potential contamination surprises. In any case, pre-cleaning with diluted nitric or hydrochloric acid (1:1) for several hours and rinsing with clean water afterwards is recommended. The containers should be rinsed with the water above the sediments immediately before the sampling procedure starts [8]. In many sampling campaigns, samples were collected in special contaminant-free lined paper bags which allowed for air-drying during the transport and in the laboratory without further sample manipulation [8]. Samples with a high organic content in contaminated areas need to be pre-dried in order to avoid the result of moldy paper bags during longer sample transports.

Containers should be appropriately cleaned in the laboratory and sealed properly to minimize contamination with components of ambient air during storage at the sampling site. A minimum cleaning procedure should involve washing the interior of the container with soap, then hot water followed by distilled or de-ionized water rinses. The initial washing is followed by either dilute nitric acid solution and a pure water rinses for analysis of inorganic constituents, or rinses with solvents (e.g. methyl alcohol, dichloromethane) and drying for organic analyses. Baking at 550°C has often been considered adequate for cleaning boro silicate glass bottles for storing sediment samples intended for organic analyses. The recommended procedure for cleaning plastic containers (Teflon and polyethylene) used for storage of sediments intended for inorganic analyses include the following nine steps:

- (1) Fill the containers with reagent grade HCl (1:1),
- (2) Allow the solution to stand for a week at room temperature, or at 80°C in Teflon containers,
- (3) Empty and rinse with distilled water,

- (4) Fill with reagent grade nitric acid (1:1),
- (5) Follow the procedure as in step-2,
- (6) Empty and rinse with distilled water,
- (7) Fill with the purest water available,
- (8) Allow to stand for several weeks or until needed Change the water periodically
- (9) Rinse with the purest water available and dry in a particle and fume free environment.

The recommended procedure for cleaning glass containers intended for organic analyses of sediment include the following steps:

- Wash with high pressure tap water
- Wash once with chromic acid and water,
- Wash once with soap and water,
- Rinse three times in organic-free water,
- Rinse twice with acetone, followed by one rinse with special grade acetone,
- Rinse twice with pesticide grade hexane, and
- Dry the containers without their caps in a hot oven at 360°C for at least 6 hours.

4.3. Precautions during sample transport

Transportation of grab and core samples from the place of collection to a field or permanent laboratory requires care and planning to ensure that the core is not disturbed. Cores of manageable length (about 1 m) should be secured in a vertical position at all times after collection. For such cores, it is often advantageous to completely fill the space from the water sediment interface to the top of the core tube with local water and to remove any air bubbles that may be trapped under the core cap. A core tube filled in this manner essentially eliminates sloshing which otherwise forms during transport by sea or by automobile. Cushioning the core with foam to adsorb vibration during transport is also desirable. These simple measures have resulted in no disturbance and <1 % settling during a 150-mile transport by car.

Sometimes longer cores must be cut into shorter sections for convenient transport. If the core can not be held in a vertical position during cutting and transport, the surface of the core, typically having a high water content, should be secured with a tight fitting plug so that slumping and mixing of the surface sediment is minimized. Placement of a Teflon sheet (about 1mm thick and cut to the interval diameter of the core tube) on the sediment surface followed by a PVC well plug having an expandable gasket and cut to the interval diameter of the tube makes a secure cap for the top of the core. The Teflon sheet prevents the sediment surface from sticking to the well plug when it is removed for sub-sampling.

Refrigeration of sediment grab and core samples during the period from collection to subsampling is important in order to reduce metabolic activity of bacteria and infauna. Burrowing organisms may continue to mix the sediments so rapid sediment processing or poisoning should be considered if this mixing interferes with the ultimate use of the core. Storing the core in a frozen state stops biological action. This storage method is often required if organic geochemistry is part of the subsequent analysis. Freezing can induce a lengthening of the core (often in the range of 3–6% depending on water content) as the interstitial water changes to ice.

5. CRITICAL PARAMETERS FOR DATA INTERPRETATION

Knowledge about the sediment matrix is critical for the interpretation of contaminant contents in sediments. The most critical and easily measured parameters are:

- Grain-size distribution or at least the percentage of fraction analyzed (e.g. percentage of fraction <0.063 , <0.125 mm separated by screening)
- Organic matter or TOC of the sediment fraction analyzed
- Percentage of water adsorbed of the sediment fraction analyzed
- Salt correction

These variables should be measured simultaneously with other elements because they provide information about the degree and mechanism of contaminant enrichment.

5.1. Particle size analysis

The determination of the particle-size distribution by wet screening, or at least the quantitative determination of the fraction screened for analyses, is a relatively quick step in the sample preparation procedure. It allows the investigator to evaluate the sedimentological history as well as the approximate surface area of the sample. As sedimentation in surface waters can be heterogeneous, the size distribution of the separated fraction from one sampling area to another can vary considerably.

5.2. Organic component role

As the organic debris of plants and organisms are good adsorbents of organic micropollutants as well as heavy metals, the total organic content should be determined.

The organic matter in the sediment sample analyzed can easily be measured for routine purposes by weight loss at 360°C (6 hours) [8]. Wet oxidation and various TOC measurement techniques are commonly used as well.

5.3. Water content of sediment

Just recently a crude method to estimate the “adsorption capacity” of fine grained sediment was suggested [8]. The estimate is based on the amount of water adsorbed and assumes that water and contaminants can occupy the same position at the surface of sediment particles. The weight loss is measured after equilibrating 1 gram of the well homogenized sediment sample at 55% relative humidity (calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$). Weight loss is measured after heating the sample at $90\text{--}105^{\circ}\text{C}$ for 16 hours. The sample is cooled to room temperature in a desiccator after heating. The weight loss values are interpreted as adsorbed water.

5.4. Salt correction for drying marine sediments

Dried sediments from the marine environment contain both dry sediment grains and dry salts, which remain after the interstitial seawater has evaporated. Since most trace metals and other contaminants are more strongly partitioned into the sediments than the interstitial water phase, the effect of the salt is to dilute the concentrations of the metals determined in the total dry sample. The amount of salt and the correction to solid phase chemical data due to its presence can be calculated from the measured salinity and water content using the equations below.

Salinity can be measured using a refractometer with a few drops of clear interstitial water or near bottom water. It can also be determined from the chloride content, conductivity, or by determining the dry mass (after drying at 105 °C) of a known mass of filtered interstitial or near bottom water.

Salinity (S) is defined as the mass (g) of dissolved solids/ 1000 g of seawater (or mg solids/g sea water) and is given by

$$S = X / (F+X) \quad (1)$$

where F is the mass (g) of fresh water and X is the mass (g) of salt. Units are typically parts per thousand and are expressed as “‰”, or “ppt.”. X is solved from eqn.(1) as

$$X = F (S/(1000-S)) \quad (2)$$

For example, assume a coastal sediment sample of 100 g wet mass with 80% water content and salinity of 35 parts per thousand (‰). In this example, 80 g is the mass of fresh water lost on oven drying at 80°C for 2 days. After drying, 20 grams of dry sediment and salt remain in which the amount of salt is calculated using equation 2:

$X = 80 (35 / (1000-35)) = 2.90$ g salt which represents 14.5 % of the mass of the dry sample. If the salt fraction is 0.145, the sediment fraction is $(1 - 0.145 =) 0.855$. This value permits one to apply a salt correction to the chemical data if desired.

One can correct for the salt by dividing any metal concentration measured on the dry sample by the sediment fraction. For example, if Pb values are 50 mg/kg in the total sample, then a salt-free amount of $50/0.855 = 58.5$ mg/kg would exist in the sediment. The correction magnitude usually decreases with increasing sediment depth because water content decreases as sediment becomes more compacted with depth. The salt correction often results in a small refinement of the metal profile but, nevertheless, it may influence the interpretations.

6. PRE-TREATMENT AND STORAGE

The scientific questions that lead to good decisions about where and how to collect sediment samples also dictate the pretreatment and storage procedures. Possible pretreatment methods include, homogenizing, compositing, splitting or perhaps selecting a specific range of grain size for analysis. Storage procedures have the objective of maintaining the sample in a state that minimizes change in the composition or concentration of the sediment components in the time between collection and analysis. Again, depending on the scientific questions, samples can be stored wet, refrigerated, dried at various temperatures, freeze-dried, or deep frozen (-30°C). Details and concerns of pretreatment and storage issues are important to address at the planning stage of a sediment sampling programme.

6.1. Drying of samples

Drying techniques should be appropriate for all subsequent analyses that are planned for the samples. A drying step is usually required because most concentrations of contaminants in sediments are reported on a dry-weight basis. The drying step also provides an opportunity to calculate water content by simply weighing the sample before and after drying. Water content

is a basic parameter of a sediment sample that is used to help interpret the sedimentary environment. For example, high water content in fine-grained sediment may suggest a site of active deposition or an area of high sediment mixing by organisms. If the sediments are from the marine environment, the salinity of the water in the sediment should be measured in order to calculate the salt left behind when the sample is dry (see section entitled “Salt correction for drying marine sediments”).

Drying can be accompanied at a variety of temperatures, depending upon the requirements of subsequent analyses.

Air drying: Place the required amount of well homogenized sample in an open container at room temperature until constant weight is achieved.

Advantages: No oven is required and many samples can be processed simultaneously.

Disadvantages: Drying at low temperatures is slow. Consideration should be given to the potential for contamination from dust accumulation during long drying periods. Water removal can be incomplete or variable depending upon humidity of the drying environment. Humidity can be a special concern for samples from the marine environment because the precipitated salt is hygroscopic.

Freeze drying:

Advantages: A major advantage to freeze drying is minimal loss of volatile compounds, such as elemental mercury, during the drying step. A second advantage is that freeze dried samples are typically easier to disaggregate, homogenize, and grind than samples that have been dried by other methods. This is true because during the freezing process, long crystals of ice form within the matrix of sediment. As the ice crystals sublime under vacuum, they leave voids in the sediment that easily collapse by shaking or by gentle grinding. The advantage is particularly noticeable when drying sediments having a high silt and clay content. Freeze drying minimizes the potential for hard aggregates (bricks) that can form during oven drying.

Disadvantages: Freeze drying requires expensive equipment. A freeze drier with the capacity of 20 samples each weighing 75 g costs between \$11,000 and \$25,000. Drying times are typically three days for this load of muddy samples and two days for sandy samples. The capacity of a freeze drier is usually less than a conventional oven.

Oven drying:

Advantages: Oven drying is potentially the fastest method of driving off moisture in a sediment sample. Many standard methods specify 100°C until constant weight is achieved. Ovens can be modified to minimize contamination. If contamination from dust or from

the heating elements is a concern, an oven can be flushed continuously with filtered air. Having all interior surfaces of the oven coated with teflon has the advantage of reducing corrosion and the potential for sample contamination. See Poppe and Polonni (2000) for a complete description of sample handling and grain size analysis procedures.

Disadvantages: Oven drying can turn silty-clay sediments into very hard aggregates (bricks). The formation of bricks can be a problem if disaggregation (ie. grinding) is a subsequent step. Placing a frozen sample into the oven often minimizes the formation of bricks. The ice crystals which separate from the sediments typically melt and evaporate before the sediment can recombine resulting in smaller fragments.

6.2. Fractionation of samples

It has often been shown that within an area with the same general exposure to contamination, the concentration of contaminants is higher in the fine-grained sediments than in the coarser sediments. This is because silt and clay sized particles have a much higher surface area per gram than sand and consequently have a higher binding capacity for many dissolved contaminants than the coarse fraction. Fractionation, or separation of a specific grain-size range in sediments, is a way to correct the spacial distribution of contaminants in the study area for the influence of textural variability.

The utility of this technique was demonstrated in a study of the distribution of drilling mud on Georges Bank, located off the northeastern US (Neff and others, 1989). Drilling mud was identified by chemically measuring the concentration of Ba, which is a major component of drilling mud in the form of barite (BaSO_4). To improve the sensitivity of detecting drilling mud (typically 96 percent of barite is finer than $60\text{ }\mu\text{m}$) in the sandy sediments of Georges Bank (95 percent of the sediment is coarser than $60\text{ }\mu\text{m}$), the sediment fraction finer than $60\text{ }\mu\text{m}$ was separated by wet sieving and analyzed separately. In samples for which the sand fraction was 95%, this step concentrated the drilling mud signal by a factor of 20. The Ba signal could be traced to distances of 65 km west (downcurrent) from the drilling operations, a considerably greater distance than was possible without this concentration step (Neff and others, 1989; Bothner and others, 1986).

6.3. Homogenization and subsampling

Because sediments are a non-uniform mixture of different particle sizes, it is critical to maximize the homogeneity of a sample selected for analysis. Starting with a representative sample that is large enough to incorporate the whole range of particle sizes present at the sampling location, the process of homogenization focuses on a thorough mixing of the sample. All steps of mixing the sample should be carried out in containers and with utensils that are non-contaminating. Mixing can be accomplished manually with standard laboratory tools or with many tools commonly used in household cooking. Commercial mixers can be obtained for sample sizes too large to manipulate manually.

Subsampling of a well homogenized original sample is accomplished by a variety of techniques. For dry sediment, a cone and quartering technique has been used to split a large

volume of starting material into representative aliquots of smaller volume. This technique specifies that the material is piled into a cone and cut into quarters (Krumbein and Pettijohn, 1938). Two alternate quarters are removed, and the remaining two are recombined, re-piled into a cone and quartered once again. This procedure is repeated until a desired mass of material is achieved.

The Jones sample splitter (Krumbein and Pettijohn, 1938, Otto, 1937), suitable for dry and disaggregated samples, consists of a hopper with a series of inclined shutters that lead the original sample to two pans on alternate sides of the apparatus. A 4-way splitter constructed by McLane (2000) is suitable for fine-grained sediment samples in liquid suspension.

6.4. Preservation of samples

Sediments consist of particles in a wide range of sizes, for example from gravel to clay and with variable amounts in different size classes. Frequently one has to decide whether the coarse material should be sieved and discarded since it contains a relatively low concentration of contaminants. Alternatively, the entire sample could be ground to suitable particle size yielding a “bulk” sediment sample for analysis. Neither of these procedures can be recommended over the other since there is still discussion as to which technique properly represents the character of the sediment. The choice depends mainly on the study objectives.

The fine sediment fraction (< 0.2 mm) is particularly useful for estimating the relative degree of pollution and to distinguish between natural (geogenic) and anthropogenic sources. The size fractions commonly selected fall into two groups: (1) coarse (<0.2 , 0.18, 0.125 mm) and (2) fine (<0.063 , <0.040 , <0.02 , <0.016 , <0.006 , <0.002) [8]. The coarse group has mainly been used for mineral prospecting and includes more rock fragments, mine tailings of operating and abandoned mines, as well as industrial particles removed by abrasion. The fine group is generally richer in contaminants and contains a greater portion of clay minerals, aluminium-, iron-/manganese-oxyhydroxides, amorphous silica and organic/humic matter, all of which actively “adsorb” and therefore concentrate solutes. This chemical adsorption is characterized by the formation of chemical associations between ions or molecules from the solution and surface particles. This includes chemisorption, ion exchange and coprecipitation mechanisms [38].

Surfacial sediment to a sediment depth of 10–20 cm typically contains large and variable amounts of water (up to 95%). To permit comparison of data, sediments are dried and analyses are carried out on dry material, or a sub sample is taken for drying to determine water content while the analyses are performed on the wet sediment. In either case, results of analyses are usually presented on a dry weight basis.

The goal of any storage technique is to maintain the sample integrity and suitability for all planned analyses as well as for any future analysis that may not be planned. There are often both short and long term storage requirements with different objectives. In some long term observations, it may be advantageous to analyze all samples in one series. In addition, it may be necessary to prepare and store duplicate samples (identically prepared aliquots), one of which remains with the user of analytical data for an independent cross check at a later time if necessary. Analytical Reference Materials are also produced in large quantities and have to be stored for years [39]. A last argument for long term storage is the conservation of ecological,

environmental and biological samples as specimen banks for use in the future [40] when new analytical techniques may become available.

It is important to consider the duration of storage as the requirement for short term and long term storage differ [39]. The storage of solid material is subjected to stringent conditions. Particle size distribution analyses should be carried out on wet sediments. Samples for this should not be frozen but stored at 4°C. Tightly sealed plastic bags, glass jars or other containers can be used to store samples prior to particle size analyses. Drying, freezing and thawing of the sediment can cause aggregation of particles and should be avoided. Freeze-drying has also been shown to generate aggregates among the fine fraction [41].

Three types of drying are commonly used to prepare solid samples prior to analysis: air-drying, oven drying and Freeze-drying. Usually air-drying should not have much effect on the trace element content, but if the speciation and organic extractable trace elements are of interest, any procedure of drying may lessen the validity of sample analysis [42]. For example, air-drying of sample markedly affects cation exchange capacity and iron speciation. Preservation of grab sediments at 4°C is a good short term storage method for the use of materials in laboratory experiments such as sorption studies.

Oven drying of sediment is usually carried out on samples collected for the determination of inorganic components, such as major and trace elements. However, oven drying is not suitable for grain size determinations since wet fine-ground sediment becomes aggregated. Oven drying is not acceptable for sediments which contain volatile or oxidizable components, whether they are organic or inorganic.

In the freeze-drying process, water in the frozen or solid state is sublimated and is removed from the material as vapour. Freeze drying (also called as lyophilization) can be used for drying sediments intended for the determination of most organic pollutants as well as for the analysis of mercury and its methyl or phenyl salts. It has been used for sediment and biological samples. Generally, freeze drying at -20°C and -30°C is considered to be the best method of drying sediment prior to long term storage because of the following advantages:

- Low temperatures avoid chemical changes in labile components and loss of volatile constituents including certain organic compound is minimized,
- Most particles of dried sediments remain dispersed and aggregation is minimized,
- Sterility is maintained and oxidation of various minerals and organic compounds is minimized or eliminated.

7. PREPARATION OF SAMPLES FOR ANALYSIS

Sample preparation procedures are of great importance for obtaining reliable experimental results. The major goal of the sample preparation is to prepare a sample in such a way that the original elemental distribution at the time of sampling is preserved and that the introduction of foreign elements is prevented. As a result of the sediment deposition process, yielding varying elemental distributions in the precipitate as a function of time, sediment samples are always stratified. The original detail of the stratified elemental distribution can only be obtained by a nondestructive analytical technique on an undisturbed sediment column. In practice, however, the specific purpose of the analysis determines the level of detail to be investigated, and the

sediment column is sliced according to the intervals necessary to meet this objective. The intervals are derived from the average settling rate over the time scale of interest. Sediment sampling tends to disturb the strata at the periphery of the sample adjacent to the coring equipment. Therefore, the outer parts of the original sample are usually discarded, leaving only the inner core for examination and analysis.

After slicing the central core of the sediment sample, the individual slices are considered as different samples by themselves. They may be homogeneous or still stratified, but at some point in the analytical process, the analyst has to decide whether the internal elemental variation and structure is relevant to the purpose of the analysis or not. When this is not the case, the slices have to be homogenized to eliminate the remaining variability in the subsamples and to average the elemental concentrations. At this point the sliced samples can be dried, preferably at a moderate temperature between 60 and 80 °C for several days or weeks until a constant weight is obtained. Adequate homogenization implies that the different mineral particles present in the sediment are equally represented in the subsamples. The fulfilment of this condition depends both on the size of the particles and on the weight of the subsample. For subsample sizes larger than 50–100 mg, satisfactory homogeneity can be obtained with particle sizes smaller than 200 mesh size or < 0.08 mm.

7.1. Non-destructive sample preparation

The main nondestructive analytical techniques applied to sediment samples for elemental composition are Instrumental Neutron Activation Analysis (INAA), Ion Beam Analysis (IBA) which includes Particle Induced X ray Emission (PIXE) as well as Nuclear Reaction Analysis (NRA) and Rutherford Backscattering Spectrometry (RBS), and X ray Fluorescence analysis (XRF). Gamma ray spectrometry is the main nondestructive technique for the determination of radionuclide concentrations from natural or man-made origin.

Sample preparation for XRF and IBA can be limited to the straightforward pressing of a suitable quantity of homogenized powder in a die to produce a pellet, with or without the use of binding additives. Also more sophisticated procedures can be applied for embedding the samples with waxes or resins under vacuum to produce a solid sample, which is adapted to the mechanical manipulations in the sample holder of the different instruments. The IAEA has published a laboratory manual on sample preparation procedures for XRF [43]. Additional information can be found in specialized handbooks on X ray Spectrometry [44] and PIXE [45]. Die pressing and embedding techniques can introduce contaminants by erosion of the moulds or from impurities present in the resins. Therefore, special care has to be taken to avoid contamination by selecting appropriate materials, performing intermediate blank pressings and embedments to clean the equipment and avoid cross-contamination, and by verifying the blank levels.

Sample preparation for INAA is essentially limited to weighing a suitable amount of homogenized powder into small quartz or plastic vials for reactor irradiation and subsequent gamma spectrometric analysis. The essential issues are to avoid contamination by careful selection of the vial material, cleaning of the vials and verification of the blank levels, and to obtain a reproducible geometry for the accumulation of the spectra. The latter usually imposes tight specifications on the vial dimensions and wall thickness in order to ensure reproducible counting efficiencies and gamma ray attenuation effects.

Passive gamma ray spectrometry to assess radionuclide concentration levels in sediment samples requires minimal sample preparation and is mainly limited to weighing a suitable

amount of homogenized powder into the counting container. Again potential sources of (cross-) contamination have to be identified and eliminated as far as possible; contamination by radionuclides, however, is easier to trace than contamination by inactive substances. Important parameters are the dimensions and wall thickness of the counting container to achieve reproducible counting efficiencies and attenuation effects. As the usual radioactivity levels measured in sediments are quite low, relatively large samples are used, which surround the detector in a near 4π geometry such as a Marinelli beaker. Unless gamma ray attenuation effects are estimated and corrected for by sophisticated algorithms, the apparent density of the sediment in the counting container should be kept constant.

7.2. Destructive sample preparation

The majority of determinations of trace element concentrations in sediments using destructive analytical techniques involve panoramic techniques, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Mass Spectrometry (ICP-MS) and single element techniques such as Atomic Absorption Spectrometry (AAS). Sometimes electrochemical methods, isotope dilution mass spectrometry, fluorimetric and spectrophotometric methods are used, but the sample preparation techniques are not different. The main difficulty is the quantitative dissolution of the sediment without introducing contaminants from the laboratory glassware and reagents used. The same sample preparation procedures are used for the determination of alpha- and beta- emitting radionuclides in sediments, but again, the risk of introducing interfering contaminants is less. The method selected for sediment dissolution will depend on its mineral composition, consisting of clayey or siliceous materials, carbonates, coral debris, basaltic or granitic erosion products, etc. Standard handbooks [46] and reference testing procedures [47] in analytical chemistry provide a variety of techniques for the complete dissolution of geological samples applicable to sediments. Current modern methods rely on the elevated temperature and pressure conditions achieved in sealed microwave-heated vessels to enhance and accelerate the dissolution process [48]. Advanced vessel designs using high density PTFE now accommodate the use of hydrofluoric acid to dissolve refractory minerals with unprecedented efficiency and speed. Dissolution procedures and heating sequences are specific for the type of microwave-furnaces and vessels used. Optimized procedures are usually available from the individual commercial equipment suppliers. A typical example for the closed vessel high-pressure dissolution of soils and sediments is given below [49] using the microwave digesters CEM (Matthews, NC, USA) model MDS-2000 and Milestone (FKV, Sorisole, Bergamo, Italy) model 2100.

TABLE IV Typical Operating Conditions for Microwave Dissolution of Soils and Sediments

Aqua Regia Procedure - 250 mg sample treated with 8 ml of Aqua Regia						
Step	1	2	3			
Power (watt)	250	400	500			
Hold Time (minutes)	2	2	10 to 30			
HF/HNO ₃ /HCl Procedure – 250 mg sample treated with 2 ml HF + 8 ml Aqua Regia (+ 2 ml saturated boric acid solution added before step 5)						
Step	1	2	3	4	5	6
Power (watt)	250	400	600	0	300	0
Hold Time (minutes)	8	4	6	2	3	2

The Aqua Regia procedure does not achieve complete dissolution for all elements in the sample. This can be achieved by the procedure involving the hydrofluoric and boric acids.

As the concentration levels of radionuclides in environmental samples are usually very low, the larger amounts (5–10 g) of sample required to obtain meaningful results are not compatible with microwave dissolution procedures. Microwave dissolution can be applied as the final step for dissolving a residual amount, after the bulk of the sample has been dissolved by acid digestion or fused salt techniques. One of the typical procedures [50] is reproduced in the appendix “Sample Preparation for Radionuclide Analysis and Nuclear Analytical Techniques in Sediments and Soils in the IAEA Laboratories”.

7.3. Quality assurance/quality control for sample preparation

Quality assurance and quality control measures during the sample preparation ensure that the sample identity and the elemental and/or radionuclide distributions in the original sample are maintained until the time of analytical determination.

To preserve the identity of the sample or subsamples an appropriate and unambiguous labelling system has to be designed, implemented and strictly followed in the analytical laboratory. The transformations applied to the samples or subsamples, such as grinding, homogenisation, transfer, dissolution, dilution, etc. have to be documented in a laboratory logbook with careful registration of date, identity, label, operator, the type of transformation and any observation of relevance to the interpretation of the final result.

Parameters, affecting the analytical result, have to be monitored by calibrated instruments and equipment, e.g. sample stability, subsample weight ratio, drying temperature, particle size, dilution factor, target surface finish (for XRF or PIXE), tap density (for gamma ray spectrometry).

To preserve the elemental and/or radionuclide distribution, all sample preparation steps have to be examined with respect to potential additions or losses of the analytes of interest. Potential additions resulting from contamination or cross-contamination can be investigated by simultaneous processing of blanks during sample preparation and careful examination of the level and variability of the blank results in comparison to the concentration level of the analyte of interest. Potential losses can occur by incomplete sample recovery after grinding and homogenization, incomplete dissolution, insufficient homogenization in solid or liquid form, wall adsorption effects at trace level concentrations. Potential losses can be identified by processing quality control materials of similar composition to the samples being analyzed. Consistent losses can be corrected for by the use of quality control materials. Variable or unpredictable losses can be corrected for by adding yield monitors or by tracing the analytes of interest with elemental or isotopic dilution before starting the sample preparation.

8. ANALYTICAL TECHNIQUES FOR SEDIMENT ANALYSIS

Most analytical laboratories use modern single- or multi-element analytical techniques for the determination of macro, micro, and trace levels of elements in sediments. Laboratories may also use a variety of nuclear instrumentation in conjunction with radiochemical separations for the determination of primordial (e.g. Ra-226, Pb-210, C-14) and anthropogenic (Cs-137, Pu-239, Sr-90) radionuclides in sediment samples. A brief description of each technique is

presented below to provide the reader with some background information which can be supplemented by consulting relevant literature and authoritative works on each technique.

Neutron activation analysis

In Neutron Activation Analysis (NAA) a sample (solid or liquid) is interrogated with neutrons and the induced radioactivity is measured and related to isotopic (elemental) concentrations of the elements present in the sample [51]. NAA is a multi element analysis technique, often non-destructive in nature where approximately 75 elements can be measured with the detection limits ranging from 10^{-6} to 10^{-12} g of element in a sample. Quantitation is accomplished by comparison with standards prepared from pure elements or compounds that are irradiated and measured under the same conditions as the samples. Typical sample sizes range from 1 mg to 1 g, however in principle much larger samples (10 kg) can be activated and the size is only limited by the capacity of the neutron irradiation facility.

Ion beam analysis

In Ion Beam Analysis (IBA) techniques a representative sample, preferably in the form of a thin film, is bombarded with charged particles like protons, deuterons or He-4 ions and the radiation produced is measured. IBA techniques are useful for qualitative and quantitative analysis. Examples are Particle Induced X ray Emission (PIXE), Nuclear Reaction Analysis (NRA) and Rutherford Backscattering Spectrometry (RBS). These are mainly surface analysis techniques as the charged particles only penetrate to a depth of a 10–30 μm and therefore trace element analysis to depth profiling of near surface layers is achieved. In PIXE analysis, the characteristic X rays are measured and therefore this technique provides a multi-element analysis capability. Sensitivities in the range of 10^{-9} g are achieved and analysis is on-line and rapid. Assuming the sample is homogenous, these techniques can provide accurate multi-element analysis by a comparison method using a certified reference material with similar composition.

X ray fluorescence analysis

Characteristic X rays are fingerprints of elements. In X ray Fluorescence (XRF) analysis, a representative sample is exposed to an energetic beam of photons and the generated characteristic X rays are measured in order to arrive at the concentrations of the elements present in the sample. XRF is a multi element analysis technique with sensitivities in the range of 10^{-8} g. Sample sizes of a few mg to one gram can be analyzed. Liquid samples also can be analyzed. XRF measurements are based on either Wavelength Dispersed XRF (WDXRF) or Energy Dispersed XRF (EDXRF). In the case of the determination of trace elements, it is better to chemically isolate or pre-concentrate the elements of interest to minimize or eliminate matrix effects and interferences. Its biggest advantage is the availability of tubes as well as radionuclides as exciting sources. Portable XRF systems are available for use in the field studies [52].

Atomic absorption spectrometry

This technique is used for single element analysis of aqueous samples and on solid samples which are introduced in the form of a slurry. Quantitation is performed using single element standard solutions from which calibration curves are prepared. One disadvantage of this technique is its limited linear dynamic range (typically one order of magnitude) which often

requires the analyst to perform serial dilutions to quantify those elements whose concentrations fall outside the linear range. The additional operations increase the uncertainty of the final results and also reduce the productivity (output). The advantages of the technique are the low capital cost and simplicity of operation, and its specificity and sensitivity for some elements which can be volatilised (e.g. Hg) or chemically converted to a volatile hydride (e.g. As, Sn). Instruments equipped with a graphite furnace vaporisation source can achieve detection limits in the range of 10^{-9} to 10^{-12} g in a 10–50 μ L aliquot for elements such as Zn, Se, Cd, Hg and Pb.

Inductively coupled plasma optical emission spectrometry

This technique is used for multi-element analysis of aqueous samples. Quantitation is accomplished using multi-element standard solutions from which calibration curves are prepared. These instruments have a wide linear dynamic range (typically 3 to 5 orders of magnitude) which permits the analyst to measure both major and trace elements in the same solution without dilution. The technique has one major disadvantage as it yields very complex spectra with many overlapping lines which may introduce a bias or increase the uncertainty in the final results. Detection limits range from 10^{-8} to 10^{-10} g/mL for approximately 70 elements.

Inductively coupled plasma source mass spectroscopy (ICP-MS)

This technique is similar to ICP-OES except that in addition to elemental analysis, it can also determine isotopic abundances and isotopic ratios for each element. It has a wide linear dynamic range (typically 4 to 5 orders of magnitude) and yields simple mass spectra which can be corrected for isobaric interferences using the natural isotopic abundances of the interfering elements. A disadvantage of the technique is the higher capital cost for the instrumentation compared to either AAS or ICP-OES, especially in the case of a high resolution magnetic sector instrument. Detection limits range from 10^{-11} to 10^{-12} g/mL for elements above a mass number of 80.

Gamma ray spectrometry

The determinations are carried out instrumentally, using HPGe γ -spectrometers. Liquid and solid samples can be analyzed with minimal sample preparation. Typical sample sizes range from 100 mL (100 g) to 2 L (2 kg). Quantitation is accomplished through energy and efficiency calibration of the γ ray spectrometer using calibrated sources of the radionuclide of interest in the same geometry as the sample. Typical limits of detection range from 0.1 to 5 Bq per sample.

Alpha spectrometry

This technique is carried out instrumentally using planar ion-implanted silicon detectors after radiochemical separation of the α -emitting radionuclide of interest. The complete procedure involves dissolution of the sample, chemical separation and co-precipitation of the α -emitter onto a carrier source. The typical sample size is 1 to 10 g of ash from soil, biological material, or air filter. Quantitation is carried out by energy and efficiency calibration of the α -spectrometer using calibrated sources of the radionuclide of interest in the same geometry as the sample source. The detection limit is typically 0.5 mBq per sample.

Beta spectrometry

This technique is carried out instrumentally after dissolution of the sample and chemical separation of the radionuclide from the matrix. A β -emitter may be determined directly on a filter after precipitation. Alternately the β -emitter can be measured in liquid form using liquid scintillation counting. Quantitation is carried out by energy and efficiency calibration of the β -detector using calibrated sources of the radionuclide of interest that are prepared under identical conditions. For a 10 g sample, the typical detection limit for Sr-90 is 0.05 Bq for a measurement time of 400 minutes.

9. CONCLUSIONS

The deliberations focused on the intended objectives of the meeting resulted in the following conclusions. It was proposed that the copies of the TECDOC could be sent to the Member States who wish to initiate the study of sediment analysis since this TECDOC would be useful to provide information about various aspects of the collection and preparation of sediments.

- (1) Since the analysis of sediments provides information on the effects of human activities on the accumulation of various pollutants, it may be worthwhile to consider organizing a workshop for providing field training as well as lectures on strategies and methodologies.
- (2) Literature pertaining to scientific information how to establish the sample integrity before elemental characterization could be prepared and distributed to the members interested in this area both through providing hard copies and maintaining an IAEA web site.
- (3) It may be worthwhile to conduct a regional workshop either by the region or IAEA to bring out various aspects of QA/QC of collection, sample preparation and analysis of sediments.
- (4) It may be helpful to carry out regular inter-comparison exercises for the analysis of sediments using nuclear and nuclear-related techniques.
- (5) IAEA should continue distributing reference materials to the Member States.
- (6) It may be noted that the dating techniques are not adequately covered in this report. In view of their importance, literature such as the contributions made by MEL, Monaco, could be placed on the IAEA web site.

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**A SAMPLE OF QA/QC STANDARD SIMILAR TO DIN 38 414 S11 USED IN
SAMPLING RECORD - FINE-GRAINED AQUATIC SEDIMENTES**

37

Annex II

SHORT REMINDER FOR DIFFERENT TYPES OF SAMPLING

Grab sampling

Grab sampling is carried out in general to survey the bottom surface area of an aquatic body using rapid and economical methodologies. The sampling equipment is simple, inexpensive and can be operated by one or two individuals.

- Check List of Items and Equipment Needed for Grab Sampling

The following general inventory is recommended for Grab Sampling:

- Inventory Check List
- Maps of the areas to be sampled
- Sampling map
- Copies of Field Standard Operating Procedures and/or Instructions
- Sample ID forms (sampling information and identification) and labels
- GPS (PI expand)
- Notebooks
- Camera (still or video) with films or cassettes and batteries
- Thermometer/pH meter with electrodes/Redox electrode/Conductivity electrode with calibration standard solutions (plus spare batteries)
- Disposable labware (beakers, tissue paper, distilled water etc.)
- Protective clothing (gloves, air masks, rainware etc.)
- Tools (hammer, axe, knife etc.)
- First aid kit
- Pre-cleaned sample containers (with protective bags?)
- Field blank containers (important for sampling areas with low levels of contamination)
- Transport containment (preferably able to maintain samples cool and in total darkness)

In addition to the above inventory the following items are needed in particular for sampling in (1) shallow water environments and (2) deep water environments

1) shallow water:

- shovel
- at least one crew member

2) deep water:

- boat or floating platform
- winch
- grab sampler (see Table X for advantages, disadvantages and costs of various grab samplers)
- buckets
- at least two crew members
- depth gauge
- anchor or a means of stabilisation
- safety gear (life jackets, flares, radio communication etc)
- spare cables and a tool kit for the winch
- underwater video camera with lights to observe sampling location (optional)

Core sampling

The following list of core sampling gear is designed to stimulate ideas during the cruise preparation stage. The best final preparation for a core-sampling cruise is to conduct a test run in or near the laboratory which requires using all the equipment actually used in the field.

Personal gear:

- Protective foot gear, hat, sunglasses, sun block, long sleeve clothing, life jackets

Core collection equipment:

- hand-held GPS receiver, some weather protection for it
- spare AA batteries for GPS receiver
- hand-held drill and bits
- weather-proof notebook
- extra end caps
- electrical tape
- life jackets
- safety harness to hold scientists on deck
- core head with check valve and baggie of Dow Corning #4 lubricant
- stainless steel weight plates
- adapter for mating core head to 3.3" fiberglass pipe
- adapter for mating core to 2.5" PVC pipe
- pre-fit pistons (piston core piston w/ eye bolt, o-ring , and face seal)
- siphon tubes (12' lengths: ½" and 3/8" inside diameters)
- stiff 1/4" polyethylene tube for siphon tip
- step-down tubing to go from ½" id to 1/4" id
- bungee cords
- hose clamps for emergency repairs
- make-a-hose-clamp kit with 24 ends
- line and tube for check valve release
- bunches of cable ties
- Refractometer to measure salinity of overlying water
- camera and film
- Titanium wire core splitting tool w/ extra wire
- Titanium spatulas
- metric tape measures
- small Kim-Wipes
- large Kim-Wipes
- large Nitrile gloves
- dish pans
- squirt bottles for rinsing.
- core collection sampling sheets and notebook
- pens, 1 pencil, and Sharpies
- 4oz specimen jars
- Ziplock 1-qt freezer bags
- Supplies for shipping cores back to laboratory
- Shipping foam
- Assorted filament, clear, and duct tape
- Limited tools:
 - regular screwdriver
 - Phillips head screwdriver
 - regular pliers
 - needlenose pliers
 - adjustable wrenches
 - jack knife
 - nut driver

COLLECTION AND PREPARATION PROCEDURE FOR ENVIRONMENTAL EVALUATION OF POLLUTED SEDIMENTS

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Abstract. A rapid procedure is described to evaluate the significance of inorganic and organic pollutants in fine-grained sediments. The air- (< 30° C) or freeze-dried samples are screened within 30 min. in stainless steel sieves (<0.04 mm) prior to chemical analysis. This procedure is also suitable for analysis of such elements as Hg and many non-volatile organic pollutants. The sediment size fraction of < 0.04 mm was chosen in order to separate the smallest grain-size obtainable by rapid dry-screening techniques; this is representative of the grain-size of suspended matter transported at low and medium river discharge (0.1-0.7 m/s). The screened fraction (<0.04 mm) of aquatic sediments is more homogeneous in grain-size and distribution, and the fine particles are more capable of adsorbing pollutants than coarser fractions. However, large differences are observed in grain-size distribution and adsorbable phases from one sample to another, even in the smallest size fractions (<0.04, <0.02, <0.002 mm). Clay minerals, Fe- and Mn-(oxi)hydrates, amorphous silica and humic substances all adsorb water at normal humidity. In order to estimate and standardise the adsorption capacity of the surface of these screened sediment fractions, the weight loss after heating at 105° C is used, instead of tedious quantification of all the above mentioned sediment phases. In addition, this procedure allows the rejection of sediment samples, unsuitable for monitoring purposes, which have very low adsorption capacities. In order to correct for the variable adsorption capacity of different sediment samples or size fractions, the weight loss (WL) at 105° C can be inserted in the widely used GeoIndex (MÜLLER 1979) formula ($I_{geo105} = \log_2 (C_{measured}/C_{background} * WL_{1058\text{ }^{\circ}\text{C}})$). This improves the evaluation of pollution in aquatic environments.

1. INTRODUCTION

Sampling and chemical analysis of aquatic sediments, as a way of indicating the regional distribution of natural and pollutant-derived concentrations of certain elements, is an efficient tool in environmental protection. The fine sediment fraction (< 0.2 mm) is particularly useful for estimating the relative degree of pollution and to distinguish between natural (geogenic) and anthropogenic sources. The size fractions commonly selected fall into two groups: (1) coarse (<0.2, 0.18, 0.125 mm) (THALMANN et al. 1989; OTTESEN et al. 1989; DARNLEY et al. 1995) and (2) fine (<0.063, <0.040, <0.02, <0.016, <0.006, <0.002) (FÖRSTNER and SALOMONS 1980; GEBHARDT and TAUX 1983; LANDESAMT f. WASSER NORDRHEIN-WESTFALEN 1986; ACKERMANN et al. 1983; MÖLLER - LINDENHOF and REINCKE, 1991; MÜLLER 1979). The coarse group has mainly been used for mineral prospecting and includes more rock fragments, mine tailings of operating and abandoned mines, as well as industrial particles removed by abrasion. The fine group is generally richer in contaminants and contains a greater portion of clay minerals, aluminium-, iron-/manganese-oxyhydroxides, amorphous silica and organic/humic-matter, which actively "adsorb" and therefore concentrate solutes (SALOMONS and FÖRSTNER 1984, REITNER and KRALIK 1997). This Chemical adsorption is characterised by the formation of chemical associations between ions or molecules from the solution and surface particles. This includes chemisorption, ion exchange and coprecipitation mechanism (SALOMONS and FÖRSTNER 1984).

Very fine grained sediments (< 0.063 mm silt and clay) in surface waters and soils filter inorganic and organic pollutants out of water and pore solutions. This is often most effective under neutral and basic pH conditions. Water pH, grain-size, humic substances, iron and

manganese oxides and clay minerals are the most important factors controlling the chemical adsorption of pollutants on very fine-grained sediments. The increase in surface area with smaller grain-sizes is enhanced due to important changes in mineral phase composition in the smallest grain-size sediments. Samples from the Danube (KRALIK and AUGUSTIN-GYURITS 1993) and other Austrian Alpine rivers (PIRKL and KRALIK (1988), as well as samples from other large rivers of the world (GIBBS 1977, IRION 1991), show a general decline in rock fragments, quartz, feldspar and possibly dolomite in the 0.02-0.2 mm fraction with decreasing grain-size, while clay minerals, organic matter, and Fe and Mn hydroxide and sometimes calcite in the <0.02 mm fraction, tend to increase. The latter mineral phases have a considerably higher adsorption capacity for dissolved pollutants.

The quantitative determination of the solid sediment phases, which control the adsorption capacity, is very difficult and time consuming. In order to make the adsorption capacity more or less comparable between samples, these phases are usually concentrated by screening followed by analysis of the very fine fractions (<0.02, <0.04, <0.063 mm). In addition, a basic requirement for the use of sediments as an environmental monitoring tool, is a high adsorption capacity. The ratio of dissolved pollutants to total suspended matter in the water column is also important. Therefore the amount of pollutants adsorbed per gram of sediment is relatively low during floods because of dilution. During normal and low water discharge, the suspended matter is considerably less concentrated and of much finer grain-size, which means it is much more suitable for pollutant adsorption.

For sampling active stream sediments, which are regarded as representative samples of the drainage basin upstream of the sample site, coarse (>0.06 mm) and fine (<0.06 mm) sediment fractions have been collected. In recent years coarser fractions have been advocated in the form of overbank sediments as a sampling medium for regional geochemical mapping (OTTESEN et al. 1989). Sampling widely spaced sections of overbank sediments therefore have the potential to provide a sampling medium for geochemical surveys which can yield both spatial (drainage basins 60-600 km²) and temporal data, and also be used as a tool for detailed studies of mining and industrial contamination (DARNLEY et al. 1995). For practical reasons and for reasons of comparability with other geochemical data, multi-element techniques are usually used to analyse total element sediment composition in regional geochemical surveys (DARNLEY et al. 1995). Compared to analytical procedures, the importance of sampling has been neglected in many publications so far. Therefore papers with detailed descriptions and quality assessment of environmental sampling are relatively rare. More detailed description can be found by GOLTERMAN et al. (1983), WHO (1982), KEITH (1991), CSUROS (1994), MUDROCH and MACKNIGHT (1994). The usefulness of these surveys was partly hampered by a lack of fine-grained sediment, by a lack of comparability between sediments from different catchment areas and confusion about analysing additional variables in the sediments (ACKERMANN 1980, HELLMANN 1992). In order to show the limits of this as a monitoring tool and to make it applicable as a quick and simple procedure for many samples, a routine procedure for sediment sampling and data-evaluation is presented. The sampling procedure was evaluated in >20 000 km² of basin and Alpine areas in Lower and Upper Austria (>2000 samples: KRALIK and AUGUSTIN-GYURITS 1994), as well as in an area of the Amazon estuary (Belem, Brazil).

2. SAMPLE COLLECTION AND PREPARATION

In order to include sampling in a Quality-Assurance and Quality-Control programme the samplers were trained and instructed in special sample handling procedures according to the

Field Standard Operation Procedure (FSOP) (CSUROS 1994). Sediments and suspended matter in surface waters are frequently very heterogeneous due to small-scale changes in hydrological regime and geomorphological changes in the catchment area. This variability is minimised by taking several sub-samples (minimum 5), which are mixed together in a composite sample (DARNLEY et al. 1995). Due to the interest in the fine sediment fraction (< 0.04 mm) a sample mass of only 1 kg (dry weight) was sufficient in most cases (Fig. 1). The variance in the sampling procedure has to be estimated by two identical sampling procedures at the same sites (duplicate sampling) from a minimum of 3% of all sample points (DARNLEY et al. 1995). This is of particular interest in anthropogenically polluted sites.

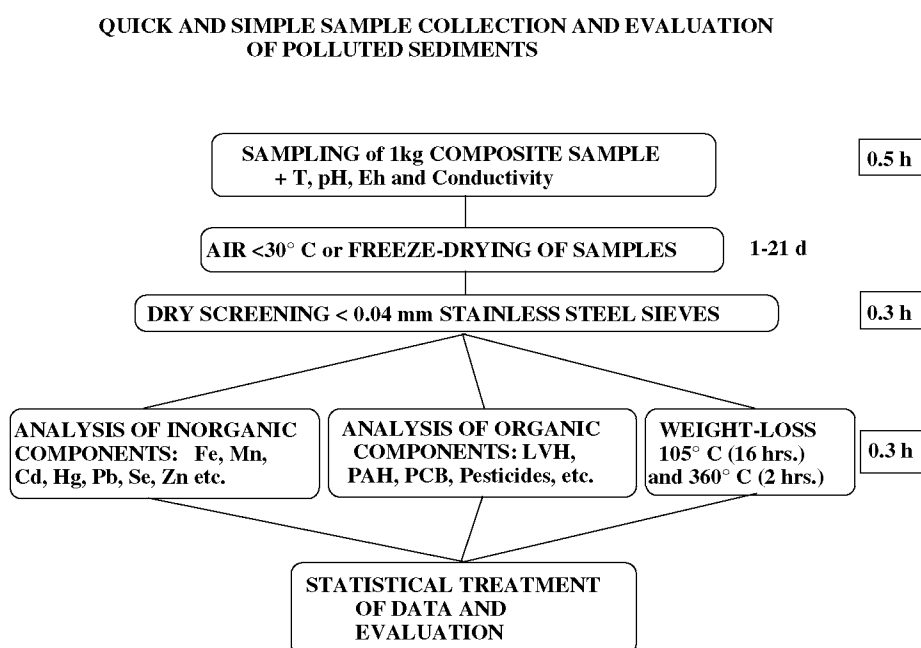


Fig. 1: Sampling and evaluation scheme for polluted sediments.

Frequently during monitoring only the recent sediments (accumulated over the last 0-6 months) are of interest. For practical reasons, at each sampling area (approximately 50-100 m on both river banks) the surface sediment (0-3 cm) is collected (GOLTERMAN et al. 1983; KEITH 1991) with a flat hand shovel as sub-samples from several points with low current velocities, in order to obtain the finest-grained sediment. Sediments settled during low and medium discharge are sampled. Sediments deposited during or after floods are normally both too coarse-grained and, diluted by freshly eroded unpolluted sediments from mountainous areas. To collect samples from deeper waters or from deeper in the sediment column for investigation of historical inputs, grab samplers or corers can be used (MUDROCH and MACKNIGHT 1994).

In order to estimate the potential to mobilise pollutants from the sediment to the adjacent water, in the case of re-suspension or deposition on land, the main factors influencing mobilisation, such as pH and Eh and temperature, were measured potentiometrically in the wet sediments. In practice the *in situ* measurement of these variables at each sampling spot is too time consuming. These 3 variables, were quickly measured in the collected composite sample, which allowed an approximate categorisation of the pH and redox conditions in the sediment at a sampling area. These measurements made in running water, including electrical conductivity, characterise the general situation in the body of water at the time of sampling.

To minimize the sampling error and to assure standardised sampling despite different persons collecting sediments, a sampling record card was completed (standard sheet similar to DIN 38 414 S11). For inorganic analyses samples were collected in contaminant-free lined paper bags which allow air-drying during transport and in the laboratory without further sample manipulation (HAWKES and WEBB 1962). Samples to be analysed for organic micropollutants should be stored in preheated (250-350°C) and extract-cleaned glass jars (teflon sealed) with a minimal head space. Samples have to be stored immediately and transported under dark and cool (4°C) conditions.

To avoid significant losses of volatile organic compounds (VOC), about 5g (dry weight) of the finestgrained sediment should be placed directly into pre-weighed head-space vials. The head space must be reduced to a constant volume (clean water, methanol etc.) and the vial immediately sealed with a gas-tight septum (PAVLOSTATHIS and MATHAVANAN 1992). For most of the inorganic pollutants, drying at 105° C is quick and effective. However, if metallic mercury is to be determined, temperatures of less than 80° C (Kralik unpublished data and IYENGAR et al. 1978) should be applied. For most pollutants air-drying in contaminant-free lined paper bags (1-3 weeks; Fig. 1) or drying in a heated cupboard at 30° C (1 night; Fig.1) is suitable. Samples analysed for organic micropollutants (excluding head-space vials) have to be freeze-dried at temperatures less than -20° C (Fig. 1). Dried samples are disintegrated gently in a mortar without grinding and screened in stainless steel test sieves on a screening machine for 10 min.

Weight loss is measured by equilibrating 1 gram of the dry-screened sample with calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) at 55% relative humidity, controlled by a hygrometer for three days. Longer periods of equilibration show only minor changes in weight loss or gain. Weight loss is measured after heating the sample at 105° C for 16 h and at 360° C for 2 h. The sample was cooled to room-temperature in a desiccator after heating. The weight loss values are interpreted as adsorbed water and organic matter, respectively (Fig. 2).

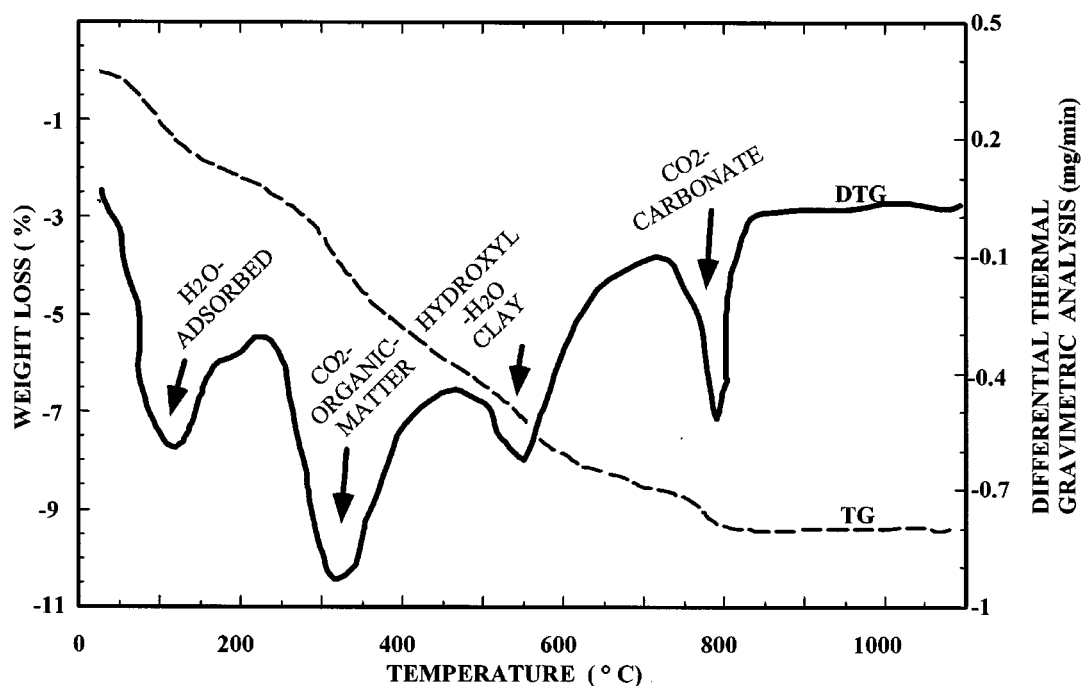


Fig. 2: Thermo-Gravimetric (TG) and Differential-Thermal-Gravimetric (DTG) determination of weight-loss during heating of a fine grained river sediment.

3. EVALUATION AND INTERPRETATION OF DATA

In order to correct for the variable adsorption capacity of the fine-fraction (<0.04 mm) the Geo-accumulation-Index used by MÜLLER (1979) was modified by replacing the factor 1.5 with the percentage of loss:

$$I_{Geo105^{\circ}} = \log 2 (C_{measured}/C_{background} * Weight-Loss_{105^{\circ}C}) \quad (1)$$

C = concentration

Samples with a weight loss (at 1058 C) of <0.3 wt. % were excluded due to insufficient adsorption capacity.

4. RESULTS AND DISCUSSION

It is not the aim of this paper to discuss all aspects of sampling and data evaluation. However, those aspects which are important for quick and simple sampling procedure are discussed at length. An experienced sampler with some training in sedimentology can collect a composite sediment sample and do the field measurements in 30 min. (Fig. 1). A common error, when sampling the water saturated upper sediments too rapidly, involves washing out the finest particles with the surface waters and concentration of the coarse sandy fraction (GOLTERMAN et al., 1983; KEITH, 1991). This can be avoided by an experienced sampler by slowly lifting the upper sediment and carefully decanting the supernatant water. MACDONALD (1989) recommends sampling of the uppermost oxidising light surface sediments separately from the somewhat deeper dark black sediments for better comparability of results. On the other hand, he did not demonstrate a significant difference in trace metal content between the two types of samples. However, KERSTEN et al. (1985) demonstrated an overall difference in the mobility of micropollutants under oxidising and reducing conditions.

The amount of pollutants adsorbed per gram of sediment is relatively low during floods with high dilution and extremely high concentrations of suspended matter. For that reason overbank sediment are in most cases better suited to trace coarse grained particulates from mines and industrial waste than soluble contaminants, which are preferentially adsorbed onto fine particles. RIDGEWAY et al. (1995) conclude from work in several Mexican basins that overbank sediments do not provide a viable medium for regional geochemical mapping. Geochemical mapping based on the systematic collection of low order stream sediment samples has been shown to be more effective in discriminating between contaminated, mineralised and background regions.

4.1. Drying sediment samples

For the investigation of inorganic and/or organic non-volatile pollutants, air-drying and heating up to 40° C is generally not thought to affect the results of the total content of pollutants (THOMAS et al., 1984; JONES et al., 1989). Drying samples with hygroscopic substances, such as water-free sodium sulphate (LANDESAMT f. WASSER NORDRHEIN-WESTFALEN 1986), does not ensure complete dryness and might therefore cause incomplete extraction of organic pollutants. The most common drying procedure for organic pollutants is freeze-drying. Freeze-drying has no adverse effects on the content of non-volatile

hydrocarbons or PCB's (MUDROCH et al., 1992). Freeze-dried sediment samples are also regarded as stable under deep frozen conditions (WELLS and KELLY, 1991). BARBANTI and BOTHNER (1993), however, reported increased aggregation between particles during freeze-drying, resulting in higher metal concentrations attached to finer particles in the coarse sieve fraction.

4.2. Grain-size separation

The normalisation of the sediment samples to a fine grain-size (<0.2 mm) should allow for the collection of representative samples with reasonably small sample mass (1-2 kg) and eliminate the gravel and coarse sand size; this is generally dominated by contaminant-free quartz, feldspar and carbonate minerals (IRION, 1991; KRALIK and AUGUSTIN-GYURITS, 1993). As these minerals have little adsorption capacity, they are not good indicators of pollution. A number of factors favour the use of the <0.04 mm size fraction: (1) this particulate size is transported at low and medium current velocities (0.1-0.7 m/s) in suspension (MÜLLER and FÖRSTNER 1968; KRALIK and AUGUSTIN-GYURITS 1993); (2) it contains considerably less quartz, feldspar and carbonate compared to the <0.063 mm fraction (Fig. 3), but represents a higher proportion of the total sample (PIRKL and KRALIK 1988) than the <0.02 and <0.002 mm size fractions with similar pollutant concentrations (Fig. 4); (3) it avoids any leaching of the pollutants either during wet-screening ($<10\%$; ACKERMANN et al. 1983) or ultrasonic treatment (1-7.3%; DONG et al. 1985) and (4) it is the smallest grain-size obtainable by dry screening in standardised (ISO 3310) stainless steel test sieves. In practice a sample can be disintegrated, screened and stored for analysis within 30 min. ACKERMANN et al. (1983) favoured the <0.02 fraction compared to the <0.063 mm fraction because of its smaller variance and enrichment of the heavy metals compared to the 0.02-0.063 mm fraction. For the environmental geochemical mapping of certain areas the fraction <0.04 mm was chosen due to a much simpler and faster dry screening procedure (NORDRHEIN - WESTFALEN 1986).

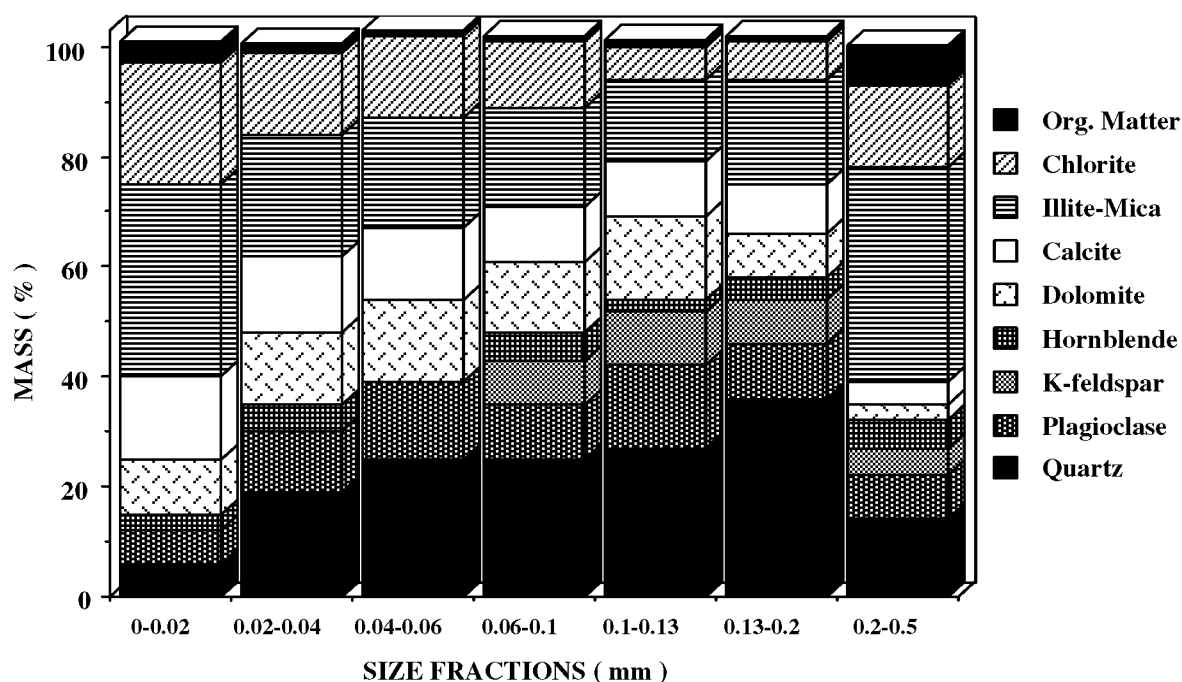


Fig. 3: Relationship between size-fraction and in mineralogy. Quartz, feldspar and dolomite content increases, while illite-mica-, chlorite-, calcite- and organic matter content decreases with increasing grain-size (Damube; KRALIK and AUGUSTIN-GYURITS 1993).

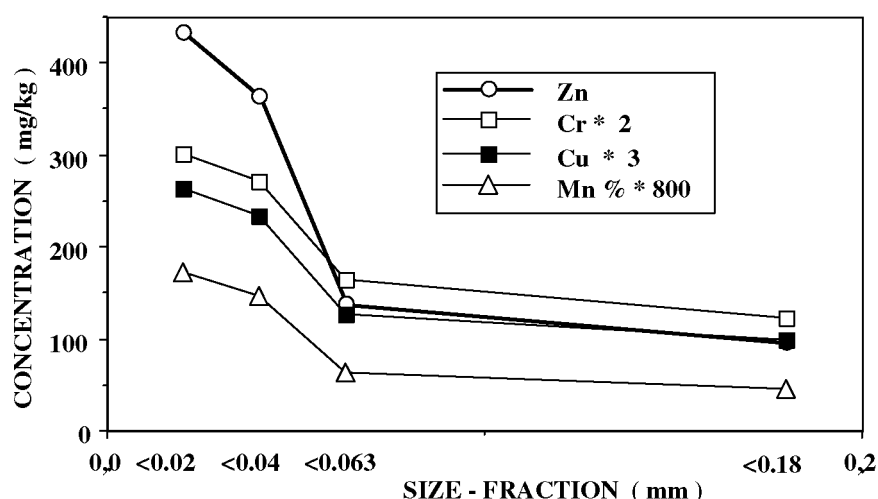


Fig. 4: Size-fraction of a sediment from the River Feistritz (Lower Austria) and heavy metal concentrations. Size-fractions <0.18 and <0.063 mm show background values, whereas the very-fine-fraction <0.04 and <0.02 indicate heavy metal pollution.

The critical point about dry screening is the gentle and complete disaggregation of air-dried, and in some cases partly, cemented samples. A comparison of two samples analysed in triplicate in the author's laboratory, shows no significant difference (<10%) between wet and dry screening (<0.04 mm) in grain-size and the concentration of 40 elements.

4.3. Characterization of sediment matrix

The determination of the particle-size distribution by wet screening, or at least the quantitative determination of the <0.04 mm fraction by careful squeezing and dry screening on a screening machine (10 min.; Fig. 1), is a relatively quick step in the procedure. It allows the investigator to evaluate the sedimentological history as well as the approximate surface area of the sample. As sedimentation in surface waters can be heterogeneous, the size distribution of the separated fraction from one sampling area to another can vary considerably (Fig. 5).

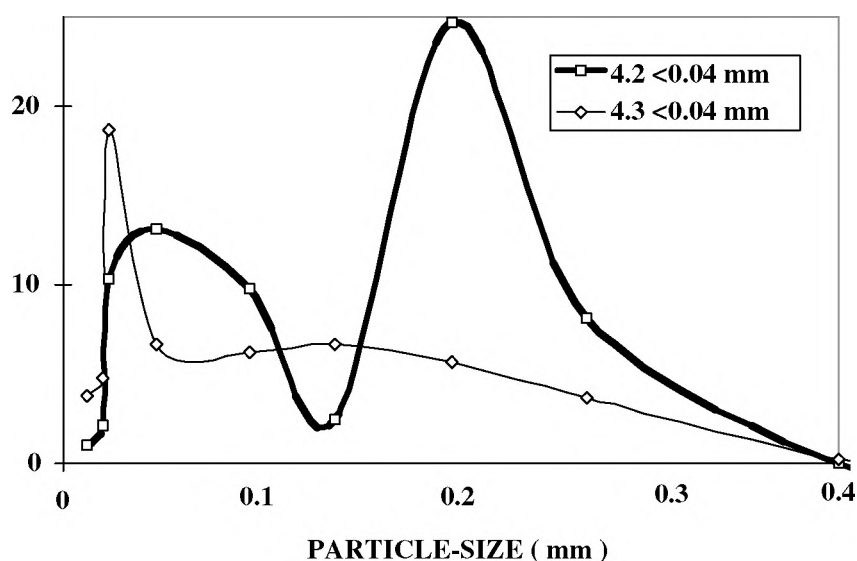


Fig.5: Differences in the particle size distribution of 2 sub-samples collected from the same area in the River Krumme Steyerling catchment (Upper Austria).

As the organic debris of plants and organisms are good adsorbents of organic micropollutants as well as heavy metals, the total organic content should be determined. Generally this is done by weight loss after heating at 550°C for 1.3 h. (DIN 38 414-3) or for 6-20 h. (ASTM D2974 1988) to oxidise even well coalified particles. This technique, however, has been questioned in recent years, because at temperatures >400° C hydroxyl-water from clay minerals is expelled and very fine grained Mg-carbonate is decarbonised. This can result in an over-estimation of the organic matter content (BRETSCHKO and LEICHTFRIED 1987; GOLDIN 1987). In conclusion, the precise estimate of the total organic matter content by measuring the organic carbon (TOC), is hampered by the sum of several analytical errors (+ analysis of carbonate carbon), including the assumption that 58% of the total organic matter content is made up of organic carbon (SCHACHTSCHABEL et al. 1982). Many investigations of fine grained sediment samples by thermal gravimetric analysis (TGA) show that the majority (>90 wt.%) of the organic matter is decomposed by continuous heating at temperatures <400° C (Fig. 2). In practical terms 2-6 hr. decomposition at 360° C in an oven has the same effect and

oxidises organic matter in surface water sediments quantitatively. Only in areas of coal mining and heavy use of high-quality coal, are temperatures of up to 550° C needed. These temperatures overlap with the temperature range of crystal water and CO₂ expulsion from minerals. A comparison of TOC analysis and weight-loss at 360° C from fine grained sediment from different areas, produces a good correlation and suggests a mean TOC-content of 52 wt.% in the organic matter of the sediments (Fig. 6).

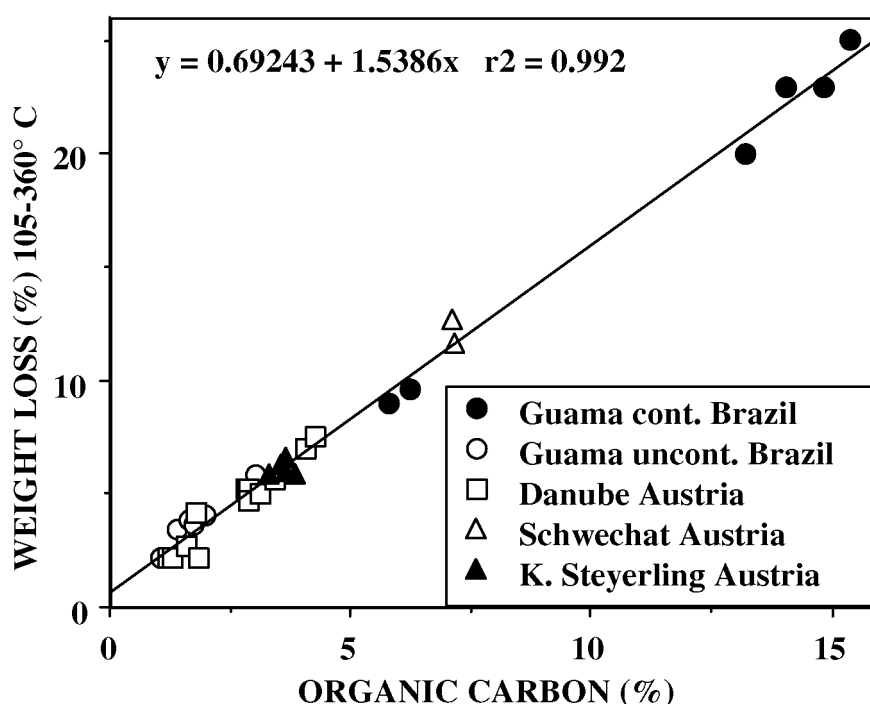


Fig. 6: Comparison of organic carbon with weight loss of different fine fractions (<0.04 mm).

The polar molecular structure of water implies that it is concentrated on the surfaces of Fe- and Mn-hydroxides and organic substances, as well as being loosely bound to clay minerals. Weight-loss at 105° C of the originally air-dried sediment depends mainly on relative humidity and the quantity of these above-mentioned phases with relatively large surface areas. The weight-loss of several phases of nearly pure clay minerals, Fe-hydroxides and organic matter after being heated to 105° C (16 hr.), indicates that between 8 - 12 % of water can be

adsorbed onto these substances after three days equilibration at 55% relative humidity ($\text{Ca}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$); Table 1). On the other hand, in fine-grained mineral phases such as quartz, feldspar and carbonate with considerably smaller surface areas and with no possibility of loose incorporation of water, the weight loss is <0.3 wt.%. Routine weight-loss determinations (105°C) of 195 fine grained river sediments from a large area in Austria shows a nearly Gaussian distribution with a maximum at 1.4 % weight-loss with some extreme values up to 3-5 % (Fig. 7).

TABLE I: WEIGHT LOSS AFTER 16 HR.
HEATING OF MODEL SUBSTANCES

Fine-grained (<0.04 mm) Pure Model Substances (Location or Company)	Weight Loss 105°C (%)*
Quartz (Merk)	0.1
Dolomite (Topla, A)	0.1
Calcite (Lafatsch, A)	0.2
Bitumn. Coal (NBS1632b)	0.79
Goethite-Hematite	6.9
Goethite Leadville (US)	9.8
Humic-Acid (Fluka)	10.2
Organ. Matter (River Schwechat, A)	11.2
Smectite	12.4

* Before heating 3 days of
equilibration at 55% relative humidity

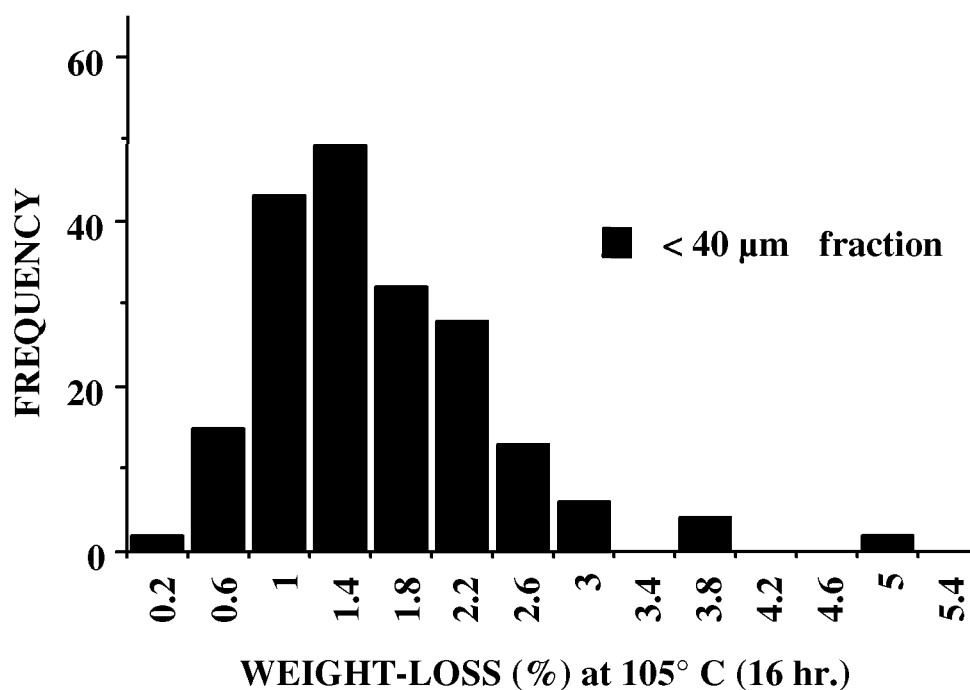


Fig. 7: The frequency distribution of weight-loss values (195) of river sediments in an area of Upper Austria after drying 16 hrs. (105°C).

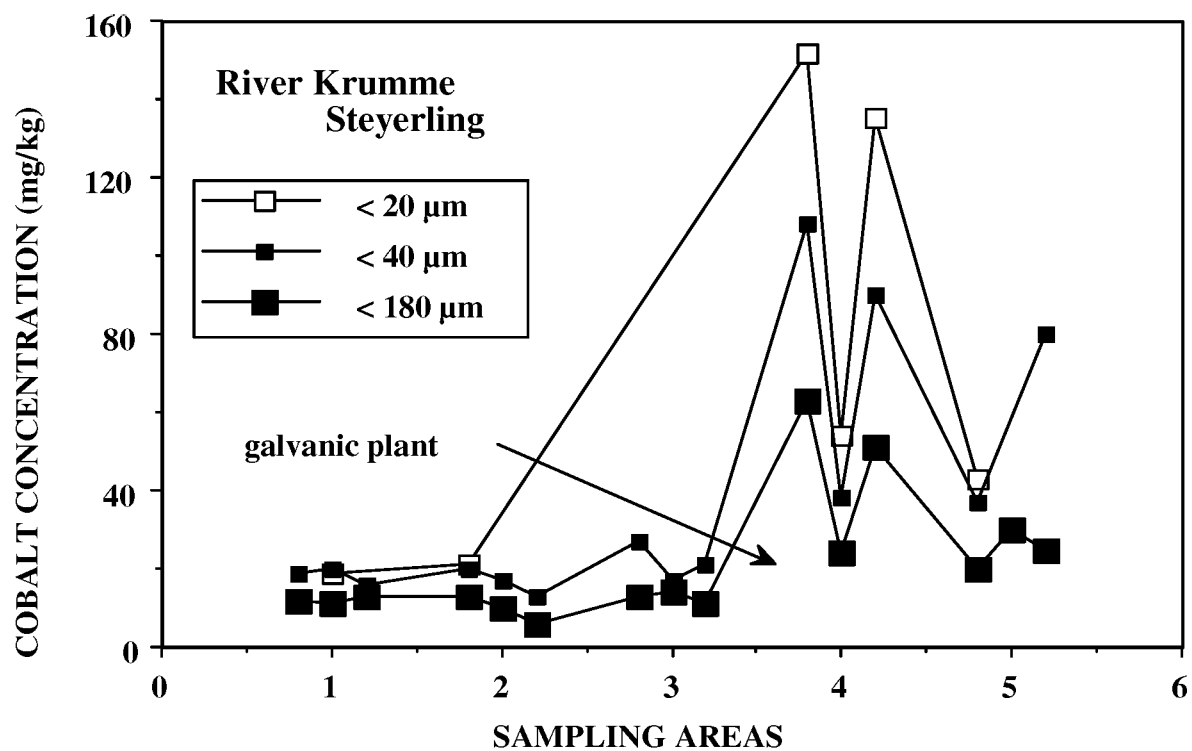


Fig. 8: Changes in Co concentration in 3 size fractions of an Alpine river sediment.

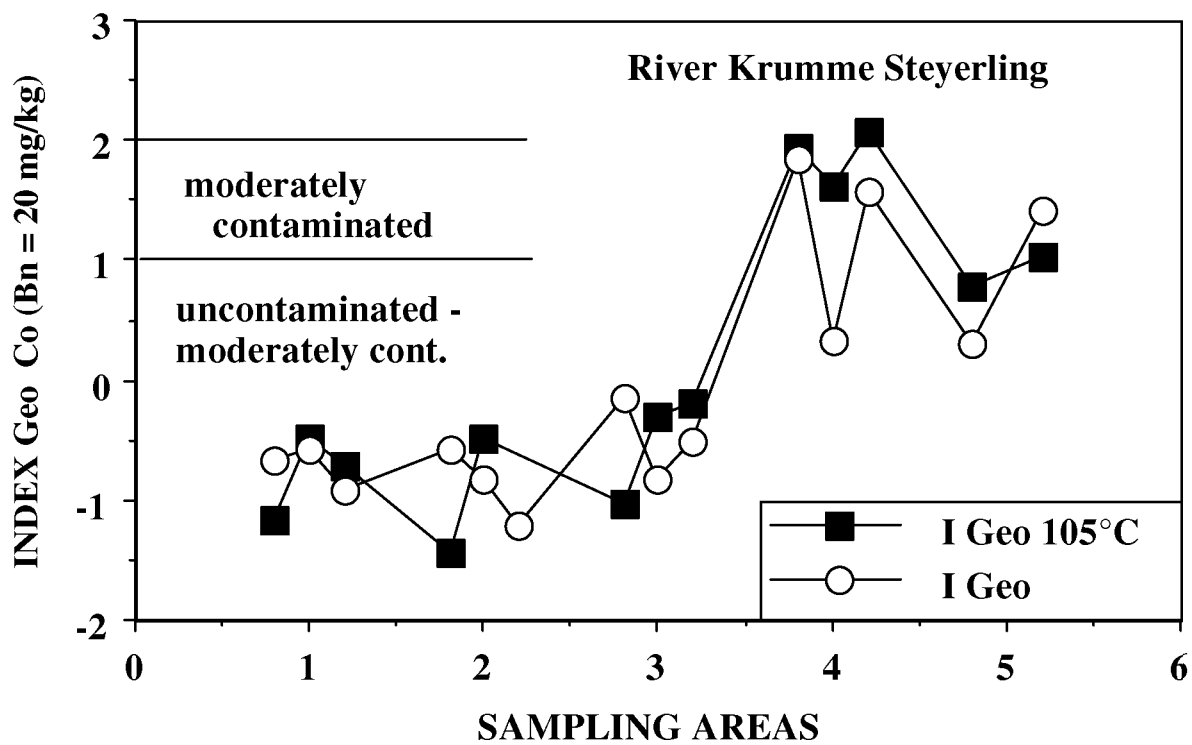


Fig. 9: Correction of the Geo-Index by weight loss at 105°C: ($I_{\text{Geo } 105^\circ} = \log_2 (C_n/B_n \times WL_{105^\circ})$). C_n = measured concentration; B_n = background values; WL_{105° = weight-loss after heating samples at 105°C (16 hrs).

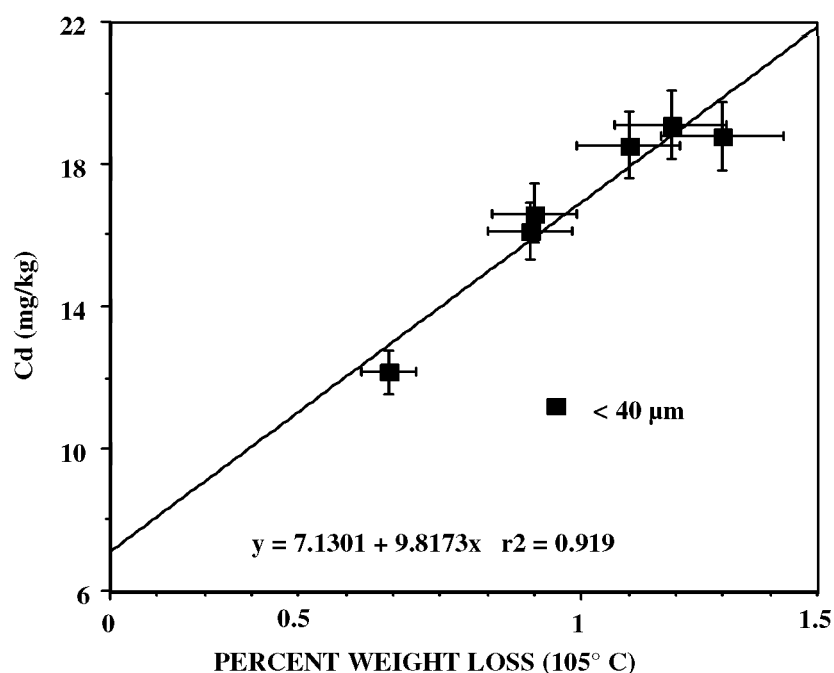


Fig. 10. Correlation of Cd adsorption (0.011 mg Cd/l; pH 7.6; 14° C; 100 min) and weight loss (105° C, 16 hr.) after equilibration of 55% (relative humidity) of different river sediment samples.

4.4. Evaluation of sediment data

A comparison of analytical data from different sampling areas is complicated by variation in the natural geochemical background concentrations of elements and differences in adsorption capacity. This is indicated by variation in the grain-size of the fine fraction (<0.04 mm) of sub-samples from a polluted sampling area (Fig. 5) in Austria. For example, the concentrations of cobalt (total XRF analysis) in three sub-samples at a sampling area next to a galvanising plant vary systematically in all the fine fractions analysed (Fig. 8), indicating variable degrees of contamination. Such a variation in contamination over a distance of a few meters within a sampling area (50 - 100 m) of a small Alpine creek 200 m below a galvanising plant is very unlikely. This is better explained by variations in grain-size and mineral-phases in the creek sediment, resulting in a difference in weight-loss (105°C) of 0.6 - 1.4 % between the three composite samples. It is suggested to correct the GeoIndex (MÜLLER 1979) by this weight loss (see formula (1)), instead of the general factor 1.5. This correction shows that moderate Co contamination is present in all three sub-samples instead of large variations in contamination at the same sampling area (Fig. 9). Fine fractions (<0.04 mm) from rivers north of Vienna (Fig. 7) indicate that the most frequent value of weight loss (1.4 %) is close to the factor of 1.5 used by MÜLLER (1979). In cases of pure organic matter, Fe-hydroxide, or clay mineral samples this 105°C weight-loss varies from 8-12 %, whereas pure mineral concentrates of quartz, feldspar and carbonates yield values of 0.1-0.2% (Tab. 1).

Using sediment fractions from variable geological backgrounds and waters contaminated with cadmium, a correlation between 105°C weight-loss and Cd-adsorption was found (Fig. 10). These preliminary results suggest that the amount (105°C weight-loss) of water (air humidity) adsorbed can be used as a simple measure to correct for different concentrations of organic matter, Al-, Fe-, Mn-oxides and clay minerals in the sediment sample. On the other hand, fine fractions with very small (< 0.3 M-%) 105°C weight-losses can be rejected because of insufficient adsorption capacity.

5. CONCLUSION

The sampling and analysis of fine-grained river sediments is an effective tool to evaluate the location and degree of pollution in large areas. Quick sample preparation procedures and rapid data evaluation are crucial. Dry screening of fine sediment fractions (<0.04 mm) minimises the time spent in sample preparation before analysis to 20 min. per sample. The measurement of the amount of water adsorbed onto the surface of these samples (weight loss 105°C for 16hr.) allows samples to be discarded with no adsorption capacity. The overall adsorption capacity in the samples is predominantly caused by variable amounts of humic substances, clay minerals, iron- and manganese hydroxides and amorphous silica (algae frustals), which can be corrected for by the amount (weight loss at 105°C) of water (air humidity) adsorbed on to the sample surface. The Geo-Index (105°C) modified by weight loss at 105°C (16hr.) allows a correction to be made for the sediment-matrix and makes the interpretation less dependent on the size-fraction selected.

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COASTAL MARINE SEDIMENT SAMPLING FOR RADIONUCLIDE ANALYSIS

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Abstract. January 1968, a B52 plane carrying 4 nuclear weapons crashed on the sea ice ~12 km from the Thule Air Base, Northwest Greenland. The benthic marine environment in the 180-230 m deep Bylot Sound was then contaminated with ~1.4 TBq ^{239,240}Pu (~0.5 kg). The site was revisited August 1997. Due to the single plutonium injection well defined in time the site is an interesting test case for sediment dating. The present data support an earlier quantification of the sedimentation rate as 3-4 mm per year, i.e. 8-12 cm during the 29 years since the accident. Biological activity has mixed accident plutonium much deeper, down to 20-30 cm, and the 8-12 cm new sediment have been efficiently mixed into the contaminated layer. In addition to the classical bioturbation mixing the upper ~5 cm, the plutonium data indicates the existence of a deeper mixing, probably also caused by bioturbation. This could have implications for the use of excess ²¹⁰Pb as a sedimentation rate chronometer in coastal environments with rich biological activity.

1. INTRODUCTION

In January 1968, a B52 plane from the US Strategic Air Command caught fire and crashed on the sea ice in Bylot Sound ~12 km from the Thule Air Base, northwest Greenland (Fig. 1). The plane carried 4 nuclear weapons. Part of the weapons plutonium was distributed over some square kilometers of the ice in the following explosive fire. The underlying sea sediments received a fraction of the weapons plutonium when the sea ice melted the following summer and probably also during the accident, as the impact caused part of the ice to break up [1].

It has been estimated from earlier sample collections (1968, 1970, 1974, 1979, 1984, 1991) [2,3,4,5,6], that the pollution remaining in the seabed in Bylot Sound by 1968 amounted to approximately 1.4 TBq ^{239,240}Pu (~0.5 kg), 0.025 TBq ²³⁸Pu, 4.6 TBq ²⁴¹Pu and 0.07 TBq ²⁴¹Am. The rich marine benthic fauna responsible for a major part of the sediment disturbances, the bio-turbation, was intensively studied in 1939-1941 [7]. Selected data from the Thule-1997 sampling have been given at recent conferences [8,9,10,11].

2. MATERIALS AND METHODS

In August 1997 we took a new set of marine samples from the contaminated area in Bylot Sound. Two different sediment corers were used. Most samples were taken with a Finnish 'Gemini Twin Corer' delivering two parallel 8-cm diameter cores. Immediately after sampling, the cores were extruded and sliced with a sophisticated sectioning equipment - normally in 1cm slices. An earlier version of the Gemini Corer, the Niemistö Corer, has been described in the literature [12]. The Niemistö Corer only takes single cores, but the slicing equipment is similar. In most cases, the same layers from the two cores taken simultaneously were pooled. At many locations, stones hampered sediment coring. In those cases the 'HAPS' corer [13], a 13.6 cm diameter steel corer used during earlier sampling cruises, had a better success rate. HAPS cores without too large stones were divided in 3-cm slices onboard.

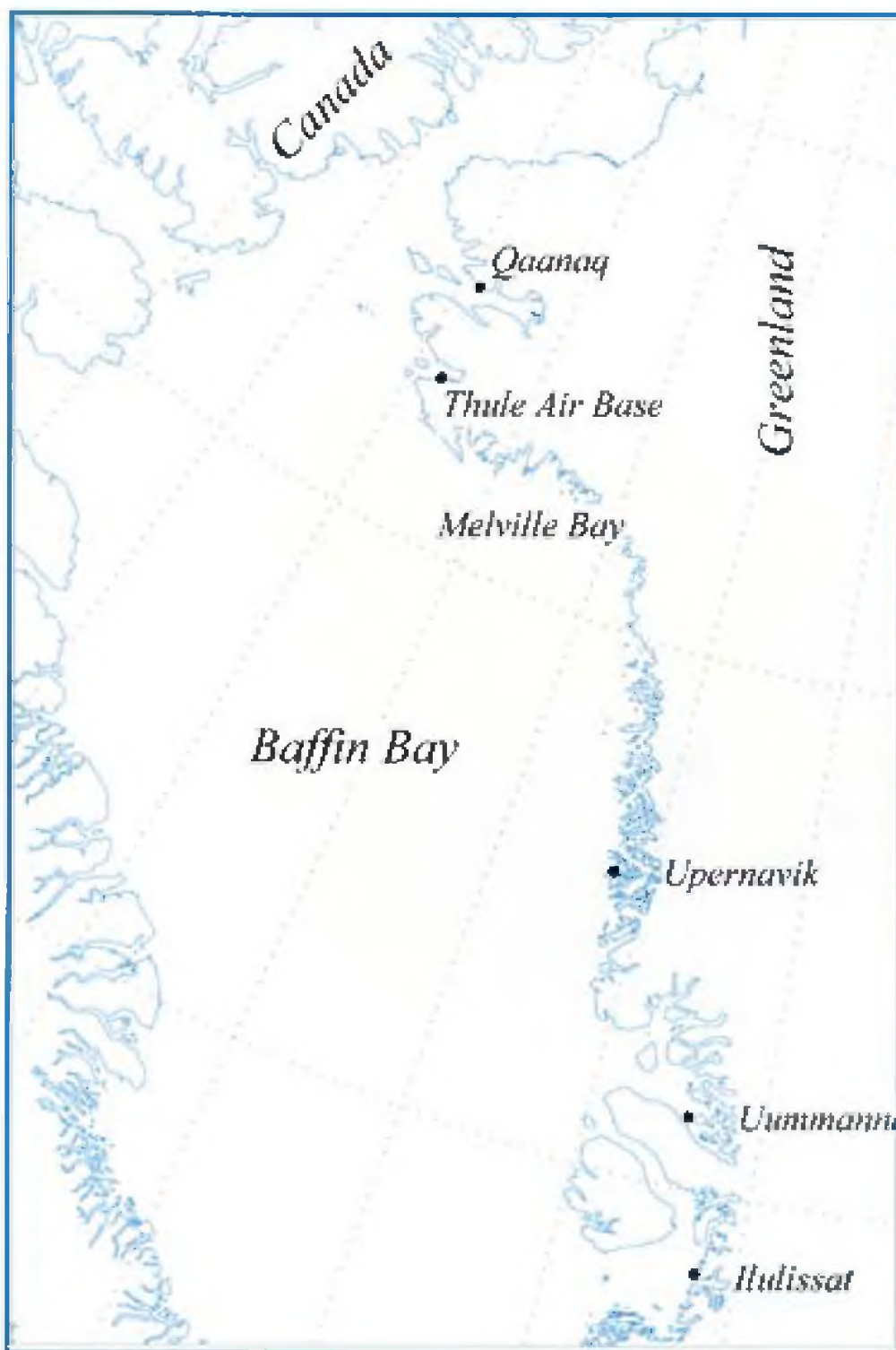


FIG. 1: Dahlgaard: Map of NW Greenland with mentioned locations. The Thule accident site is situated in the sound ~12 km W of the Thule Air Base.

Plutonium was analysed by alpha spectrometry after radiochemical separation and electrolysis on stainless steel discs [14]. Analyses were performed on one gram aliquots except for background samples taken outside Bylot Sound, where 5 gram aliquots were used. Pb-210 was analysed by HPGe semiconductor gamma spectrometry on 10-15 g aliquots. All data referred to here are excess ^{210}Pb calculated by subtracting the in-situ supported ^{210}Pb level based on ^{226}Ra calculated from the same gamma spectrum.

3. RESULTS AND DISCUSSION

Examples of $^{239,240}\text{Pu}$ and excess ^{210}Pb concentration profiles versus sediment depth are given for two contaminated sediment cores, locations 20 and P (Fig.2). An apparent exponential decrease in concentration with depth is observed for excess ^{210}Pb as well as for $^{239,240}\text{Pu}$. The indicated regression lines are given in the figure text. For location 20 (Fig. 2) an alternative excess ^{210}Pb regression line might be placed at 16-25 cm, if the ^{210}Pb distribution in the 0-16 cm layers are assumed to be caused by a biological mixing gradually decreasing with depth. The example illustrates that there are possibilities for personal judgement when interpreting sedimentation data. Such judgements may have a significant effect on the results.

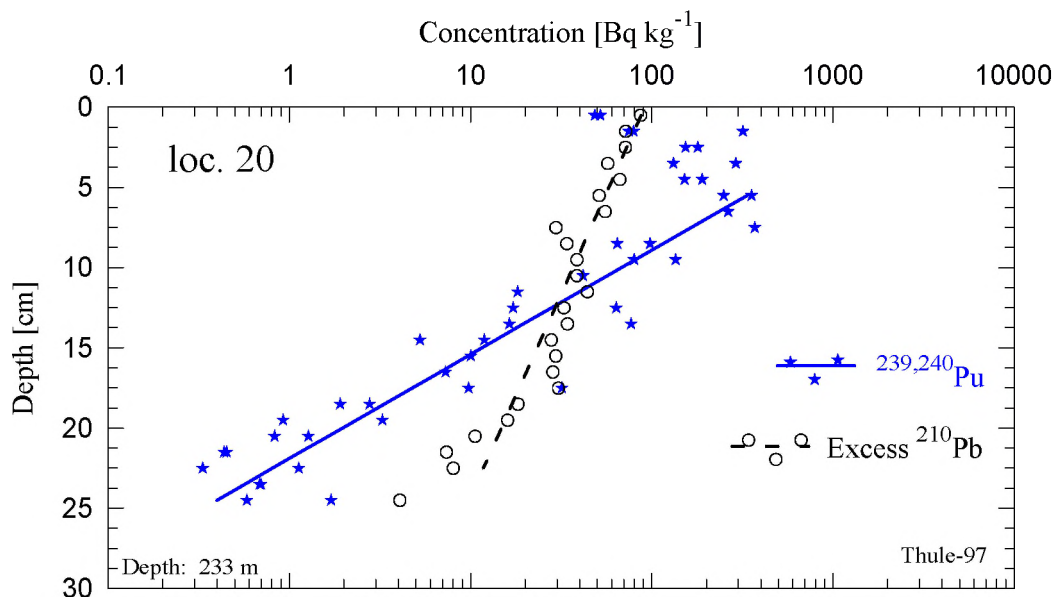


FIG. 2: Dahlggaard et al: Thule-97. Two different sediment $^{239,240}\text{Pu}$ and ^{210}Pb concentration (Bq kg^{-1}) profiles with sediment depth (cm). Loc. 20 and loc. P. The regression lines are:

Loc. 20: $\ln(^{210}\text{Pb} [\text{Bq kg}^{-1}]) = 4.52 - 0.091 * d$, 0-23 cm, $r^2=0.84$.

Loc. 20: $\ln(^{239+240}\text{Pu} [\text{Bq kg}^{-1}]) = 7.77 - 0.35 * d$, 5-25 cm, $r^2=0.90$.

Loc. P: $\ln(^{210}\text{Pb} [\text{Bq kg}^{-1}]) = 4.66 - 0.21 * d$, 1-15 cm, $r^2=0.86$.

Loc. P: $\ln(^{239+240}\text{Pu} [\text{Bq kg}^{-1}]) = 4.81 - 0.30 * d$, 1-15 cm, $r^2=0.89$.

d is mean depth of sediment layer in cm.

A set of further plutonium sediment profiles are given in Fig. 3 for weapons plutonium contaminated cores from Bylot Sound as well as for assumed background cores taken outside Bylot Sound (ny-3, 1410 and Schades Øer). In all cases, plutonium seems to be well mixed in the upper 3-5 cm sediment layers. In the first 8 examples in Fig. 3, the 1968 plutonium pulse then shows gradual decreasing activity concentrations, down to 20 – 30 cm sediment depth in some cases. However, in some of the cores a uniform contamination level was seen throughout the whole column. This indicates that in those cases we have not managed to penetrate the corer sufficiently deep to account for the total contamination and further, that some of the cores are from sediments that may have undergone a-typical mixing. Many explanations could be given for this, e.g. penetration in an area, where previous trawling or dredging has disturbed the layering, or maybe the effects of sediments sliding along submarine slopes. The sampling was performed “in the blind”, i.e. without any side scan sonar or similar sediment mapping.

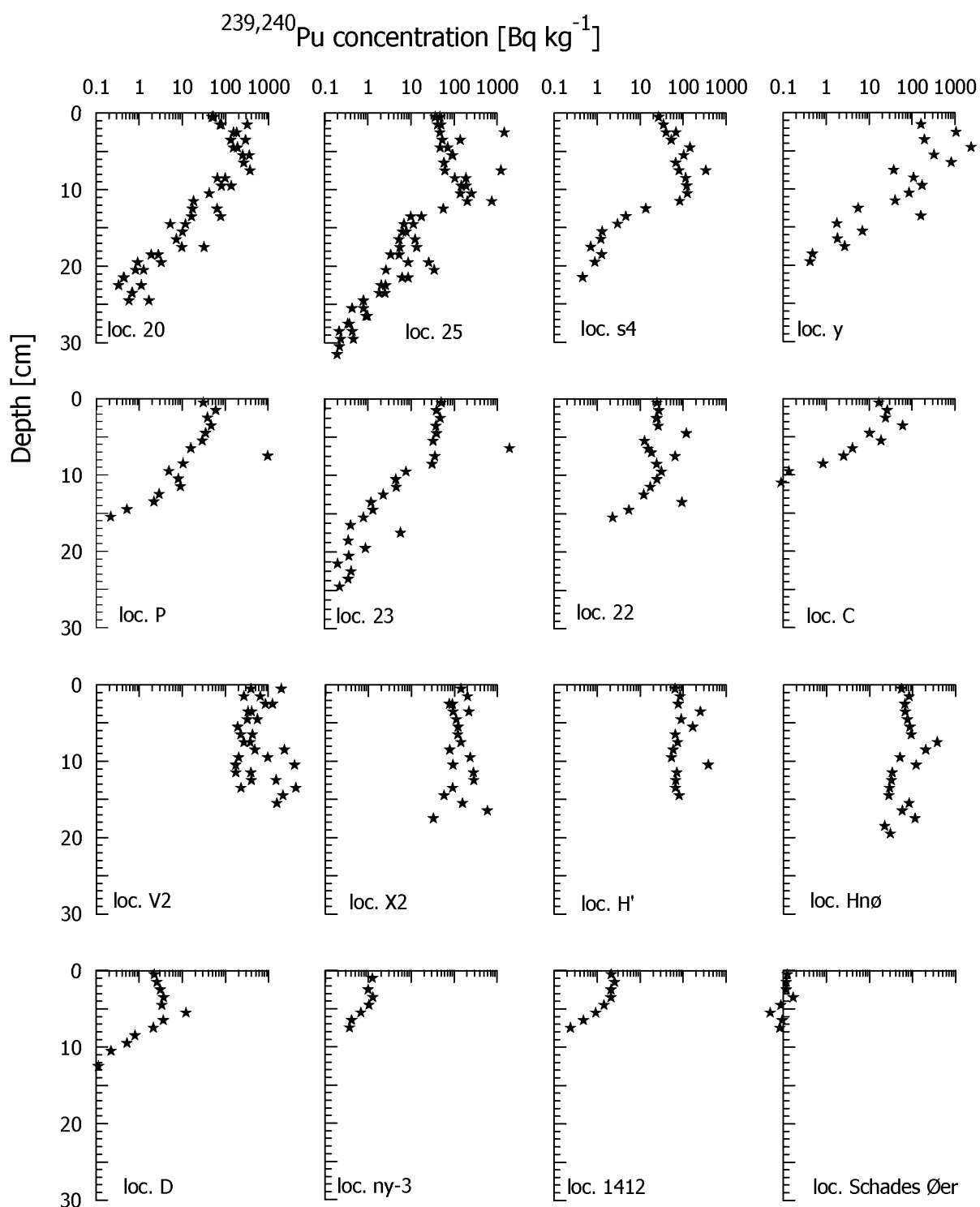


FIG. 3: Dahlgaard et al: Sediment $^{239,240}\text{Pu}$ concentration (Bq kg^{-1}) profiles with sediment depth (cm).

It should be noted that the concentration axis in Fig. 2-3 is logarithmic. In spite of this, the large variation of observed plutonium concentrations is obvious. This is caused by hot particles. In several cases reanalysing a second aliquot, where orders of magnitude differences are sometimes observed, supports this. In an ongoing study, the frequency and the analysis of these hot particles are being further studied.

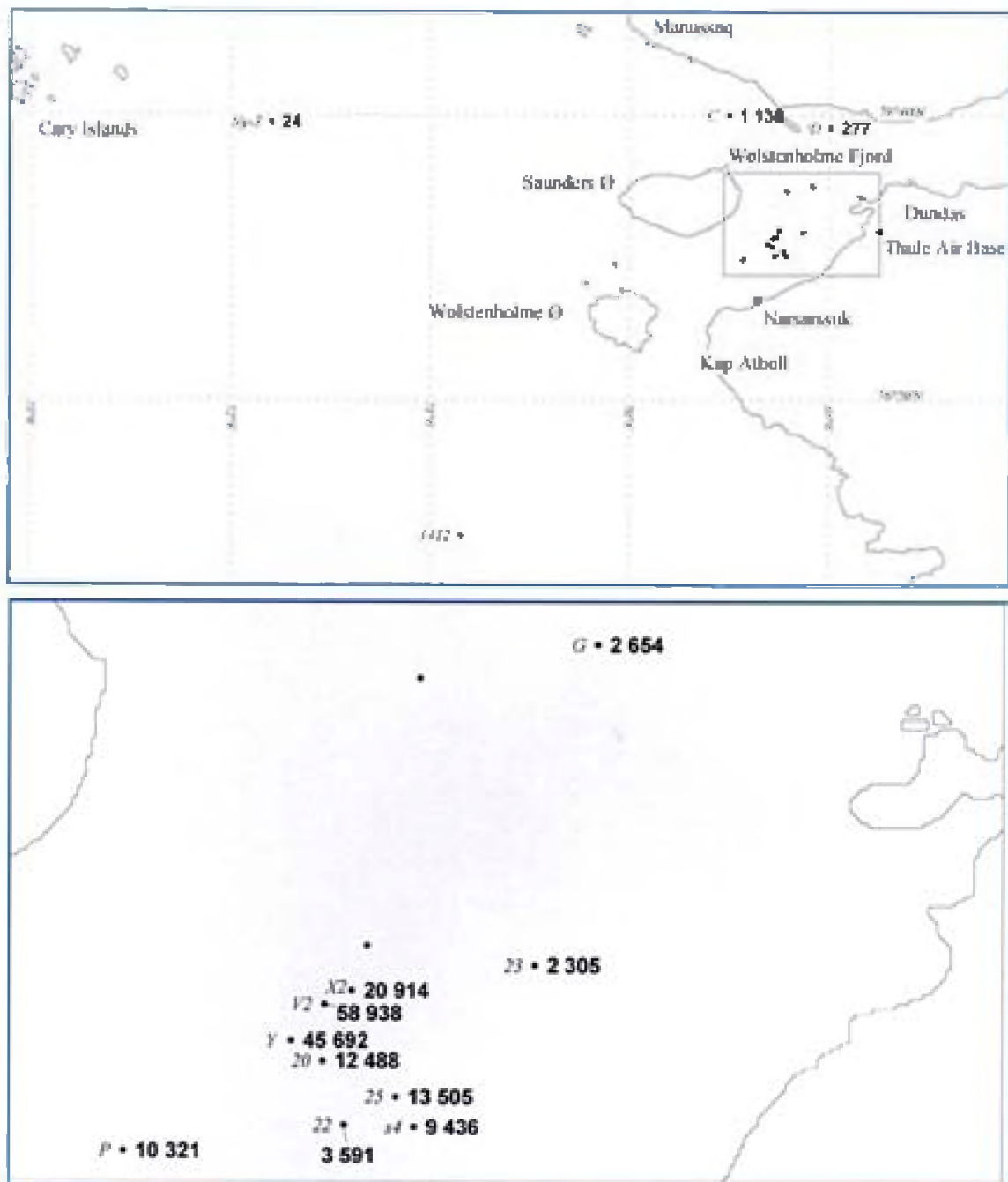


FIG. 4: Dahlgaard et al.: Thule-1997. Plutonium inventories integrated over the full sediment column taken, expressed as Bq $^{239,240}\text{Pu m}^{-2}$. Location names in *italics*, inventories in **bold**. The point of impact was on the sea ice 180 m above the location marked V2.

If the deeper part of the high-concentration layer is assumed to correspond with the accident in 1968, 29 years before the sampling, a sedimentation of 5-12 cm, i.e. 2-4 mm per year, has taken place since then. This corresponds well with ^{210}Pb dating of earlier cores [15]. The penetration of plutonium to much deeper layers and the absence of very low concentrations in the top layers are both thought to be caused by biological mixing processes performed by the rich benthic community. The apparent penetration of accident plutonium far deeper than the assumed 1968 depth plus the depth of the surface mixed layer could have implications for the use of excess ^{210}Pb as a sedimentation rate chronometer in coastal environments with rich biological activity.

If the explanation is a small but significant deep biological mixing in addition to the fast bioturbation of the surface layer, this should be accounted for when comparing the slope of the excess ^{210}Pb depth distribution with its 22.3 year physical half life. Bioturbation in the upper mixed layer was included in the earlier sedimentation modelling [15]. Data from the present sampling have not yet been finally evaluated concerning sedimentation rates.

It was not possible to retrieve sediments in areas shallower than 100 m due to rocky bottoms. During the sampling expedition much effort was devoted to obtaining additional sediment samples from Upernavik, Melville Bay and the area between Cary Islands and the mainland. The success rate for this effort was very low due to stones in the sediments – even far from land and at large depths. The stones are probably dropped from the numerous icebergs in the area.

Plutonium inventories integrated over the full sediment columns taken, expressed as $\text{Bq } ^{239,240}\text{Pu m}^{-2}$, are given in Fig. 4. The accident site – around location V -with the highest inventories is situated at a depth of 180 – 230 meters. A preliminary integration of the data in Fig. 4 gives a total inventory estimate of 1.8 TBq [10]. This is not considered significantly different from previous estimates. A possible error in the inventory estimates caused by the lack of quantitative knowledge of the hot particles is currently being investigated.

4. CONCLUSIONS

- The Thule weapons accident site is an interesting test case for sediment dating due to the single plutonium injection well defined in time.
- The present Thule 1997 data support an earlier quantification of the sedimentation rate as 2-4 mm per year, i.e. 5-12 cm during the 29 years since the accident. Biological activity has mixed accident plutonium much deeper, down to 20-30 cm, and the 5-12 cm new sediment have been efficiently mixed into the contaminated layer.
- If the explanation for the occurrence of accident plutonium far deeper than the assumed 1968 depth plus the depth of the surface mixed layer is a small but significant deep biological mixing in addition to the fast bioturbation of the surface layer, this should be accounted for when comparing the slope of the excess ^{210}Pb depth distribution with its 22.3 year physical half life.
- Retrieving well defined sediment cores from a rugged coastal area under constraints of logistics, time and budget is much more difficult than it is to define ideal requirements for the quality of sediment samples.

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COLLECTION AND PREPARATION OF LAKE SEDIMENTS FOR DATING AND TRACE ELEMENT ANALYSIS BY NUCLEAR TECHNIQUES

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Abstract. Aquatic mediums are the recipients of the liquid effluents from variety of industries. Both the suspended and bottom sediments of the mediums, owing to their great absorption capacity for many of the toxic pollutants, could become effective indicators of the pollution status of the medium when sampled, stored and analyzed with appropriate care. The determination of metal levels in sediments can play a key role in detecting the sources of pollution. The analysis of pollutants coupled with measurement of sedimentation rates in the medium using radiometric methods can reconstruct the history of discharge into the medium. Sampling modes of suspended solids bottom surface sediments and bottom core samples are presented in this presentation. The significance of sample storage procedures for the maintenance of sample integrity is also discussed. The choice of container materials for the storage of samples should receive utmost attention, especially for wet samples. Many type of the containers made from relatively inert materials like Teflon, quartz, polyethylene, hard glass and so forth have both attractive and undesirable attributes. The duration of storage and the requirements of short term and long term storage are also discussed. The pre-treatments of the samples, i.e. preparation of samples ready for analysis is a crucial step in generating representative data. The problems associated with pretreatment procedures are presented in order to avoid contamination of the sample during sampling operation, through operating personnel and sample preparation. The importance of control analysis with standard reference materials and participation in inter laboratory comparison exercises are emphasized. The dating techniques using natural Pb-210 and anthropogenic Cs-137 applied to determine recent sedimentation rates in Lake Naini, in Uttar Pradesh, India are discussed in detail. Recent sedimentation rates, estimated by Pb-210 has found to be fairly constant at one location (mean dry mass sedimentation rate being 0.112 ± 0.010 g cm⁻² a⁻¹) but varying in other locations in the lake (the dry mass sedimentation rates varying from 0.026 ± 0.010 to 0.421 ± 0.050 g cm⁻² a⁻¹). At all locations the short term rates (for the last three decades) derived from the fall out radio nuclide Cs-137 have been observed to be marginally higher compared to long term (last 120-150 yr.) deduced from Pb-210. The spatial and depth wise distribution of both the radio nuclides obtained from sediment cores of the lake along with their textural properties like porosity and water content provide preliminary information on the existence of differential depositional zones throughout the lake and on the physico-chemical nature of the sedimentation process in the lake.

1. INTRODUCTION

Over the last two decades there has been increased attention directed towards interaction of pollutants with solid matter in aquatic medium. The interest originally focused on the simulation of the settling of organic matter produced by eutrophication and their subsequent decomposition in the bottom sediments. Today the need for understanding the characteristics of both suspended and bottoms sediments has been heightened by the fact that many toxic substances associate with solid matter. In some systems, solids are considered a pollutant in their right; e.g.reproduction of some endangered fish can be affected by sediment deposition on spawning beds. Both the suspended solids and bottom sediments represent an environment that must be investigated adequately to understand the fate of pollutant in an aquatic system.

Tracing of pollution sources by means of water analysis frequently gives rise difficulty, which may be usually associated to sampling procedures and physicochemical conditions pertaining to the species rather than to accuracy and precision of analytical techniques. A special difficulty arises from contaminants, which are not soluble but become rapidly fixed to particulate matter in the receiving water body. This applies in particular to heavy metals like Cr., Hg and Pb, because even close to the point of input their concentration in water decreases to ambient level making detection difficult, except by means of close knit system of water sampling. The determination of metal levels in sediment can therefore play a key role in detecting sources of pollution in an aquatic system. Although sediment analyses do not represent the extent of intoxication, they may be employed on a semi-quantitative basis in comparative studies to trace the sources of pollution such as surreptitious discharges from close-by industries. Furthermore, it is possible to determine the development of pollution intensity from dated sediment cores provided they contain fine-grained depositions, in which the sorbed, precipitated, organically bounded metals concentrations are accumulated. Finally the investigation of sediment particles is more useful from analytic point of view since trace element in particulate matter is about 3-4 orders of magnitude higher than the corresponding metal content in the aqueous phase.

The history of the impact of man on the environment evidences that in many places the greatest impact has been effected within the last 150 years. Lakes and estuarine sediments provide a basis for reconstructing many aspects of this impact, for estimating rates of change and for estimating a baseline in environmental monitoring programme (Eakins, 1983; Walling and He, 1993). In such studies, the establishment of accurate chronologies of sedimentation is of very importance not only for dating events but also for determining sediment accumulation rates. Furthermore, sedimentation rates based on palynological or stratigraphy methods often provide historical averages involving many meters of the sediment. Such measures may not reflect adequately the rates within upper 20-40 cm where significant sediment-water exchanges occur.

Radiometric methods have been successfully employed for studying sedimentary geochronology. Krishnaswami et al (1971) evaluated the use of ^{210}Pb as well as three other radio nuclides (^{32}Si , ^{55}Fe , ^{137}Cs) for dating recent fresh water lake sediments and they concluded that ^{210}Pb is an ideal tracer for dating lake sediments as old as a century or so. Koide et al (1973) further validated the utility of the method and determined sedimentation rates in a series of lakes. Edgington et al (1991) and Saravana Kumar et al (1999) used anthropogenic ^{137}Cs and natural radionuclide ^{210}Pb to estimate recent sedimentation rates in Lake Baikal and Lake Naini respectively. In addition, their results could provide information on the timing of paleolimnological events, on the existence of different depositional zones in the lake and for the development of mass-balance models for the sediments and contaminants.

The total ^{210}Pb activity in Lake Sediments has two components. Supported ^{210}Pb is that component of the activity, which derives from in-situ decay of the parent isotope ^{226}Ra within the individual soil or rock particles. It is transported into the lake in particulate form (along with the associated ^{226}Ra) as a part of erosive input from the catchment. The second component, called unsupported ^{210}Pb derives from a fraction of the ^{222}Rn atoms formed in the atmosphere due to interstitial diffusion through the soil into the atmosphere, where they decay through a sequence of short-lived isotopes to ^{210}Pb . This is removed from the atmosphere by precipitation or dry deposition falling on to land surface or into lakes or oceans. ^{210}Pb falling directly into lakes is scavenged from the waters and is deposited on the bed of the lake with sediments. In most situations, the supported ^{210}Pb can be assumed to be in radioactive

equilibrium with the supported ^{226}Ra activity and the unsupported activity at any level is obtained by subtracting ^{226}Ra activity from the total ^{210}Pb activity. The unsupported ^{210}Pb in each sediment layer declines with its age in accordance with the usual radioactive decay law and can be used to date the sediment. The determination of ^{210}Pb content can be effected either through a simple radiochemical separation scheme based on an anionic ion exchange followed with lead chromate precipitation and beta counting of ^{210}Bi or through ^{210}Pb leaching followed with alpha measurement of its grand daughter ^{210}Po deposited on a Silver planchette (Godoy et al, 1998).

Similarly the basis of using ^{137}Cs to derive chronologies for lake sedimentation during the past 30-40 years revolves on the fact that the weapon released atmospheric radio cesium is washed away by precipitation and is rapidly and strongly bound to fine particulate of land surface. Through run off it gets washed away from land surface and settles on the lake bottom. Assuming that post-depositional migration is insignificant, the distribution of ^{137}Cs in sediments reflects the chronology of the sediment deposition. The first appearance of this radionuclide in the sediment profile was observed in 1950s and the vertical distribution of ^{137}Cs in sediment profiles can be related to the known record fall –out for the subsequent period. The peak fall-out levels that occurred in 1963 have often been used to date sediments deposited at that time.

2. PRINCIPLES OF ^{210}Pb CHRONOLOGY

The three processes that are expected to influence the concentration-depth profile of unsupported ^{210}Pb in a sediment core are radioactive decay, sedimentation and sediment mixing. If the sedimentary particle mixing is considered as a diffusive process, the variation in the concentration of unsupported ^{210}Pb with time is given by:

$$\partial (\rho C)/\partial t = \partial / \partial z (K \partial (\rho C)/ \partial z) - S \partial (\rho C)/\partial z - \lambda (\rho C) \quad (1)$$

Where C is the concentration of unsupported ^{210}Pb (Bq/g) at time t, ρ is the in-situ density of the sediment (g/cm^3), K is the mixing or diffusion coefficient (cm^2/y), z is the depth below the sediment-water interface, S is the linear sedimentation rate (cm/y) and λ is the decay constant of ^{210}Pb (0.031 y^{-1}). Assuming steady state condition; and K, S and ρ are constant with time and depth, the Eq (1) can be rewritten as:

$$K (\partial^2 C / \partial z^2) - S (\partial C / \partial z) - \lambda C = 0 \quad (2)$$

Three solutions of this differential equation can be written (Krishnaswami and Lal, 1978) with the general boundary condition $C(z) = C_0$ for $z=0$ and $C(z) = 0$ for z tending to ∞ . By imposing constant flux and specific condition $K=0$; the solution for Eq (2) is given as

$$C(z) = C_0 \exp [-(\lambda z/S)] \quad (3)$$

This formulation assumes Constant Initial Concentration (CIC model) of unsupported ^{210}Pb at the sediment-water interface. The value of C_0 is the ratio of the deposition rate of the radionuclide ($\text{Bq} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$) to the deposition rate of the sediment ($\text{g} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$) at the interface. If the sedimentation rate is constant over the time interval t, then the Eq (3) is translated as:

$$C(z) = [\phi / S \rho(z)] [\exp(-(\lambda z/S)] \quad (4)$$

where ϕ is the flux the radionuclide ($\text{Bq. cm}^{-2} \text{ y}^{-1}$) and ρ is the in-situ density at depth z . The plot of $\log C(z)$ versus depth should be a straight line if both the deposition rates of isotope (ϕ) and sediment (S_p) are constant. The formulation is called as Constant Flux and Constant Sedimentation rate (CFCS model).

However, if the sedimentation rate has changed during the dating interval, the ages of different strata in the sediment column can be deduced from the integrated activity of the isotope in the core. Assuming Constant Flux (CF model) and steady state between supply and decay, the time taken to deposit a sediment layer of thickness z in continuously depositing sediment is

$$t = 1/\lambda \ln [(A_{\infty} / A(z))] \quad (5)$$

where A_{∞} represents the total unsupported ^{210}Pb (Bq. cm^{-2}) in the sediment column and $A(z)$ that beneath the sediment depth z from the surface. Since a new value of $A(z)$ is available at various depths of the core, it is possible to calculate their age and hence the sedimentation rates between depth intervals.

3. LAKE ENVIRONMENT

Standing water bodies range from small detention ponds to huge systems like the Great Lakes. Lakes can be either Natural or Artificial (Reservoir or Impoundment). Although there is tremendous amount of variation within these two categories, there are some generalizations that typify each in a general sense. In particular, Impoundments often have controlled outflow while the natural lakes are controlled. Damming a river always creates artificial impoundment and consequently they tend to be elongated or dendrite since they consist drowned river valleys. In contrast, natural lakes tend to be less elongated and more circular.

The two aspects of size namely Residence time (τ) and depth (H) have a strong bearing on the water quality. In general the Lakes are divided into short ($\tau < 1\text{y}$) and long ($\tau > 1\text{y}$) residence time systems. Further they are classified as shallow ($H < 7\text{m}$) and deep ($H > 7\text{m}$) based on the average depth. This latter classification is significant because deep lakes are often subject to thermal stratification during certain periods of time. In wind- and current-induced turbulence leads to the accumulation of coarser solid matter in shallow water and finer particles at depth. This process referred to as Focussing, means that a fine- grained solids deposition zone will be formed at the center of the lake.

4. SEDIMENT ENVIRONMENT OF LAKE

The lake sediment environs can be categorized into two components viz.: - Suspended solids and Bottom sediments.

4.1. Suspended Solids

The concentration values of suspended solids in natural waters range from below 1 mg/L for extremely clean waters to over 100 mg/L for highly turbid systems. Some typical values (Chapra, 1997) are given in Table-1. Though the concentrations of suspended solids are expressed on dry weight basis, their dynamics require a more in-depth characterization of their composition.

TABLE I: SUSPENDED SOLID CONCENTRATION ENCOUNTERED IN NATURAL WATERS

<i>Serial Number</i>	<i>System</i>	<i>Suspended solid (mg/L)</i>
1	Great Lakes	
	Superior/Huron	0.5
	Saginaw Bay	8.0
	Western Lake Erie	20.0
2	Flint River, Michigan	8-12
3	Clinton River, Michigan	10-120
4	Hudson River, New York	10-60
5	Potomac Estuary	5-30
6	Sacramento-San Joaquin Delta, California	50-175

Solids in natural waters have two primary origins: the Drainage basin and the photosynthetic process. Particles from these two sources are referred as allochthonous (drainage) and autochthonous (photosynthetic) solids respectively. Allochthonous solids originate from soil erosion and therefore have lower organic content and higher density. Autochthonous solids are generated from plant cells during photosynthesis and hence have high organic content. They tend to have low density. Allochthonous solids tend to cover a wide spectrum of sizes. Although Autochthonous solids also range in size, the principle type of autochthonous solids (unicellular plant cells called phytoplankton) tend to reside at lower end of the sizes.

4.2. Bottom Sediments

Some of the suspended solids are eventually deposited and become part of the water body's bottom sediments. The suspended solids constitute only a minute fraction of the water volume whereas the situation is different in case of bottom sediments. This is because a significant fraction of the sediment volume is solid and such systems are referred as porous medium. This leads to definition of some more parameters. For example the porosity refers to the volume of sediment that is in the liquid and is interconnected (Engelhardt, 1977). This would exclude isolated pore space that is considered as a part of the solid phase, however such isolate pores are rarely found in fine-grained sediments (Berner, 1980). The porosity, θ , is defined as the fraction of the total volume that is in liquid phase as given by;

$$\theta = V_1 / V_2 \quad (6)$$

where V_1 is volume of the liquid part of the sediment layer (m^3) and V_2 is the total volume of the sediment layer (m^3). The fraction of the sediment that is in the solid phase immediately follows as:

$$1-\theta = V_p / V_2 \quad (7)$$

where V_p is the volume of the solid or particulate phase of the sediment. Another quantity that is required in chronology study of the porous media is the in-situ density, ρ (g/cm^3), which can be represented as:

$$\rho = M_2 / V_p \quad (8)$$

Where M_2 is the mass of the solid phase in the sediments (g).

5. SAMPLING AND STORAGE OF SEDIMENTS

The lateral variations in the chemical composition of surface sediments act as a guide to local pollution centers. The qualitative profiles of sediment data along with the course of lake can be used to evaluate the characteristic influences of industrial, municipal and agricultural sources especially when the grain –size effects, which strongly influence the concentration values of metals, are taken into account. On the other hand, the study of vertical profiles from the fine-grained deposits in lakes and impoundment obtained through sediment cores can provide historical events occurring in the watershed of a particular lake and enable a reasonable estimate of background level and changes in input over a period of time. However, this necessitates the determination of sedimentation rate in the particle aquatic system using modern dating techniques (Forstner and Wittman, 1979).

5.1. Sampling

Several devices have been developed and marketed for the sampling of surface sediments, sediment cores and suspended solids. In most cases, the particular apparatus serves only one purpose as discussed below.

5.1.1. *Suspended Solids*

The recovery of suspended material requires method that can estimate concentrations as low as 1 mg/L. Large volumes of water samples are collected in polyethylene containers and filtered through 0.45 μm membrane filter. The Millipore filtration Apparatus is generally used for this purpose.

5.1.2. *Bottom Surface Sediments*

Sampling and storage of soils, rocks and dry sediments present fewer problems than those encountered with water and biological samples (Forstner and Wittman, 1979). In general tools which are either encased in Teflon or made up of polycarbonate are preferred; in all cases the material selected for analyses should be collected from inner part of the sample material which has not been in direct contact with metal of the sampling device. When sampling beneath the water coverage, great care must be exercised to leave the top layers undisturbed.

Sampling of surface sediments depends on the type of sample required. Coarse grained and consolidated material may be recovered by means of a mud grab. This spring loaded device is constructed from non-corrosive material and capable of extracting samples from depth of 15 cm.

The fine-grained bottom sediments are collected with the aid of a sediment grab of the Van Veen type (Figure-1). The catch that keeps the two bowl shaped sections of this Dredger apart is released upon making contact with the bottom sediment; withdrawal leads to a closure of the half-sections and capture about 2 Kg of sediment material with penetration depth of about 20 cm.

The Ekman-Birge grab is more suitable for collecting undisturbed sediment samples. The box is furnished with two flaps, which are spring-loaded and enclose the material upon withdrawal.

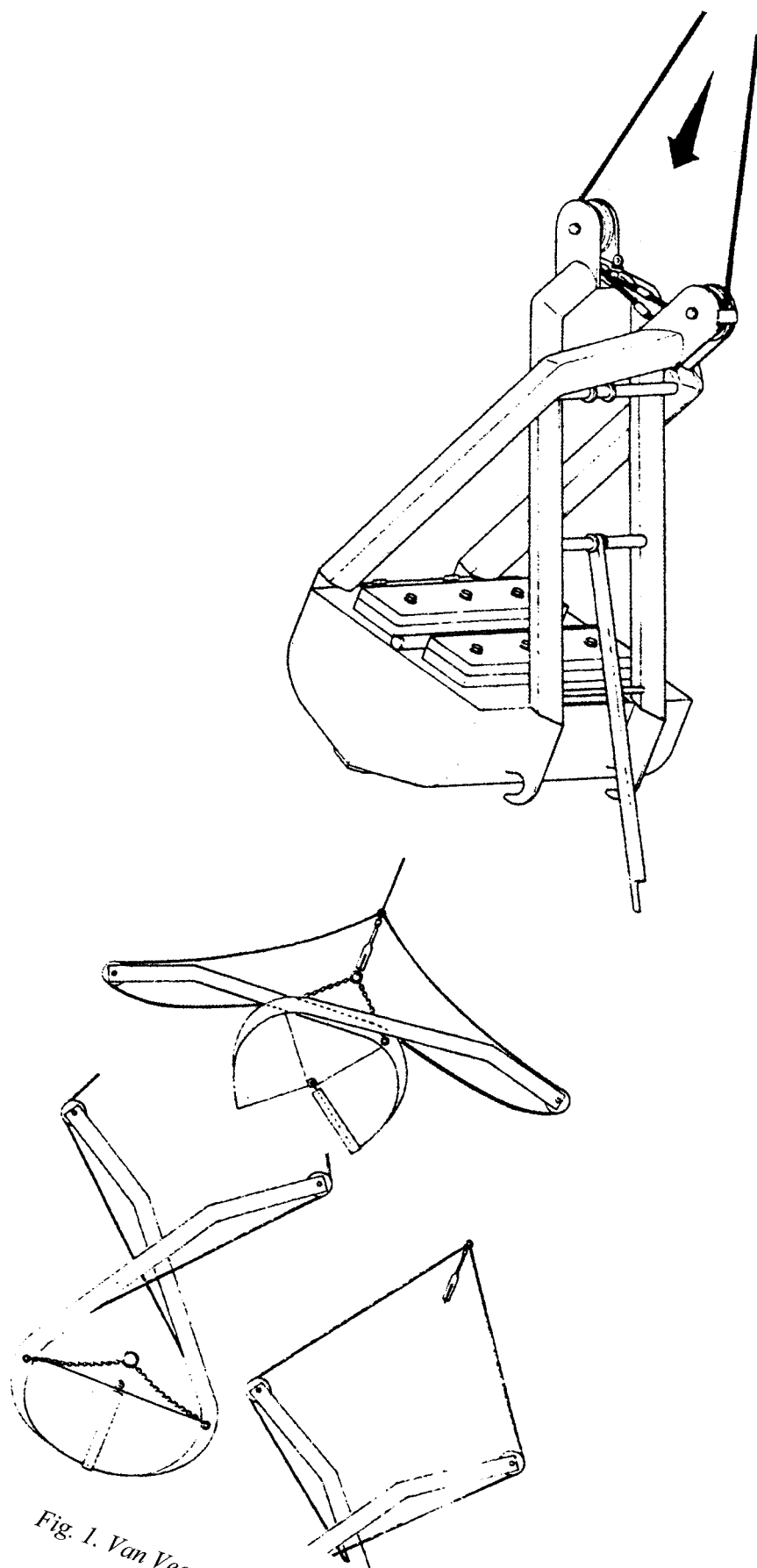


Fig. 1. Van Veen type sampler.

5.1.3. Bottom Core Samples

The need for reconstructing historical development of pollution influence has led widespread sampling sediment cores. Such profiles may cover the last two hundred years of industrial development and in accordance with an average sedimentation rate of 1-5 mm/y applicable for moderately humid climate; the procedure entails sampling core 20 cm to 1-m length. In areas where sedimentation rate is high due to erosion, longer cores are required.

Corers are commercially available and the sampling tubes are made up of Stainless steel AISI 316 as standard; it is also available in shockproof transparent polycarbonate. The tube is driven to the bottom to bring up a core. The tube is driven into the bottom by allowing a heavy weight to drop automatically upon the head of the tube when its foot touches the bottom. Adjustable piston rod with silicone packing accessory is used to dislodge slowly the core sample from the tube.

Gravity corers are used particularly in the study of sediment structure and evaluation of paleoclimatic changes for which cores of 2-3 m length are required. Box corer is used when undisturbed cores with large cross sections are required. The cores collected with these set up may not be of use for pollution tracing studies.

5.2. Sample Storage

Storage of samples obtained after sampling procedure may have several purposes. First, the sample may have to be kept awaiting sample preparation and the following analytical steps, if they cannot be performed immediately after sampling. This is important in long term investigation when it is desired to analyze all the samples in one series. Second, it may be necessary to prepare and store duplicate samples (identically prepared aliquots): one of which remains with the user of analytical data for independent cross checking at a later time if necessary. Analytical reference materials are also produced in large quantities and have to be stored for years (IAEA, 1983). A last argument for long-term storage is the conservation of ecological, environmental and biological samples as specimen banks for use in future (Sansoni and Iyengar, 1980).

The goal of any storage technique is the maintenance of sample integrity. Consideration of container materials is necessary regarding adsorption from solution on the walls, leaching from the walls, loss through volatilization, degradation through photochemical or biological activity, and other factors. Many type of containers made from relatively inert materials like quartz, Teflon, polyethylene, hardglass and so forth have both attractive and undesirable attributes.

An overriding consideration may be duration of storage and the requirement for short term and long term storage differ distinctly (IAEA, 1983). The storage of solid material is subjected to stringent conditions. Usually air drying should not have much effect on the trace element content, but if the speciation and organic extractable trace elements are of interest, any procedure of drying may lessen the validity of sample analysis (Maienthal and Becker, 1976). For instance, air drying of sample markedly affects cation exchange capacity and iron speciation. Preservation of grab sediments at 4°C is a good short term storage method for the use of materials in laboratory experiments such as sorption studies while deep freezing is needed for long term storage of geochemical and biological samples. In the opinion of many authors, freezing at -20° and -30°C is the best method for long term storage.

6. SAMPLE PREPARATION

Pretreatment of the samples, i.e., preparation of samples ready for analysis is a crucial step for representing the data. The contamination of the sample could occur during sampling operation, through operating personnel and sample preparation. During sampling operation contamination may arise from dust and volatile contaminants in the air. The sampling tool can contribute to a marked degree. Numerous possibilities exist for the contamination of samples from operating personnel. Sansoni and Iyengar (1980) have summarized the types of contamination, which may occur in a laboratory environment

The preparation of sample for radio nuclide and trace element analysis involves homogenization of bulk material, which include fragmentation and powdering. The problems due to homogenization require special attention while analyzing bulk sample. Samples prepared from homogeneous samples of small particle sizes are expected to be representative of the original sample. However, the disadvantage of pretreatment is the possible contamination. The homogenization of the bulk sample is usually carried out in a microdismembrator comprising of a Teflon vessel in which the sample is vibrated rapidly together with a Teflon-covered metal ball, at liquid temperature. Other suitable materials for grinders and homogenizes include ultrapure quartz, polymethylmethacrylate and high purity titanium.

6.1. Targets for XRF analysis

Solid samples may be analyzed as, or may be reduced to slices, powders or solutions. If the sample is analyzed in as-received state, the analysis is usually rapid and convenient. Kivits (1980) has demonstrated usefulness of thin targets ($< 1 \text{ mg/cm}^2$) with slice samples (especially to study depth-wise profile). Any surface treatment may result in unwanted contamination and/or in selective removal of certain constituents. The use of cutting tool across the surface causes smearing of soft constituents and in spectral enhancement.

6.1.1. Thin Targets

The thin targets for powdered samples may be prepared by spreading into thin layers (Kivits, 1980), dry or as slurries. In the dry technique, the sample powder is spread onto an adhesive surface (e.g., scotch tape) or can be spread out over a support, adding fixative later. Sometimes a measured amount of sample powder is placed on a Mylar film and distributed as uniformly as possible. A second Mylar film is then stretched over the sample powder and the first film, thus enclosing the sample layer (Rinsvelt, 1977). Brady and Cahill (1973) have used static charge for holding thin layer of powder onto Mylar and Mylar onto adhesive coating. In practice, it is very difficult to obtain a uniform thin layer of the sample using dry technique (IAEA, 1983).

In the slurry technique, a small amount of sample powder and binding material is slurried in an appropriate solvent. The slurry is spread over a microscopic slide. Some of the suggested solvents are amylacetate, chloroform and Dioxane. The recommended binding materials include nitrocellulose, ethyl-cellulose and polystyrene. Both these dry and slurry techniques could introduce sources of analytical errors such as contamination and loss of elements.

Alternatively small amount of sample powder is temporarily formed into a turbulent suspension succeeded by rapid filtration onto a Millipore type filter to obtain uniform thin

targets. The target is then coated with acrylic spray after determining mass of the deposition. Kivits (1980) employed the following steps for the preparation of thin targets:

A solution is prepared consisting of 5 gm Formvar in 100 ml Dioxane. The powdered sample is mixed with this solution (10% sample weight fraction) with the aid of whirlmixer. A selection filter is rotated at 3000 RPM and saturated with 0.5-ml water and 0.2 ml of sample-Formvar-Dioxane mixer is immediately dispensed on the wetted rotating filter. The resulting Formvar foil is pulled from the Selection filter and alpha particle absorption method is used for estimating area density ($< 1 \text{ mg/cm}^2$). This method of thin target preparation had a failure rate of only 10%.

6.1.2. Thick Targets

Small amount of sample coupled with low concentrations of the elements of interest limits the sensitivity of thin targets. The thick target technique involves use of about 500 mg of homogeneous sample powder obtained via grinding or lyophilization coupled with grinding. This powder is then spread onto a dye (about 3-cm diameter) and pressed into a pallet with a 20-ton hydraulic press. A cellulose binder must be mixed with the sample prior to pallet formation. The disadvantage of this technique lies with self-absorption of such thick targets, which are hardly optimum for light elements. The increase of sample size has resulted in better precision and sensitivity by increasing the X-ray intensities from the trace elements. Though the use of binder may be useful for making good uniform pallets, excess use of binder will dilute the sample size and hence it is necessary to establish an optimum ratio of sample to binder (Table-2). In general, sample to binder ratio of 1:1 is found to be useful. The commonly used binder materials are either Methylcellulose or Chromatographic cellulose (which consists of 72% Methylcellulose with 28% paraffin base powder).

TABLE II: EFFECTIVENESS OF BINDER AND BACKING MATERIALS*

<i>Sample to binder ratio</i>	<i>Binder</i>	<i>Backing</i>	<i>Results</i>
100 :0	-	Methyl cellulose	Sample does not adhere to backing; pallet surface cracks
95:5	Chromatographic cellulose	Methyl cellulose	Sample does not adhere or adheres poorly to the backing
85:15	Chromatographic	Mixture A*	Homogeneous surface, sample adheres rigidly to the backing
75:25	Chromatographic	Methyl cellulose	Homogeneous surface, sample adheres rigidly to the backing

* IAEA TECDOC-300

6.2. Targets for INAA Analysis

A known amount of homogenized sample powder is packed in polythene envelopes with a 2 mg of Cu or Co foil as a flux monitor. The sample is irradiated for 7 hours in a Swimming Pool Research Reactor, APSARA in neutron flux of $10^{12} \text{ n. cm}^{-2} \text{ s}^{-1}$. Suitable standards of similar matrix as the samples are also irradiated along with the samples for quantification of elements.

7. MEASUREMENT PROCEDURES

7.1. EDXRF Analysis

X-ray fluorescence method consists of exciting samples by either photons or charged particles and measuring the intensities as fluoresced X-rays. The fluoresced x-rays were measured by Wavelength Dispersive Spectrometer till the advent of high-energy resolution Si (Li) detectors. The Si (Li) detectors have made possible simultaneous measurement of fluoresced x-rays from a number of elements in the sample

In XRF analysis samples can be excited by photons either from radioisotopes or from the X-ray tube. For trace element analysis of environmental samples, photon excitation has been demonstrated to be more practical and advantageous than the particle excitation. K x-rays are generally measured to estimate light elements (atomic number <55) and L x-rays for heavy elements. This entails X-ray measurement in the range of 1-30 KeV, which is also useful energy range for Si (Li) detectors. The excitation efficiency and detector sensitivity for any element is dependent on excitation energy. It is however, not feasible to have a range of excitation energies to obtain maximum detector sensitivity for each element. Therefore, excitation energy that provides reasonable sensitivity for a range of elements is adopted in the study. In X-ray tube source, it is possible to vary the energy by using different secondary targets. Monochromatic sources are preferred in XRF analysis so that the scatter of the background in the fluoresced x-ray region is minimum.

Convenient radioisotopes for use as primary radiation sources are ^{55}Fe , ^{125}I , ^{109}Cd and ^{241}Am . Of these ^{241}Am is used in secondary fluorescence mode which would give varying target x-rays. Some of the commonly used excitation sources and the range of elements, for which the sensitivity is high, are given in Table-3.

TABLE III: SOME OF THE EXCITATION SOURCES USED IN EDXRF ANALYSIS

<i>Serial Number</i>	<i>Source</i>	<i>half-life (years)</i>	<i>Useful radiation emitted (keV)</i>	<i>Range of application (atomic number)</i>
1	Fe-55	2.70	5.9 (Mn K x-rays)	9-30
2	Co-57	0.74	γ (122.1, 136.4)	70-94
3	Pu-238	86.4	12-22 (U L x-rays)	23-38/56-82
4	Cd-109	1.3	22.1, 25.1 (Ag K x-rays)	23-46/68-94
5	I-125	0.16	27.2 - 31.7 (Te K x-rays)	33-51/73-94
6	Am-241	458	59.5 (γ) and with secondary targets	28-69
7	X-ray targets* Cu, Mo, Rh, Sn, Dy	-	8.4-46**	14-51

The target samples were irradiated by ^{55}Fe radioactive source for the estimation of Si, S, Cl, K, Ca, Ti and V. The elements like Fe, Cu, Ni, Zn, Se, Rb, Sr and Pb were measured using a low power X-ray tube with Mo secondary fluorescer. The measurement times were 3000 seconds and 2000 seconds for source irradiation and tube irradiation respectively. The statistical errors for EDXRF analysis of samples for most elements vary from 5 to 15 % except for Al and Si wherein the errors can be as high as 20%

7.2. Instrumental Neutron Activation Analysis

The Instrumental Neutron activation Analysis is based on the fact that irradiation of a stable element in a target sample with a high flux of neutrons for a period of time produces radioactive isotope which can be measured using radioactive measuring systems. Nuclear reactors have provision for irradiating the samples for activation. The compound radioactivity formed can be measured immediately or after a certain period of time called the Cooling Period. The radioactive isotope is characterized by two important parameters viz., the Energy emitted by the radioactive product while decaying and the Half-life of the product. Mostly gamma rays emitted by the activation product are measured in radiation monitoring systems.

The samples are encased in waterproof polythene envelopes along with standard reference materials in APSARA Reactor for about 7 hours. The irradiated samples are counted in a Gamma spectrometer with HPGe detector coupled to 8K channel Analyzer. The samples are counted after two different cooling times for the analysis of short/medium and long –lived isotopes. The list of elements/isotopes measured at these times is given in Table-4. The detection limits for various elements are given in Table-5 for a typical aerosol sample collected on a 5-cm diameter Whatmann 541 with a collection volume of 12 m³.

TABLE IV: INAA- NUCLEAR DATA FOR ELEMENTS MEASURED AFTER DIFFERENT COOLING PERIODS

<i>Element</i>	<i>Isotope</i>	<i>Half-life</i>	<i>γenergies used (keV)</i>
Short lived isotopes (after 5 days cooling)			
As	As-76	26.3 h	559.1, 657.0
Br	Br-82	35.3 h	554.3, 776.5
K	K-42	12.36 h	1524.7
La	La-140	40.23 h	328.8, 487.0, 1596.2
Na	Na-24	15.02 h	1368.4, 2754.1
Sb	Sb-122	67.20 h	564.0
Sm	Sm-153	46.70 h	103.2
Long-lived isotopes (after one month cooling)			
Ce	Ce-141	33.0 d	145.4
Cr	Cr-51	27.7 d	320.0
Co	Co-60	5.3 y	1173.2, 1332.4
Eu	Eu-152	13.6 y	1408.0
Fe	Fe-59	44.6 d	1098.2, 1291.6
Hf	Hf-181	42.4 d	482.2
Hg	Hg-203	46.6 d	279.2
Sb	Sb-124	60.2 d	603.0, 1691.0
Sc	Sc-46	83.8 d	889.3, 1120.5
Se	Se-75	118.5 d	136.0, 264.7
Ta	Ta-182	115.0 d	1221.4
Tb	Tb-160	72.4 d	879.4
Th	Pa-232	27.0 d	311.9
Yb	Yb-175	4.2 d	396.3
Zn	Zn-65	243.8 d	1115.5

TABLE V: DETECTION LIMITS FOR VARIOUS ELEMENTS IN FILTER DUST SAMPLES USING INAA AND EDXRF TECHNIQUES

<i>Minimum Detection limit</i>		<i>Minimum Detection limit</i>	
<i>Element</i>	<i>INAA (ng/m³)</i>	<i>Element</i>	<i>EDXRF (μg/m³)</i>
As	0.38	Ca	0.28
Co	0.21	Cl	0.45
Cr	2.00	Cu	0.03
Fe	100.0	Fe	0.56
K	0.42	K	0.05
La	0.09	Pb	0.05
Eu	0.01	Rb	0.84
Zn	20.00	Zn	0.10
Mn	0.11	Se	0.05
Na	2.78	S	0.32
Sc	0.01	Si	2.44
Ce	0.01	Sr	0.07
Ti	0.11	V	0.04
Hf	0.01	Ni	0.15

For INAA: Neutron flux 10^{12} n. Cm⁻² .s⁻¹ ; Whatmann-541 5 Cm. Diameter; Volume 12 m3

7.3. Measurement of ²¹⁰Pb in sediment samples

The methods employed for the determination of ²¹⁰Pb can be divided into two categorized: one deals with measurement of total ²¹⁰Pb/ ²²⁶Ra dealing with low energy gamma spectrometry or total sample dissolution and ²¹⁰Pb and ²²⁶Ra radiochemical determinations and the other utilizes leaching procedures for either ²¹⁰Pb or ²¹⁰Po followed with deposition of ²¹⁰Po on a silver disc from 0.5M HCl medium. The ²¹⁰Pb standard solutions are obtained by gravimetric dilution of a 3.7×10^4 Bq.g⁻¹ Amersham ²¹⁰Pb standard solution. Marine sediment reference samples from IAEA, IAEA-135 and IAEA-368, were analyzed to validate the method. Godoy et al (1998) proposed leaching of 5-g dry sediment sample with 100 ml 0.5 M HBr and 1 g hydroxylamine hydrochloride. An ion-exchange separation with Dowex 1x8, 50-100 mesh, Br⁻ form is followed. Lead is eluted with 1 M HNO₃ and precipitated as PbCrO₄. The chemical yield is determined by gravimetric technique and 10 days later the ²¹⁰Pb content is obtained through the beta counting of ²¹⁰Bi that is developed. A low background gas-flow proportional counter was used for measurement of ²¹⁰Bi. The efficiency of beta counting was about 30% with a detector background of 0.2 cpm. This proposed method was applied to sediment cores from Guanabara Bay, from the Amazon River estuary and from the Infernao lagoon, a part of the Mogi-Guacu River flood area. Many authors (Jha et al, 1999; Carpenter et al., 1981, 1982) followed the HCl leaching procedure for the sediment and the determination of ²¹⁰Pb content is based on the alpha measurement of its granddaughter ²¹⁰Po activity that is assumed to be in secular equilibrium with its parent. The basic radiochemical procedure involves adding of ²⁰⁸Po as a yield tracer, leaching the sediment samples with aqua regia, the residual solids are filtered off and the solution is dried and converted to chloride form with concentrated HCl. The final solution is taken in 0.5M HCl. Polonium nuclides are then spontaneously deposited on silver planchette by adding ascorbic acid prior to alpha counting in a Si Surface barrier detector coupled to multi channel analyzer. This method is used for the determination of ²¹⁰Pb in the estuarine and Lake Sediment cores (Jha et al, 1999; Saravana Kumar et al; 1999).

7.4. Measurement ^{137}Cs in sediments

The ^{137}Cs activity in each section of the core is determined by gamma counting of the oven dried samples using HPGe detector coupled to Multi Channel Analyzer. A ^{137}Cs standard, having essentially same geometry and density is used for obtaining efficiency of measurement system. The samples were counted for about 500 minutes to obtain statistical accuracy. The detection limit for ^{137}Cs by this method is about 0.25 mBq. g^{-1} and the standard counting error are less than 10% in the core sections.

8. STUDY AT NAINI LAKE: A CASE STUDY

8.1. About the Study Area

Crescent shaped Lake Naini is tectonically formed sub-tropical and eutrophic Lake situated at an altitude of about 1937 m and above mean sea level (Latitude $29^{\circ}24'$ N and Longitude $79^{\circ}23'$ E) in the Nainital district of Kumaun Himalayas. The lake divisible into a Mallital (Northwest) basin and Tallital (Southwest) basin due to the presence of a submerged transverse ridge running east-west about 8 m below the Lake surface. The northwestern part is made up exclusively argillaceous limestone and marlites whereas the southwestern part comprises of dolomite with limestone and black carbonaceous slates (Valdia, 1988). Maximum and average depth of the lake is 27.3 m and 18.5 m respectively. Surface area and volume of the lake are $465,000 \text{ m}^2$ and 8.5 Mm^3 respectively. . The catchment area of the lake is about 4.9 Km^2 . The lake, in addition to being a picnic spot, is the only drinking water source to the Himalayan City.

The annual rainfall in the catchment of the lake Naini ranges from 2200 and 2500 mm. The monthly maximum rainfall is about 630 mm in August and minimum is about 3 mm in March. Besides rainfall, there are occasional snowfalls in and around the lake basin during winter varying between 20 and 60 mm in recent years.

8.2. Sampling and Analytical Techniques

Core samples were collected at different locations in the lake using bottom corer, its inner and outer diameter being 5.2 and 6.0 cm respectively. Most of the sampling stations are from the eastern side of the lake since a large number of gullies loaded with considerable amount of sediments join the lake basin at those stations. The length of the core ranged from 15-60 cm. With the help of an adjustable piston rod with silicone packing, the obtained cores were extruded vertically and sliced at 2-cm intervals.

An aliquot (2-5 g) of the sliced core were used for measuring physical characteristics of the sample including bulk density, water content, porosity and remaining part of the sliced core sections were freeze dried and stored in laboratory for radionuclide measurements (^{137}Cs and ^{210}Pb). The clay mineral assemblage of this lake mainly consists of montmorillonite, illite, kaolinite and chlorite besides the mixed layer mineral, which are typical of high altitude clays (Jauhari and Hashmi, 1994).

8.3. ^{210}Pb profile in sediment cores:

A few selected core samples collected from locations V and S (in Tallital basin) and Q in Mallital basin) in the lake were analyzed for ^{210}Pb (Figure-2) and ^{137}Cs (Figure-3). The

available porosity and water content profiles are shown in Figures 4 and 5. The depth profiles of total ^{210}Pb in the core collected at location V showed an approximate exponential decrease in concentration with depth to a constant value maintained by in situ decay of ^{226}Ra . At other locations, the total ^{210}Pb concentration profiles do not approximate to an exponential (i.e., non-monotonic type). Accompanying measurements of ^{137}Cs indicate that the top portions of the sediment deposit were not lost during coring. The mean global atmospheric ^{210}Pb fall-out is about $0.0165 \text{ Bq. cm}^{-2} \cdot \text{y}^{-1}$. (Krishnaswami and Lal, 1978) and therefore the mean atmospheric inventory should be about 0.53 Bq. cm^{-2} . In Lake Naini, the mean total ^{210}Pb inventories in surface sediments of the core is slightly higher than the global mean (i.e., about 0.96 Bq. cm^{-2}). (Table-6)

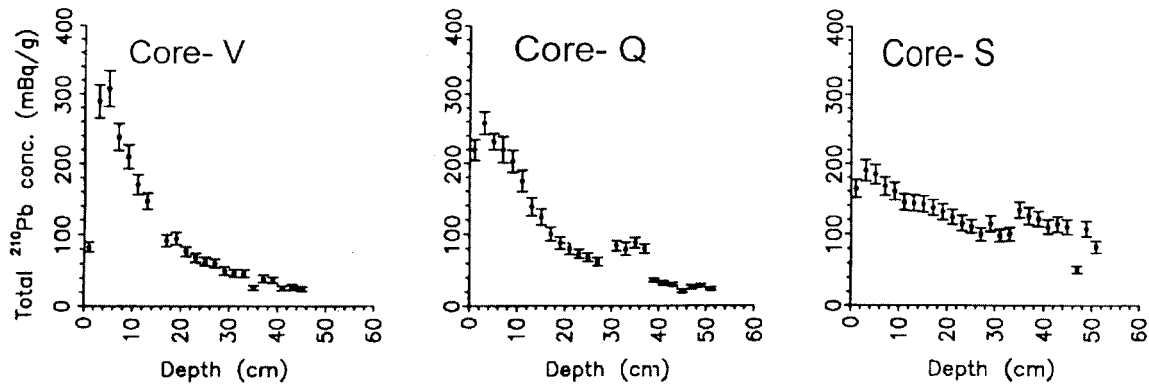


Fig. 2. ^{210}Pb profiles in sediments from Lake Naini.

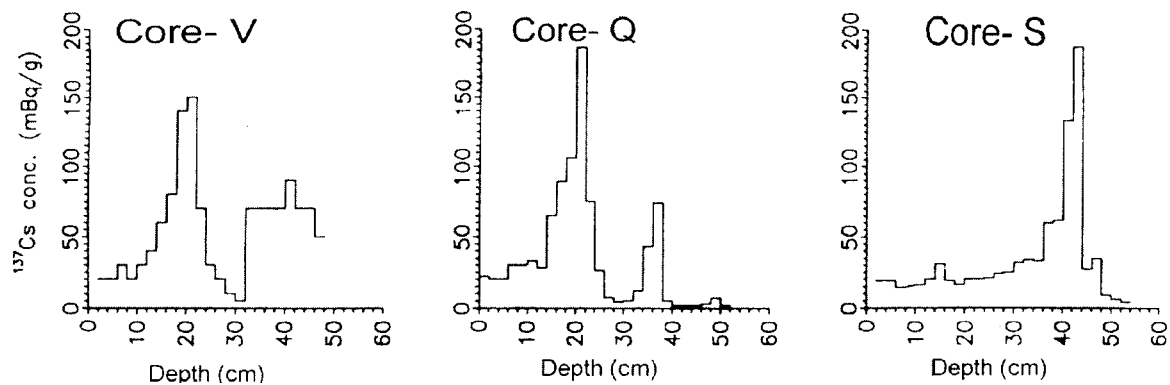


Fig. 3. ^{137}Cs profiles in sediments from Lake Naini.

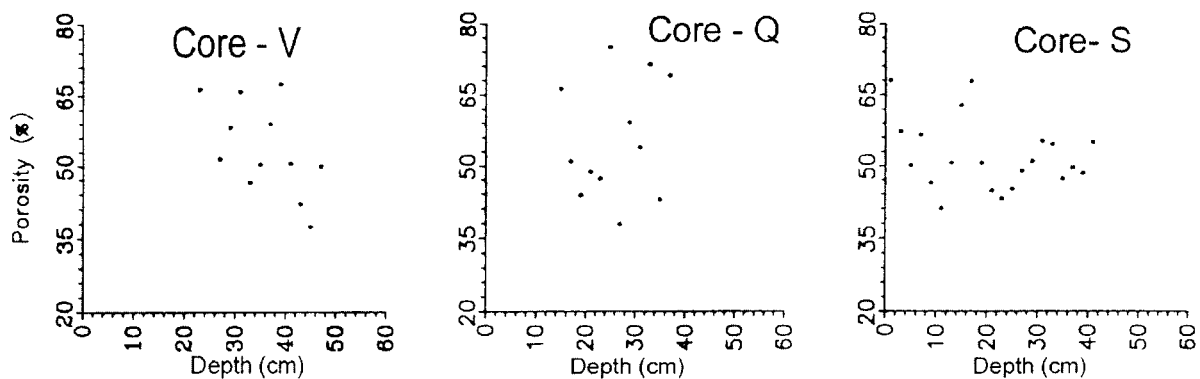


Fig. 4. Sediment porosity from Lake Naini.

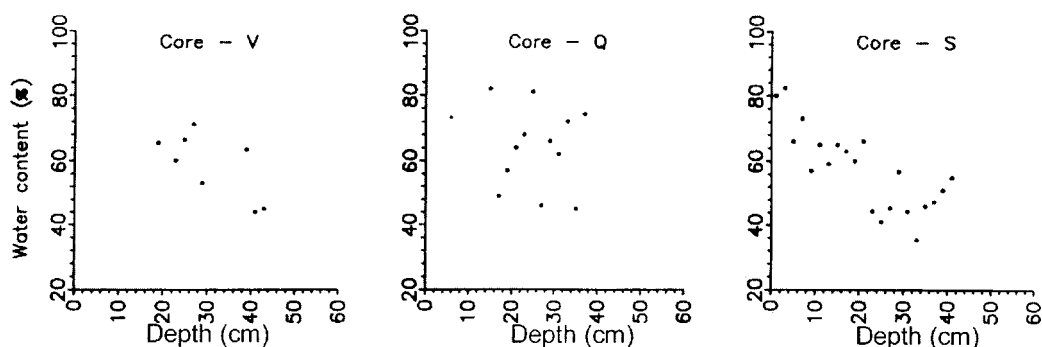


Fig. 5. Water content in sediments from Lake Naini.

TABLE VI: SEDIMENTATION RATES AND INVENTORIES OF ^{210}Pb AND ^{137}Cs IN LAKE NAINI

		Average sedimentation rate			
		Pb-210		Cs-137	
Sampling Station (water depth in m)	Model used	Linear sedimentation rate (Cm/y)	Mass sedimentation rate (g/Cm ² /y)	Linear sedimentation rate (Cm/y)	Mass sedimentation rate (g/Cm ² /y)
V (24)	CFCS	0.48 ± 0.40	0.112 ± 0.010	0.60 ± 0.07	0.140 ± 0.016
Q (20)	CF	0.64 ± 0.18	0.150 ± 0.041	0.70 ± 0.03	0.168 ± 0.007
S (20)	CF	1.24 ± 0.44	0.289 ± 0.104	1.35 ± 0.05	0.315 ± 0.018

As mentioned earlier, the three different models viz., CFCS, CF and CIC are being widely used for dating thorough ^{210}Pb measurements, however none of these models are universally acceptable (Robbins and Edgington, 1975; Eakins, 1983). In practice, the type of model to be used is usually decided on the depthwise distribution of ^{210}Pb concentration (Crickmore et al, 1990). The estimated sediment accumulation rates in Lake Naini using ^{210}Pb dating technique (both linear and mass units), along with the ^{210}Pb models used are given in Table-6.

8.4. ^{137}Cs profile in sediment cores:

The ^{137}Cs profile at sampling station Q in the lake (Figure-3) closely parallel its weapon fall-out record pattern reported by earlier investigators (McHenry et al., 1973; Livingston and Camnray, 1978) revealing initial appearance in 1952-53, a subsidiary peak in 1957-58 and a major peak in 1963-64. Using depths recorded in 1963-64 as the datum levels, the average sedimentation rate (both linear and mass units) of Lake Naini has been computed and listed in Table-6.

The close similarity between deposition and fall-out pattern of ^{137}Cs probably indicates that the residence time of ^{137}Cs in the lake water is small and post depositional mobility of the radionuclide in the sediment core, if any, is insignificant. However, the ^{137}Cs profile of Lake Naini must still be viewed as an ideal case, as there have been many studies in which ^{137}Cs profile in a lake sediment does not closely match that associated with the fall-out record mainly due to post-depositional mobility of ^{137}Cs resulting from bioturbation (Sholkovitz and Mann, 1984), molecular diffusion (Davis et al., 1984), sediment focusing i.e. resuspension of deposited sediments in shallower zones by waves and water currents with subsequent transport to and settling in deeper zones (Brunskill et al., 1984; Balis and Kaiff, 1995), higher residence time of ^{137}Cs in lake waters (Edgington et al., 1991) and influence of delayed input of radiocaesium from drainage basin of a lake (Miler and heitt, 1986).

TABLE VII: QUALITY ASSURANCE OF THE MEASUREMENT TECHNIQUES

<i>Serial Number</i>	<i>Nuclide</i>	<i>Standard Material</i>	<i>Reference</i>	<i>Standard Material value (Bq/kg)</i>	<i>Our Measured value (Bq/kg)</i>
1	Cs-137	IAEA soil-375		5281 ± 80	5174 ± 100
2	Cs-137	QAP USDOE soil		810 ± 40	786 ± 3
3	Cs-137	IAEA soil-327		25.1 ± 2.1	30.4 ± 0.6
4	Ra-226	IAEA soil-327		35.2 ± 12	21.5 ± 1.2
5	Pb-210	IAEA-135 sediment	Marine	48.0 (acceptance range 42.2 – 54.1)	44.8 ± 3.5

TABLE VIII: TRACE ELEMENT DEPTH-WISE DISTRIBUTION IN LAKE NAINI

<i>Concentration of element (µg/g)</i>					
<i>Station</i>	<i>Depth (Cm)</i>	<i>Cadmium</i>	<i>Lead</i>	<i>Copper</i>	<i>Zinc</i>
Station V	0 - 2	0.22	77.6	40.9	140.8
	2 - 4	0.31	95.1	48.2	156.8
	4 - 6	0.23	66.6	47.0	137.9
	6 - 8	0.54	71.9	41.2	147.8
	8 - 10	0.17	81.2	39.6	168.1
	10-12	0.23	84.9	46.8	175.0
	12-14	0.28	93.2	56.6	199.3
	14-16	0.32	77.7	40.4	225.8
	16-18	0.26	69.2	45.0	247.9
	16-18	0.29	75.1	47.6	250.4
	18-20	0.30	71.8	46.3	234.4
	20-22	0.42	78.5	50.4	266.3

Due to short lengths of the cores obtained and/due to higher sedimentation rates (Table-6), the initiation and subsidiary peaks of 1952-53 and 1957-58 are not clearly seen in core samples V and S respectively (Figure-3).

8.5. Quality assurance of measurements

The reliability of results is a function of precision (reproducibility) and of accuracy. The precision of results can easily be determined by internal measurements. The determination of accuracy, however, requires more detailed procedures. This includes alternatives such as analysis through as many different methods, analysts and instruments as possible; control analysis with standard reference materials (i.e., materials similar in composition to the materials to be analyzed) and participation in inter laboratory comparison exercises. The radiochemical measurement technique for ^{210}Pb and ^{137}Cs are validated through the use of different Standard Reference Materials (SRM) as shown in Table-7. In their absence, independent analytical techniques should be used on a subset of samples in order to obtain a measurement of accuracy. A number of institutions and agencies are involved in manufacturing, testing and distributing of SRM. In Europe, a number of Standard Reference Materials can be obtained from the Analytical Quality Control Services (AQCS) provided by International Atomic Energy Agency (IAEA). The depth-wise distribution of some typical trace elements (Pb, Cd, Cu and Zn) in a particular station V is shown in Table-8.

8.6. Residence time of ^{210}Pb in lake water

If ϕ_w and ϕ_s are the fluxes ($\text{Bq. Cm}^{-2} \cdot \text{y}^{-1}$) of ^{210}Pb in the lake water and sediments respectively, and their corresponding inventories I_w and I_s (Bq. Cm^{-2}), then the residence time of radiolead in water can be derived using the first order kinetic relation as shown below:

$$dI_w/dt = \phi_w - \{ [\lambda_{\text{Pb}} + (1/T_w)] I_w \} \quad (9)$$

$$dI_s/dt = \phi_s - \{ [\lambda_{\text{Pb}} + (1/T_s)] I_s \} \quad (10)$$

Where λ_{Pb} is the radioactive decay constant, T_w and T_s are the residence times of ^{210}Pb in the Lake Water and Lake Sediments respectively. At steady state, the inventory of unsupported ^{210}Pb in the lake water, I_w is the difference between atmospherically supported inventory, I_{atm} ($0.802 \text{ Bq. Cm}^{-2}$), and the mean sedimentary unsupported ^{210}Pb inventory of the lake, I_s ($0.798 \text{ Bq. Cm}^{-2}$). Thus the relationship for the derivation of residence time of ^{210}Pb in Lake Water, T_w , can be obtained from the above equations as :

$$T_w \approx \{ (I_a - I_s) / (\lambda_{\text{Pb}} I_s) \} \quad (11)$$

since $\lambda_{\text{Pb}} \ll 1/T_w$, $\lambda_{\text{Pb}} \gg 1/T_s$ and $I_w = I_a - I_s$. The residence time of ^{210}Pb in the lake water calculated from equation-5 is about 2 months.

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OPTIMIZING THE QUALITY OF SEDIMENT SAMPLES COLLECTED FOR GEOCHEMICAL MEASUREMENTS IN COASTAL MARINE ENVIRONMENTS

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Abstract. The quality of sediment samples can be improved by choosing sampling locations and sampling tools that meet the carefully considered goals of the geochemical project. Design of the sampling location plan is aided by using remote surveying techniques, such as sidescan sonar, high-resolution swath bathymetry, acoustic backscatter, and seismic reflection. Information from these techniques can be used to map sediment types on the sea floor and to infer transport processes for sediment and associated contaminants. Several innovative devices have been designed to collect high-quality sediment samples without disturbance or loss of material from the water-sediment interface. These devices include a hydraulically damped gravity/piston corer and a freeze corer that provide an intact surface and a recovered core up to 1 meter long. Devices have been designed for use by SCUBA divers or from a manned submarine to collect near-bottom flocculent material that is known to be mobile in strong bottom currents. Clam-shell type grab samplers are used to take large volumes of material from the upper 20 cm of sediment. A video camera can be attached to any of these bottom sampling devices to further enhance the efficiency of collection and sample quality by providing real-time information about sediment type or local anomalies on the sea floor. The sea-going platform for collecting bottom samples can be complex or simple. The U.S. Geological Survey HoverProbe consists of a coring platform built on a 21-foot hover craft that can travel over very shallow water or marsh grass. A simpler platform can be made of floats with a tripod mounted over a central moon pool for deploying sampling equipment. A key component to assure sample quality on any platform is precise navigation provided by the Differential Global Positioning System.

1. INTRODUCTION

Many dissolved contaminants introduced to coastal waters are quickly bound to suspended and bottom sediments. Consequently, processes affecting these sediments influence the transport pathways, chemical interactions, biological availability and ultimate deposition of contaminants. Knowledge of the distribution of contaminants in bottom sediments in space and time and the processes which control their mobility is critical for understanding environmental threats as they presently exist and for predicting the outcome of management plans for remediation. Degraded environmental conditions, contaminated fish and shellfish, and threats to human health are commonly associated with contaminated sediments near coastal population centers throughout the world. Contaminated sediments have also impacted the economic viability of major shipping ports. In New York and Boston Harbors, for example, dredging for larger ships has been slowed because dredged bottom sediments are too toxic to safely discharge in other marine areas, and alternative forms of disposal remain prohibitively expensive.

This review focuses on a number of tools and a multi-disciplinary survey approach that improves both the quality of sediment samples collected for geochemical analysis and the scientific value of the results. A few examples of results will be taken from our on-going environmental studies in Boston Harbor and Massachusetts Bay where modern tools and

sample-handling procedures have been developed to meet specific scientific needs. The quality of results from any sampling programme depends not only on the tools but also on the ancillary information gathered. Ideally, a sediment sampling programme should be multi-disciplinary and take advantage of recent developments in other fields of marine science. Advances in mapping techniques using swath bathymetry and sidescan sonar now permit rapid identification of bottom types over hundreds of square kilometers per day. A comprehensive analysis programme should also be undertaken, which supplements the primary chemical analysis with data on the physical, and biological parameters of the sediment. This multi-disciplinary approach aids the interpretation and expands the utility of results.

2. SAMPLING STRATEGY

2.1. Selecting Sampling Sites

Maps of the sea floor geology are a significant aid in the design of a bottom sediment sampling programme in any new area for geochemical study. Sidescan sonar, seismic reflection and swath bathymetry techniques (Fig. 1, Butman, 1998, Schwab and others, 1999) have been used to provide continuous coverage of the seafloor. The resulting synthesis maps in Massachusetts Bay and on the Continental Shelf off New York can identify the location and extent of fine-grained deposits where contaminants are likely to accumulate and areas of coarse-grained sediments or outcropping bedrock where erosion is common (Knebel and others 1995). Such maps are critical in designing an efficient sampling programme. Sampling sites can be selected with fewer samples representing larger areas, thus reducing the ship time, number of samples, analyses, and the overall project costs. Knowing locations of coarse sediments or bedrock prevents unproductive sampling efforts in areas where the risk of damage to sampling equipment is high.

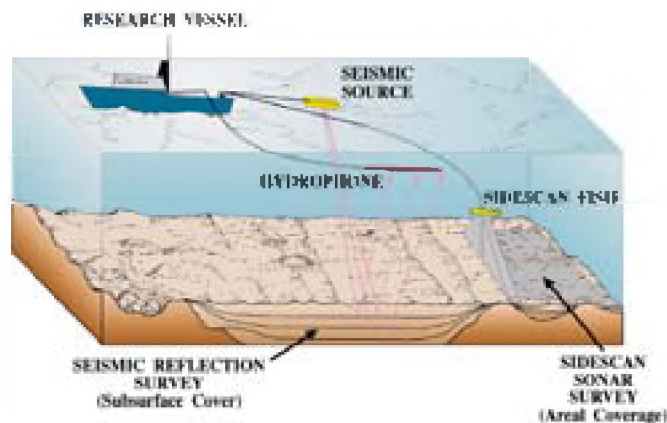


Figure 1. The sea floor is remotely mapped by sidescan sonar and high-resolution seismic reflection profiling. These systems use the strength of reflected sound to characterize the sea floor and sediments below it.

On a much smaller spatial scale, bottom video and photography have been a tremendous aid in characterizing the sea floor prior to sampling. Video cameras on the sampling tools make it possible to view and select the specific sampling site and to assess disturbance and other measures of quality as the sample is being collected.

2.2. Navigation

The differential global positioning system (DGPS), can provide precision to within 3 meters. This system can be a significant aid in long-term studies where repeated sampling is conducted at the same location or in sampling specific targets identified by general surveying tools. For example, sampling near barrels of industrial and/or radioactive wastes in Massachusetts Bay (Lindsay, 1996; Wiley, 1992) found by sidescan sonar techniques has been possible because of the precision of DGPS navigation.

3. COLLECTING UNDISTURBED SEDIMENT

A common objective of geochemical research in marine sediments is to interpret contaminant concentration profiles in sediment cores in order to estimate sedimentation rate, history of contaminant inputs, and contaminant inventories. The contaminant concentrations in surface samples are of special importance because they may reflect the most recent contaminant fluxes and may provide insight into the bio-geochemical or physical processes that are occurring at the water-sediment interface. When considering sampler design, it is essential that a sampler collect a core with minimal disturbance of both the water-sediment interface and the subsurface strata. Further design criteria include successful operation in both sandy and muddy sediments. The USGS has developed a hydraulically damped gravity/piston corer with these concerns in mind in order to collect undisturbed cores in sandy sediments of the continental shelf as well as in muddy sediments in estuaries or the deep sea. A video camera system is often attached to the coring frame in water depths shallower than 150 m.

3.1. The USGS hydraulically-damped gravity/piston corer (HDC)

This instrument (Fig. 2) consists of a four-legged frame with a central sliding shaft that holds a 318 kg weight stand and a clear polycarbonate core barrel (1 m long and 10.7 cm id). The apparatus is constructed of aluminum, plastic, and stainless steel in order to minimize contamination by heavy metals. A hydraulic damping mechanism, the key feature of this corer, consists of a water-filled piston which empties at a selectable steady rate. In this respect, the corer follows a design described by Pamatmat, 1971, and recently updated by Jahnke and Knight, 1997. When the corer contacts the bottom and releases tension on the winch wire, the water filled piston connected to the sliding shaft controls the speed at which the core barrel enters the sediment. Full travel of the core barrel is typically set for 10-15 seconds. As the core tube enters the sediment, a mechanical switch changes the ping rate of a sonar transducer, providing a confirming signal on the ship's depth recorder. After sufficient time for full core travel (about 20 seconds), the instrument is winched out of the bottom. A check valve seals the top of the core barrel. If a piston is used (useful in soft sediment) the piston is connected to the core frame and remains close to the water sediment interface as the core tube slides around it. At full penetration, the piston is fixed in position using a jam cleat and provides the seal at the top of the core. When the core bottom clears the water-sediment interface, a spring-loaded paddle slides against and seals the cutting edge of the core tube. Therefore, both sediment and ambient overlying water are captured by seals at the top and bottom of the core tube at the moment of pullout. As soon as the corer is on the deck of the ship, the core quality and sedimentary features are described by visual inspection through the clear core barrel. The core is then removed from the frame, capped and taped at both ends, and stored under refrigeration. Cores are secured in a vertical position at all times. Overlying water is left to completely fill the head space above the water sediment interface for transport and storage. We have found that a sealed core barrel completely full of water (no air space

above sediment) can be transported by ship or car without resuspension or other disturbance. As a precaution against contamination, all core barrels, sampling utensils, and sample containers are carefully cleaned prior to use. All core barrels and caps are acid washed with 5% nitric acid and rinsed with distilled water and methanol. Subsamples from the cores are taken with spatulas, knives, and spoons custom made from high purity titanium, a material with low contamination potential for both organics and trace metals.



Figure 2. U.S.G.S. hydraulically damped gravity/piston corer. This instrument takes sediment cores up to 60 cm long with minimal disturbance of the water-sediment interface. Design plans are available from the author.



Figure 3. Core extrusion rack. An adjustable clamp held between uprights hold a core barrel vertically. A piston inserted at the bottom of the sediment core extrudes the sediment under controlled movement of the hydraulic jack. Sediments are sliced off the top of the core barrel with depth resolution of 0.5 cm.

Cores are sectioned onboard the ship or in a shore-based laboratory by inserting a cleaned piston into the bottom of the core barrel and clamping the barrel in a vertical rack (Fig.3). The sediment core is extruded from the barrel by pushing a piston upward using a long-throw hydraulic jack. Sediment in direct contact with the core barrel is trimmed off and discarded, a further precaution to avoid contamination and smearing. This apparatus provides excellent mechanical control on the rate of extrusion and one-half cm resolution is easily achieved if desired.

3.2. Alternative designs of a HDC

Another corer utilizes a water filled piston to control penetration (Fig. 4, Jahnke and Knight, 1997). This instrument takes 4 piston cores simultaneously separated laterally from each other by about 1 meter. The core tubes are plastic (1 m long and 8.9 cm id) and no core catcher is required for silty or clayey sediments. The corer is not presently designed for operation in sand which would require the addition of a sealing mechanism for the bottom of the core barrel. Like the USGS corer, this instrument also recovers water from the sediment-water interface and has been successfully used for studies of interstitial water.

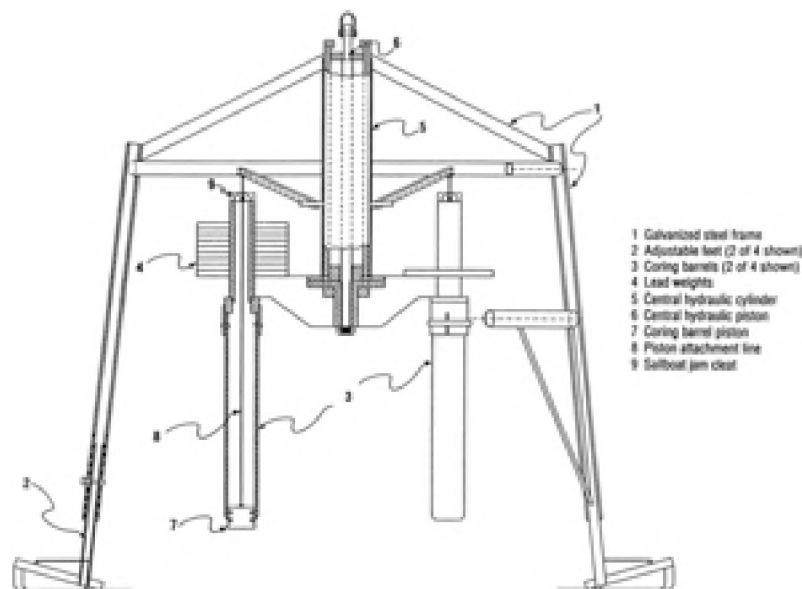


Figure 4. Schematic representation of the gravity-driven, hydraulically-damped multiple piston corer. The unit is approximately 1.5 m wide and 1.8 m tall. Exact dimensions vary with leg positions (Jahnke and Knight, 1997).

These two corers using a hydraulic damping mechanism have two advantages over conventional gravity and piston corers. First, their ability to take undisturbed cores is enhanced because the penetration rate is decoupled from the winch speed and the heave of the ship. They also remain vertical even if penetration is minimal. Conventional piston and gravity corers (and many other sampling tools) oscillate near the bottom with the roll of the ship, thus making the penetration rate unpredictable in rough seas. The conventional corers, lacking an outer frame, also can fall over when penetration is low. One relative disadvantage of the damped corers is their typically shorter core length compared to corers that free fall into the bottom.

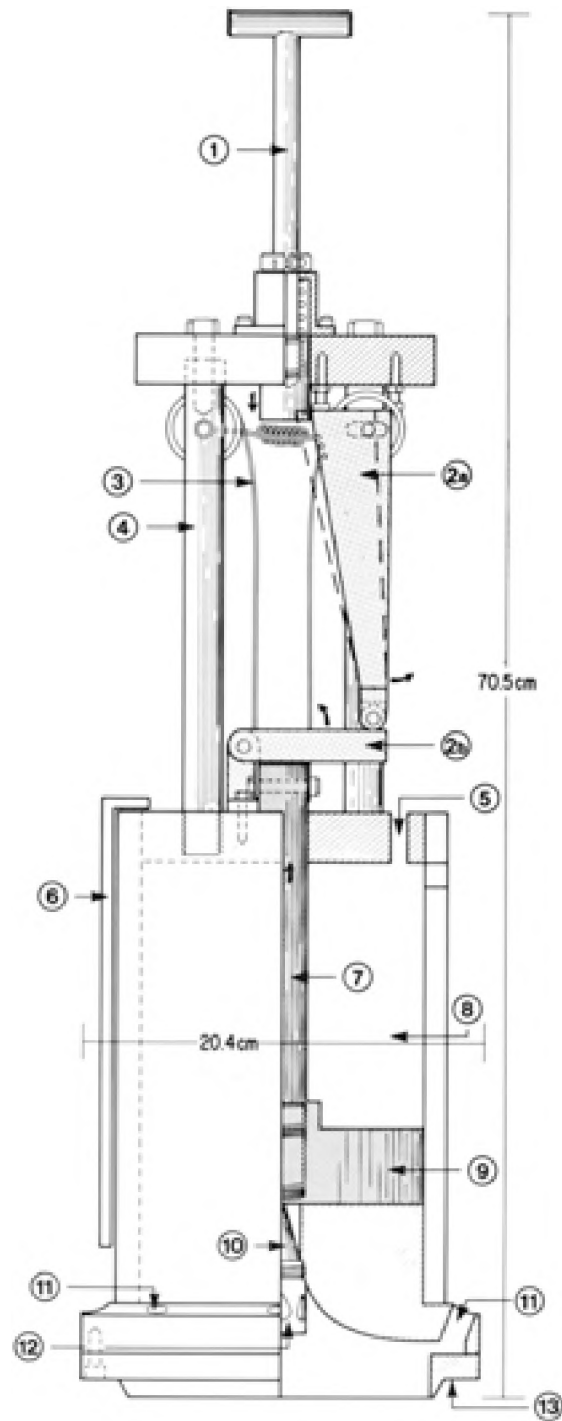


Figure 5. Components of the water-sediment interface sampler, cutaway view: 1) spring-loaded handle; 2a and b) release mechanism; 3) constant-tension spring; 4) support rod; 8) sample chamber (2 liters); 9) piston; 10) duckbilled check valve; 11) intake port; 12) intake to sample chamber; and 13) support base. As the instrument is lifted out of its container, the "T" handle assembly moves up approximately 1 cm, which allows movement of the triangular plate (2a) to the position of the dotted line. When the instrument weight is transferred to the sea floor, spring tension in the "T" handle assembly rotates plate 2a off bar 2b, which frees the piston. Arrows show relative motion of pieces as the instrument is fired.

3.3. Freeze corer

A new device utilizing a hollow wedge filled with dry ice and alcohol has been developed to collect a frozen core in soft sediment having high water content (Lotter and others, 1997). It has a hydraulic system for controlling the rate of sediment penetration. Two slabs of frozen sediment are recovered having dimensions of up to 100 cm long, 20 cm wide and 5 cm thick. Cold room facilities (-8 to -10 degrees C) are useful for convenient post collection processing.

This instrument has successfully recovered varved sediments in lakes without disturbance. It weighs a total of 115 Kg and can be disassembled and transported in a minibus. It can be operated from a small boat, raft, or through the ice.

3.4. Surface samplers

Large volumes of surficial sediment are commonly collected with grab samplers that vary greatly in design. Clam shell type grab samplers, such as the Van Veen or Smith-MacIntyre samplers, have opposing buckets that bite into the sea floor when the sampler hits the bottom using leverage from the samplers lifting arms (Van Veen, 1935; Smith and MacIntyre, 1954). The Smith-MacIntyre grab has a spring loaded initial thrust into the sediment as contact is made, which provides some advantage in hard sediments. A Shipek grab (Shipek, 1965) has a spring-loaded half cylinder that rotates 180 degrees through the water-sediment interface when the sampler contacts the bottom. Because there are no opposing jaws, this sampler sometimes mixes or completely inverts any stratigraphic structure originally present in upper few cm of the sediments (Dean A. McManus, oral communication, 1999).

The USGS has incorporated a Van Veen grab sampler into a camera frame which includes both still cameras and forward and downward looking video (Valentine and others, 1999). This tool has improved sample quality by providing an opportunity to observe local variability in sediment type and to select representative sites on the basis of live video observations. Camera surveys provide information about bottom features that complement both the detailed sampling at specific locations and the wide-swath bathymetric and sidescan-sonar surveys. Habitat assessment is one example of the application of the combined sidescan-sonar/camera/grab surveys. This survey approach has documented the negative impact of net dragging on the micro and macro benthic fauna attached in the gravel areas of the once-rich fishing grounds of Georges Bank and Stellwagen Bank off the Northeastern United States. Surveys show that biological overgrowth on coarse sand and gravel can be completely stripped by commercial dragging. The overgrowth offers protective habitat to juvenile fish (Watling and Norse, 1998). In test areas, where net dragging has been prohibited in order to monitor recovery, significant re-colonization of this overgrowth has been observed within a few years (P.C. Valentine, oral communication, 1999). Data collected during the combined survey have been useful in setting and evaluating the effectiveness of different resource management strategies in these fishing areas.

3.5. Sampling flocculent material at the water sediment interface

We have developed an instrument to collect fine-grained and flocculent material from the water-sediment interface for chemical and mineralogical analysis (Bothner and Valentine, 1982, Fig. 5). The instrument works like a spring loaded syringe that suspends and collects surface material from the sea floor. The sampler can be used by a diver in shallow water or from a manned submersible. In areas of active sediment deposition, the material collected

represents the most recently deposited sediment. This material is of interest for determining the concentration of anthropogenic contaminants at the sea floor. Such sediment may be a more sensitive indicator of early contamination than bulk samples collected by means of conventional corers or grab samplers. The instrument also may be well suited for sampling freshly flocculated or precipitated material from the sea floor, for example in estuaries or around thermal vents on mid-ocean ridges.

The goal of collecting flocculent material was also accomplished using a submersible pump downstream of a Millipore cartridge filter and flexible tubing. This equipment was used successfully by divers in shallow water and from the 3-man submersible ALVIN in the deep sea. A plume of resuspended “fluff” is generated by waving a rectangular plastic paddle (22 X 28 cm) just above the sea floor. The end of the flexible tubing is inserted into the plume and the pump turned on. The solids are retained on the filter. Using ALVIN this procedure recovered 10-20 grams of material from the top few mm of bottom sediment in about 20 minutes. The instrument was also used like a vacuum cleaner to collect recently deposited sediments from coral reefs in the Hawaiian Islands (Fig. 6). The goal was to recover and identify the relative magnitude of soil particles transported to the reef from the adjacent island of Molokai after unusually heavy rains. The increased erosion, thought to be a result of recent agriculture, shoreline development, and overgrazing by feral pigs and goats may be linked to degraded health of the reef in some locations.

3.6. Sampling platforms for collecting sediment cores in coastal marine areas

There is a wide variety of vessels that can be fitted with appropriate lifting hardware for recovering sediment cores. Two unusual platforms are briefly described here. The first is an extremely simple catamaran, the second a unique and highly sophisticated hover craft.

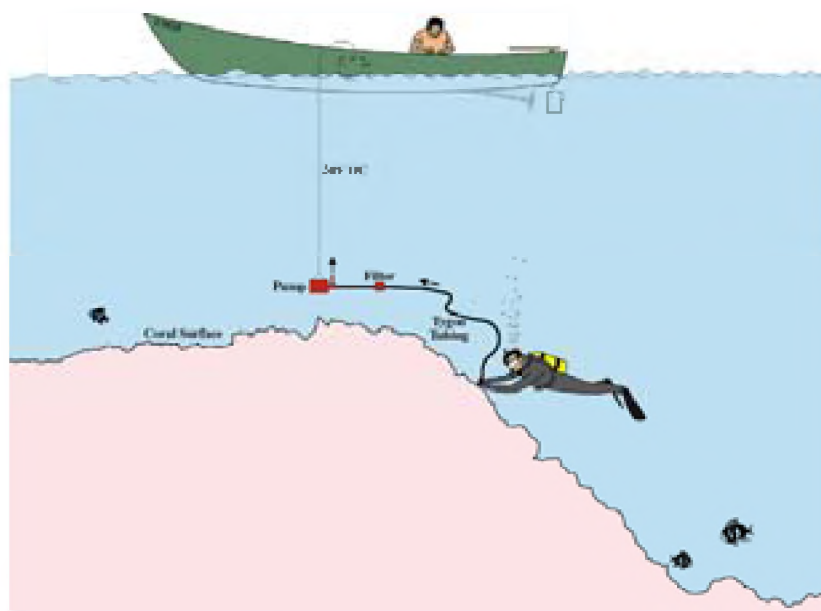


Figure 6. Diver- or submersible-operated “fluff” sampler for collecting easily resuspended sediment (top few mm) from the water-sediment interface. A 24 V DC submersible impeller pump draws water through a Millipore cartridge filter. The end of the flexible tubing is used to draw sediment from an induced plume of resuspended sediment or to vacuum sediment off a hard coral or artificial flat surface.

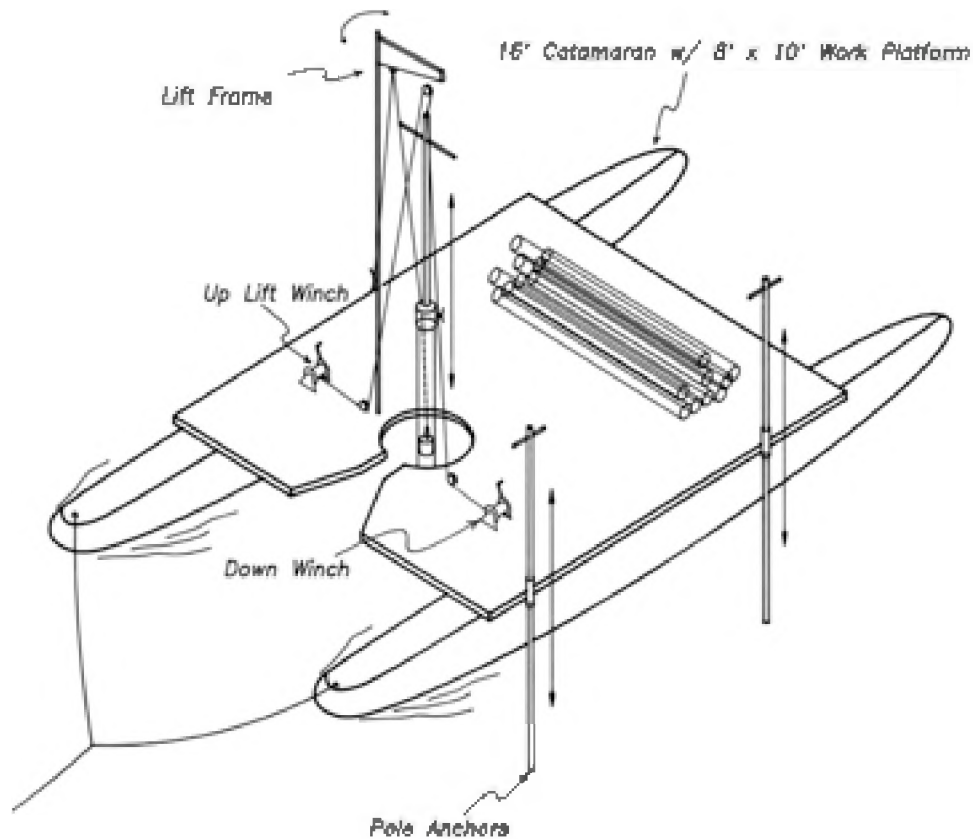


Figure 7. This catamaran is an example of a floating platform with a central opening through which piston or gravity corers can be deployed. In shallow water (<10 m), a stiff rod or pipe can be fixed to the core head and the core can be pushed into the sediment by hand or forced in using the down winch. The penetration rate can be controlled using either method.



Figure 8. U.S.G.S. HoverProbe a coring platform designed on a hovercraft. This vessel is being used to collect piston and gravity cores in shallow water environments that are difficult or impossible to reach with conventional boats. Rotary drilling and vibra-coring is also possible from this platform. More information on this vessel can be obtained from Wayne Newell or Donald Queen, USGS, Reston VA.

The catamaran platform (Fig. 7) can be constructed from two fiberglass hulls supporting a rectangular deck with a “moon pool” opening in the middle. A tripod or lifting post is erected over the moon pool. The platform can be towed to location, thus eliminating the need for independent propulsion. Anchors at three or four positions around the platform are used to keep the platform on sampling location.

In shallow water (<10 m), piston or gravity cores can be collected using a stiff pipe attached above the core head and sampling barrel. The gravity core assembly is pushed into the sediment as far as possible by hand and then pushed farther using the deck winch which pulls down on the pole at a selected rate. In the piston core configuration, the piston is held at the water-sediment interface by a line attached to the deck while the core barrel is forced down around it. After maximum penetration is reached, the piston line is attached to the pole, and the deck winch line is fed through a block on the tripod to a lifting point on the corer. The core barrel and piston, now fixed in position relative to each other, are pulled out of the sediment together. This design has been used successfully in Florida Bay and in shallow areas of Boston Harbor. Within the water depth limitation of 10 m, coring can be accomplished without utilizing heavy weights to assist core penetration.

The USGS HoverProbe is a coring platform built on a 21 foot hover craft, 8 feet wide which travels about 1 foot above any flat surface (over water or land) on a cushion of compressed air (Fig 8). The craft is specifically designed to collect sediment cores in shallow areas or on salt marshes over which transport of sampling gear is often difficult or impossible. The probe is equipped to collect piston, gravity, and vibra cores and to conduct rotary drilling. The craft has been fully operational for a few months. Details of the construction and capabilities of the craft will be described in a WWW page in the near future.

4. SUMMARY

This report briefly describes some new equipment designed to collect sediment cores with minimal disturbance of material at the water-sediment interface. A number of these devices have a hydraulic damping mechanism which permits the operator to select the rate at which a piston or gravity corer is forced into the sediments. The penetration rate is decoupled from the motion of the ship and the pay-out rate of the lowering winch. A sediment core with minimal disturbance permits analysis with fine-scaled depth resolution which may yield new insights about the accumulation of contaminants and about bio-geochemical processes.

One general recommendation is to incorporate multi-disciplinary components to the design of a bottom sampling programme. Bottom sediment mapping, using some of the modern sidescan and bathymetric survey tools, has provided valuable insights into the nature and distribution of sediments. Designing a sampling programme after obtaining this basic regional information has made our geochemical surveys off the New England coast more successful and more cost effective. With continued population growth and with the continuous generation of new chemicals, the need for understanding and predicting the fate and effects of contaminated sediments in the worlds lakes, rivers, and oceans will increase. The tools and procedures used to make assessments of contaminated sediments will change in response to new scientific questions. Past accomplishments in equipment design serve as a guide and encouragement toward solving future sampling challenges.

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SAMPLE PREPARATION FOR RADIONUCLIDE ANALYSIS AND NUCLEAR ANALYTICAL TECHNIQUES IN SEDIMENTS AND SOILS IN THE IAEA LABORATORIES

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Abstract. Sampling and sample preparation for radionuclide analysis and nuclear analytical techniques applied to sediments and soils in the IAEA laboratories in Seibersdorf and Monaco are described and illustrated by examples taken from the IAEA' contribution to international radiological assessments of contaminated sites. The sample is defined as a function of the objective of the sampling campaign and the information and conclusions expected to be derived from the sample analysis. Typical marine and terrestrial sediment and soil samples and the techniques for selecting and obtaining them are described. The application and procedures for in-situ screening techniques to assist in the selection of sampling sites of interest is documented and examples are given. Sample treatment techniques for marine and terrestrial samples, including depth profiling of contaminants are described. Depending on the type of analysis to be performed, drying, homogenisation, bulk analysis or subsampling and different dissolution techniques might be applied to the samples. Specific techniques for identifying and sampling hot spots and for the isolation of hot particles are illustrated. Handling and preparation of hot particles for microanalytical techniques are provided and illustrated. Quality assurance and quality control aspects related to sampling and sample preparation are described, as being essential to provide full trackability of sampling operations, unambiguous identification and documentation of the samples, and full records of important observations.

1. INTRODUCTION

An important activity of the IAEA laboratories in Seibersdorf and Monaco is to participate in the assessment of the residual radiological risk resulting from accidental or intentional contamination of the environment by radionuclides. In this context the IAEA Laboratories co-ordinated and participated in the sampling campaigns conducted to assess residual contamination in regions affected by the Chernobyl accident, and at former nuclear weapons test sites in Khazakstan, French Polynesia and the Marshall Islands. A large number of terrestrial, aquatic, biological and vegetation samples was collected and procedures for sample collection and preparation were established. This review covers the collection and preparation of sediment samples collected during the sampling campaigns for sediments and soils at the Mururoa and Fangataufa atolls [1].

2. DEFINITION OF THE SAMPLE

The ultimate objective of sample collection and preparation for radioactivity measurements is to provide data on the radioactive contamination by measuring the radionuclides of interest. Contaminants in solid samples such as sediments and soils tend to have heterogeneous distributions and radionuclides are no exception. Accidental and intentional airborne contamination by radionuclides is due to the dispersion of radioactive particles or condensation of radioactive gases and their deposition on land or water (fall-out). The physico-chemical processes involved produce a range of particle sizes and dispersing vectors produce an heterogeneous pattern of deposits in the terrestrial and aquatic environments. Sediments contaminated by radioactive effluents consist of different minerals and species whose chemical affinity, adsorption and ionic or isotopic exchange properties differ for the

various elements and hence also for radionuclides. Small samples, like sediment and soil, will therefore always be heterogeneous and consist of different particles with varying concentrations of different radionuclides. The definition of the sample therefore is dependent on the specific interest of the final user. Interest may be on the average radionuclide concentration on an area or weight basis in order to obtain data for external radiation dose assessments or the average radiological burden. A representative sample should be sufficiently large in order to average radionuclide concentration in many different species. Before subsampling for analysis the sample should be homogenized and often the preparation procedure includes volume reduction, preconcentration stages and bulk separation techniques to isolate groups of, or single radionuclides. Alternatively, interest may be on the individual radioactive species in the sample in order to obtain a detailed description and understanding of the source term, the dispersion process or the migration characteristics for different radionuclides. A representative sample in this case would therefore include the different species involved. Rather than being homogenized, the individual particle sizes and species should be sorted and individual particles of interest should be isolated and analyzed. Sample preparation and separation techniques should not only be designed to distinguish between different radionuclides but also between the species of the same radionuclide. F. Macasek [2] recently made an in-depth review of this issue. Table I reproduces his summary of sampling and pre-analytical treatment. It is essential to collect several replicate samples in order to assure that the sample is appropriate for the intended use and to evaluate the confidence limits of the sampling procedure.

3. DESCRIPTION OF MURUROA AND FANGATAUFA SAMPLES

3.1. Marine sediment samples

The sampling sites and the number of samples to be collected were agreed on before the sampling campaign. They were chosen with a view of keeping the IAEA study as independent as possible and completely covering the Mururoa and Fangataufa lagoons. Sediment samples consisted of Kullenberg core samples, box core samples and grab samples. The box and grab samples were collected in triplicate. One set was distributed among the network of laboratories participating in the project (MARINALABS), the second set was kept by the Commissariat de l'Energie Atomique (CEA) in France and the third set was kept as an archive at IAEA-MEL in Monaco. The total number of samples was 139 and the total weight to about 500 kg. A large volume of sediment (about 200 kg) was collected for an intercomparison exercise (IAEA-384) planned within the framework of the IAEA's Analytical Quality Control Services programme. The samples collected by the box corer were sub-cored in triplicate using a plastic tube of 10 cm diameter and split into slices of 0-1, 1-3, 3-5, 5-10, 10-15, 15-20 cm etc. The Kullenberg cores were also split into slices after inspection. Grab samples were analyzed as bulk samples. All sediment samples were freeze-dried before analysis.

3.2. Soil samples

The main purpose of sample collection and preparation was to obtain representative environmental samples from bedrock and the surface layer and prepare them in a way that would ensure the homogeneous distribution of all radionuclides in the final subsamples. The samples were divided into three sets: two sets were intended for measurements either by the members of the ALMERA network or the Agency's laboratories in Seibersdorf and the third to be kept in Seibersdorf as an archive. The amount of material sampled took into account the mass needed to reach adequate detection limits in each of the three subsamples to be provided.

TABLE I: THE ENVIRONMENTAL ANALYTE FUNCTION ONTOLOGY
SAMPLING AND PRE-ANALYTICAL TREATMENT AS A FUNCTION OF THE PURPOSE OF ANALYSIS

SAMPLING	ENTROPY GENERATION (*)		
	HIGH	MEDIUM	LOW
	HOMOGENISATION	RANDOM REPLICATE ANALYSIS	STRATIFIED RANDOM SAMPLING and SPECIATION ANALYSIS
PURPOSE of ANALYSIS	Gross mass balance Regional abundance and availability of analyte	Natural distribution of analyte Heterogeneity indications for non-parametric evaluation methods	Physico-chemical description of different species and their interactions
Inventory	Differences between areas Contour maps		
Impact	Regional environmental impact Integral exposure evaluation	Assessment of stochastic action of the analyte	Specific action of different analyte species
Mobility	Regional spatial dynamics of the analyte in a pseudocontinuous environment	Average mobility in a multi-component medium (near- and far-field studies)	Specific mobility and transfer properties of different species in different matrices

(*) Shannon information entropy H in the sample defined by $H = - \sum x_i \ln x_i$ for i species with fractional abundance x (i.e. $\sum x_i = 1$)



FIG 1: Template used for topsoil sample collection. The sample was sieved and big stones were discarded.

Samples were taken at the atolls of Mururoa, Fangataufa and Tureia. At Mururoa samples were collected in the inhabited part of the atoll, where low contamination was expected, as well as at locations at test sites where higher contamination levels were expected. Sampling at Fangataufa was carried out at three locations in order to assess the contamination level due to fall-out from the atmospheric tests. A few samples were also collected at Fakamaru on the inhabited atoll of Tureia, which may have been heavily contaminated during the series of atmospheric test. Samples of topsoil and soil profiles were collected at Tureia.

Knowledge of total soil contamination gives an estimation of the deposition of the various radionuclides, whereas depth profiles provide information on the possible transfer of radionuclides to vegetation through roots. The depth profiles are expected to change with time as a result of downward particle transport or migration of chemical species. Topsoil samples were collected using a collection template (Fig. 1) designed to scrape off the top two centimeters of a 20 x 30 cm area.

Depth profiles were taken by scraping off the top 2 cm layer with the template, then coring the next 40 cm with a square section coring tool of 10 x 10 cm (Fig. 2). The 40 cm long core was subdivided into four 10 cm layers in order to study radionuclide migration in the soil. The vertical radionuclide distribution must be known in order to calculate the calibration and self-shielding corrections of in-situ gamma-spectrometry measurements.



FIG 2: Box coring tool to collect soil profile samples. Collection of the third layer ranging from 12-22 cm depth is shown.



FIG 3: Loose coral rocks



FIG 4: 10 cm Bedrock core with porous structure

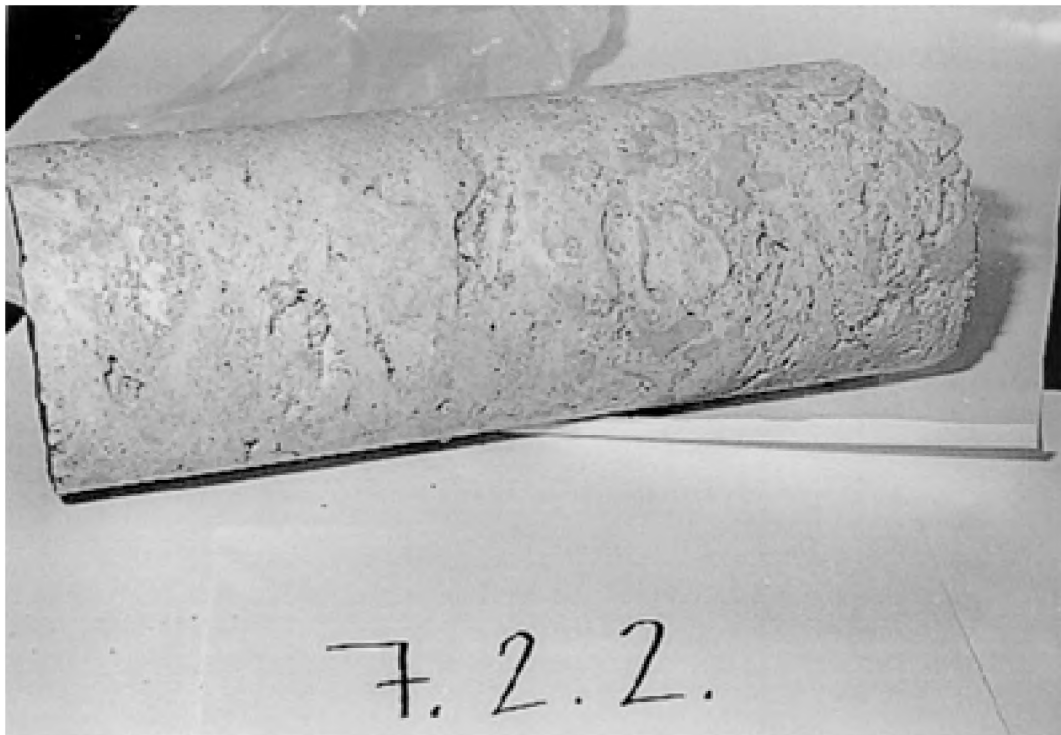


FIG 5: 40 cm Bedrock core with fine structure



FIG 6: Bedrock sampling with core drilling equipment

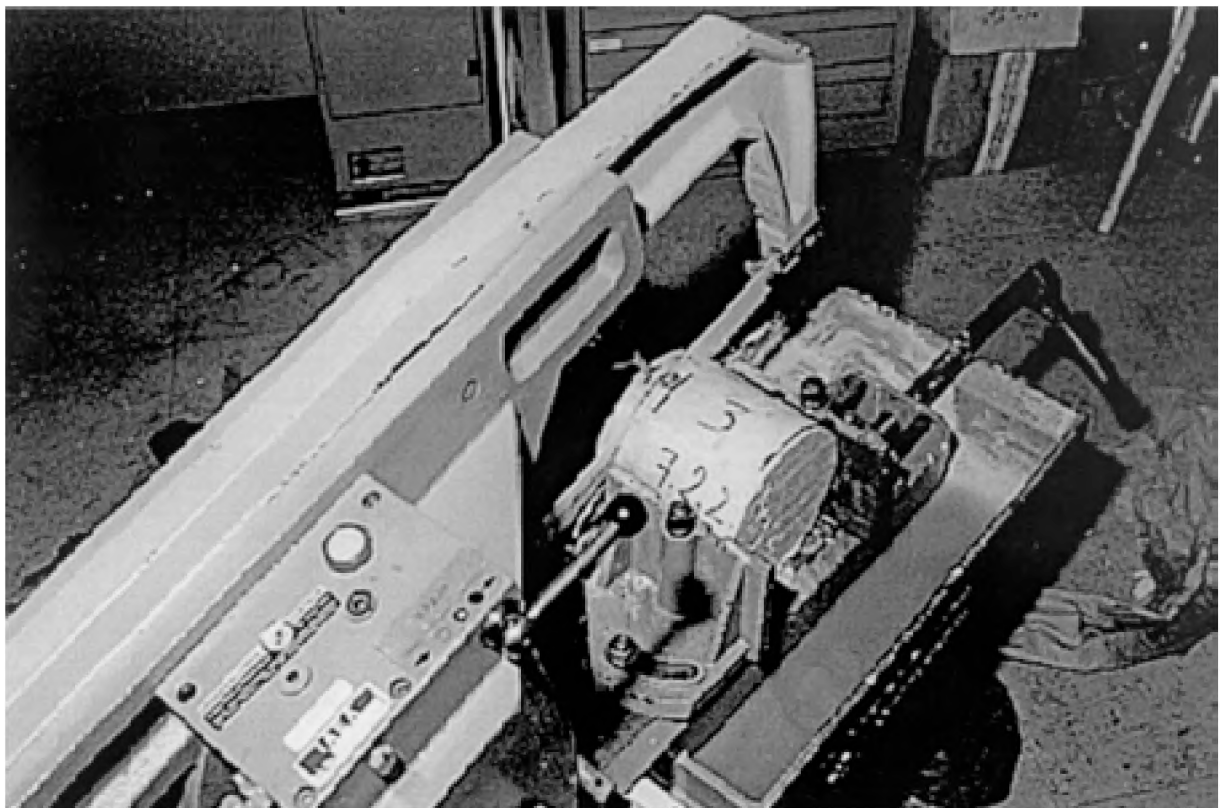


FIG 7: Band saw cutting a bedrock sample

In some areas, the collection of soil profiles was prevented by coral debris, sand or ground water in the lower layers. The collection of soil profiles at Tureia was also hampered by sand and coral debris in the lower layers.

In areas where there was no soil available, loose corals (Fig. 3) and sand samples were collected to obtain information on surface contamination. The sand samples from beaches were collected using a small shovel at a random number of places at a single site and mixed to give one composite sample. Loose coral rocks were also collected at random on beaches.

Cores of coral rock were sampled in order to determine whether radionuclides had migrated downwards in the coral rock. This information was needed to calculate the total radionuclide deposition per unit of surface area. The vertical concentration profile was also an important parameter for the calculation of overall radionuclide inventories from in-situ gamma-spectrometry measurements. Although it was expected that most of the radionuclide activity would remain adsorbed in the top layer, migration through small channels in bedrock could not be excluded (Figures 4 and 5).

The cores were collected using a coring device (Fig. 6) designed for coring concrete. Usually cores of 14 cm in diameter were taken. The maximum core length possible was 80 cm, but the cores ranged from 10 to 40 cm, depending on the location and the structure of the bedrock. Several cores broke during coring.

After pre-tests including autoradiography and gamma-spectrometry measurements, it was decided to cut all cores into two top layers of 1 cm each and the rest into layers of 10 cm (Fig. 7).

4. IN-SITU MEASUREMENTS OF RADIONUCLIDES IN SEDIMENTS AND SOILS

4.1. Marine sediments

Underwater gamma-spectrometry was used for in-situ measurements of gamma-emitting radionuclides with the purpose of identifying the most contaminated areas for subsequent sample collection. The survey was carried out inside the lagoons of the atolls. The rugged bottom topography prevented towing of benthic devices and measurements were carried out at a discrete network of points. The most contaminated areas were found in locations subject to direct contamination from atmospheric nuclear weapons tests.

The measurements were performed with a NaI based gamma-spectrometer. The main components of the spectrometer are shown in Fig 8. Spectra were recorded from the detector placed on the sea-bed at depths between 30 and 45 m. Energy calibration spectra were recorded at regular intervals. Background spectra were measured with the detector placed in the water column. For each site the total recording time was selected according to the measured count rate in order to optimize counting statistics. Counting times ranged from 5 to 20 minutes for seabed spectra and up to 100 minutes for the background spectra. ^{60}Co and ^{137}Cs were easily identified in the recorded spectra, as well as natural radionuclides ^{40}K and ^{214}Bi (Fig 9). Because of the important site-to-site variation of the depth distribution of radionuclides in sediment, an in-situ efficiency calibration of the detector was not possible nor was an evaluation of the radionuclide inventories in sediment from the recorded spectra alone. Nevertheless reasonable predictions were obtained on the basis of a simple calibration for ^{60}Co using the average activity concentration in the top 10 cm of the sediment layer. The

distributions of ^{60}Co and ^{137}Cs in lagoon sediments due to different origins and geochemistry are not necessarily the same as for plutonium, which is the major contaminant in lagoon sediments. However the investigations have shown that the distributions of ^{60}Co and ^{137}Cs correlate well with plutonium distribution patterns. Relative determinations to identify locations of enhanced radioactivity for the selection of sampling sites was therefore successful. Following the survey, Kullenberg cores were taken at sites identified as having local contamination maxima. Later, calibration measurements carried out in the laboratory enabled calculation of ^{60}Co and ^{137}Cs inventories from the in-situ measurements, and after establishing some correlations, of the $^{239+240}\text{Pu}$ inventories as well. The obtained results were in reasonable agreement with direct assessments by Osvath [7]. Underwater gamma-spectrometry proved to be an efficient technique for on-site identification of areas of interest on the sea-bed, a process which otherwise would have required time-consuming sampling, sample preparation and counting sequences.

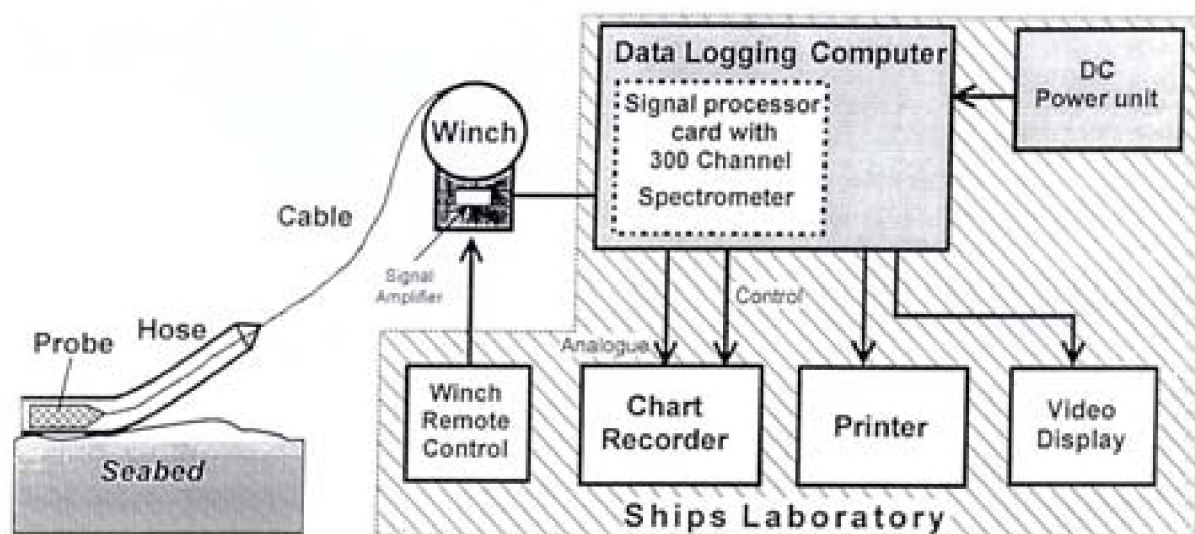


FIG 8: Seabed spectrometer equipment (schematic).

4.2. Emerging coral bedrock

Some of the test sites are composed of exposed coral bedrock, covered by a thin layer of sand, sediments and coral debris as a result of regular flooding by seawater. On these sites a heterogeneous distribution of radioactivity was expected.

The ^{239}Pu concentration in 10m x 10m squares was initially determined with a portable detector equipped with an X probe, placed at 3 cm above the terrain, with the window adjusted to detect the 59.5 keV radiation of ^{241}Am . The counts per second of the detector over each 100 m² area were then converted to ^{239}Pu areal activity (MBq/100 m²) using a $^{239}\text{Pu}/^{241}\text{Am}$ ratio which ranged between 40 and 50. The $^{239}\text{Pu}/^{241}\text{Am}$ ratio was determined by collecting 26 samples at random and determining directly, after radiochemical separation, the Pu and Am activities. The data show that the measured $^{239}\text{Pu}/^{241}\text{Am}$ ratios are spread over an interval of 23 to 158 and have two maxima. Therefore the use of an average $^{239}\text{Pu}/^{241}\text{Am}$ ratio for indirectly calculating ^{239}Pu through the measurement of ^{241}Am may have lead to considerable uncertainties and a new series of 21 in-situ gamma-spectrometry measurements were performed on these sites by the IAEA team.

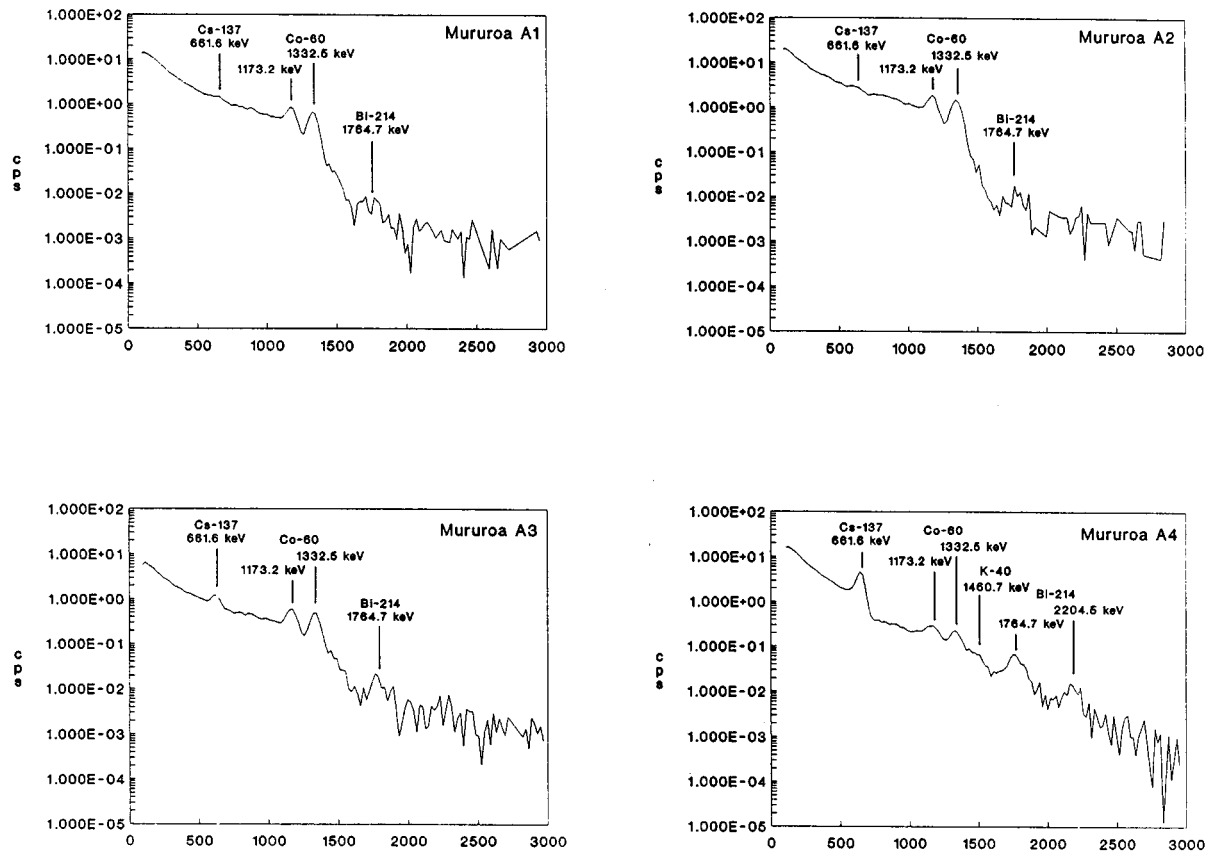


FIG 9: Mururoa transect A, sites 1-4.

Dose-rate and contamination monitors were used on-site as a guide and as screening devices to indicate places of interest for sampling, in particular to locate hot spots. However, no quantitative data however can be obtained from these measurements.

The in-situ gamma-spectrometers shown in Fig 10 were used to collect information on surface and subsurface radionuclide inventories. This technique allows for rapid and efficient identification and quantification of gamma-emitting radionuclides in the soil at a specific site. A gamma-ray detector is positioned at a defined height (usually 1 m) above ground level and a spectrum of gamma-emitters is collected. The main source of uncertainty was usually poor knowledge of the distribution pattern of the radionuclide of interest in the soil. In some cases, an uneven distribution of the radionuclide on the soil surface may have played a dominant role in the overall uncertainty.

A total of 106 gamma-ray spectra were recorded with three portable gamma-spectrometers at selected locations on the Mururoa and Fangataufa atolls. Five control spectra were collected at the laboratory on Mururoa and a few repetition measurements were carried out to assess the reproducibility.

Each spectrometer used consisted of a high purity germanium detector (HPGe), associated electronics and rechargeable batteries. The detectors used were:

(1) Canberra Extended Range model GX2018 (20% efficiency at photon energy of 1.3 MeV relative to 3" x 3" of NaI(Tl) detector, and resolution of 1.80 keV at 1.3 MeV);



FIG 10: In-situ gamma measurements using high purity Ge detector.

(2) EG&G Ortec model (n-type, 30% relative efficiency, resolution of 1.90 keV);

(3) Canberra model GC2019 (p-type, 20% relative efficiency, resolution of 1.90 keV, enclosed in a magnesium capsule).

Each detector was equipped with integrated nuclear electronics of the InSpector type (Canberra Industries, Inc., USA). The first two detectors were suitable for detection of low-energy gamma-emitters, in particular ^{241}Am (59.5 keV), and ^{239}Pu (129 keV). The gamma-spectrometry analysis software package GENIE-PC (Canberra) was used for spectra acquisition and evaluation.

The measurements were performed in conventional way with the detector mounted vertically on a tripod, facing the soil/rock surface at a distance of 1 m. Data collection time was optimized according to the activity concentration at the site. It ranged from a few minutes in the most contaminated areas to one hour in the least contaminated zones. The following radionuclides were identified and quantified at various locations: ^{214}Am , ^{239}Pu , ^{137}Cs , ^{155}Eu , and ^{60}Co . The limit of detection, calculated according to Currie, [3] was of the order of 750 Bq m^{-2} for ^{241}Am and ^{155}Eu , 90 Bq m^{-2} for ^{137}Cs , 60 Bq m^{-2} for ^{60}Co , and 2 kBq m^{-2} for ^{239}Pu .

Results are presented as the total inventory of a radionuclide in a soil column at a specific location expressed in terms of activity concentration in units of Bq/m^2 . As radionuclides are not only present in surface layers but may have migrated downwards into the soil, appropriate absorption correction factors for the different gamma rays had to be calculated. It was assumed in the data evaluation that the soil had an atomic composition similar to CaCO_3 with

an average mass density of 1300 kg m^{-3} . Another parameter necessary for the calculations was the vertical distribution of a radionuclide of interest in the soil at a specific location. All available data on depth distributions were critically evaluated and compiled for all radionuclides at different locations. The activity profiles at some locations closely follow an exponential distribution, but at other locations display a flat distribution corresponding to disturbed soils. The shape of the exponential distribution is determined by the relaxation mass per unit area L_r (kg/m^2). Values of the parameter varied from 30 kg/m^2 to 200 kg/m^2 which corresponds to a range of 2.3 to 15 cm for the relaxation length. A value of $L=15 \text{ cm}$ for instance, means that 63% of activity contained in a whole soil column is deposited in the 15 cm thick top layer of the soil.

The surface activity concentrations of ^{241}Am and ^{239}Pu were calculated using an exponential depth distribution in the coral bedrock, with the relaxation mass per unit area $L_r = 0.3 \text{ g/cm}^2$ (L is the relaxation length in cm and r the density of the coral rock in g/cm^3). This implies that 50% of the total activity is contained in the $< 0.9 \text{ mm}$ layer and 90% in the $< 3 \text{ mm}$ layer. A relaxation mass per unit area of $L_r = 0 \text{ g/cm}^2$, corresponding to a uniform distribution of the activity on a perfectly smooth surface of zero thickness would lead to surface activities which would have to be multiplied by the factor 0.70 for ^{239}Pu (129keV) and 0.57 for ^{241}Am (59.5keV) (the same conversion factors would apply to the uncertainties and level of detection). Nevertheless the assumption of having the activity confined to a perfectly smooth surface of zero thickness appears unrealistic in view of the great unevenness of the surface, cracks where radioactive material may have penetrated, coral debris of variable thickness covering the bedrock, coral rocks and sand, and the presence of scattered low vegetation. Therefore all surface activities were calculated with a relaxation mass per unit area $L_r = 0.3 \text{ g/cm}^2$. This hypothesis is supported by the experimental data in which the results for the radioactivity profiles of ^{239}Pu and ^{241}Am were measured for three bedrock core samples collected at random in the center of the test site. These bedrock cores were collected by an electric-motor-driven corer normally used to drill concrete. They had a diameter of 14 cm and a length of about 40 cm. The cores were then cut in the laboratory by a water cooled electric saw into slices of different thicknesses. Unfortunately, due to the fragility of the coral rock, it was not possible to cut slices of less than 1 cm thick. The data (Figures 11, 12, 13) indicate that practically all activity ($>99 \%$) is confined in the first centimeter, with the exception of one sample, where the first centimeter contains only 90 % of the overall activity. This was due to the presence of large cracks in the bedrock surface.

The activities of ^{239}Pu and ^{241}Am , separately calculated from the 59.5 keV (^{241}Am) and 129 keV (^{239}Pu) peaks, were determined. The ^{239}Pu limit of detection was about 0.7 MBq/100m^2 . It appears that Pu activities directly measured by gamma-ray spectrometry are about two to six times higher than those indirectly evaluated through the counts of a NaI probe. This can be explained by the initial measuring technique, requiring the setting of a threshold of the probe, which can easily lead to missing a high ^{239}Pu “background” (up to 100 MBq/100 m^2 or even higher, depending on the threshold value). How a relatively high background radiation can be missed when using this measurement technique is explained below, in the paragraph dealing with the results of the search for hot-spots in a $10 \text{ m} \times 10 \text{ m}$ area. The procedure used the ^{241}Am radiation measured by NaI detectors, which are sensitive to changes in temperature and require a threshold setting to eliminate low-energy background radiation. Also a single value for the $^{239}\text{Pu}/^{241}\text{Am}$ ratio, which has been shown to vary from place to place was used to calculate the ^{239}Pu activity. More reliable data were obtained by direct measurement of ^{239}Pu by HPGe detectors using its gamma radiation.

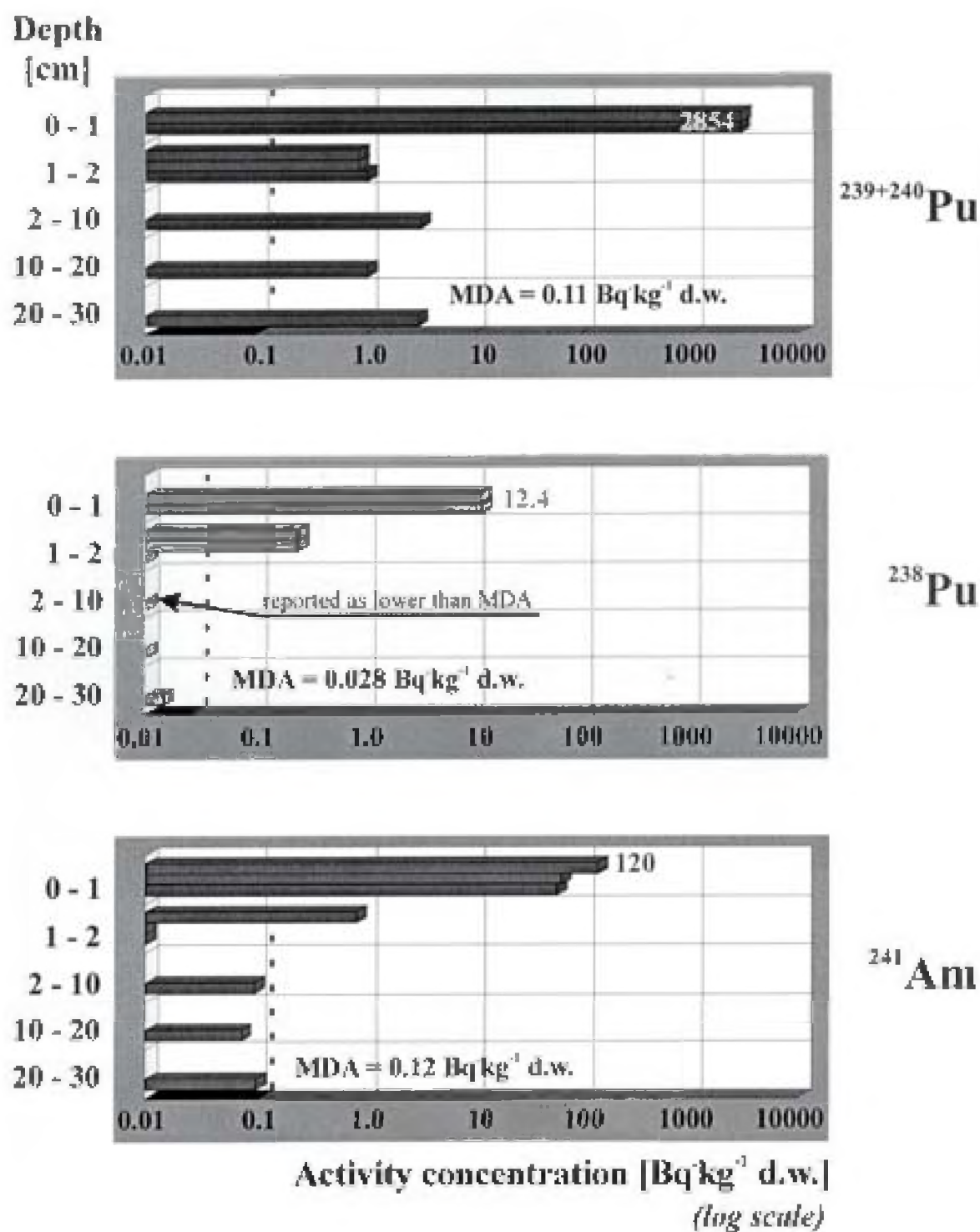


FIG 11: Activity concentrations of ²³⁹⁺²⁴⁰Pu, ²³⁸Pu and ²⁴¹Am versus depth in the Colette area bedrock (location 7.2.1.1-6).

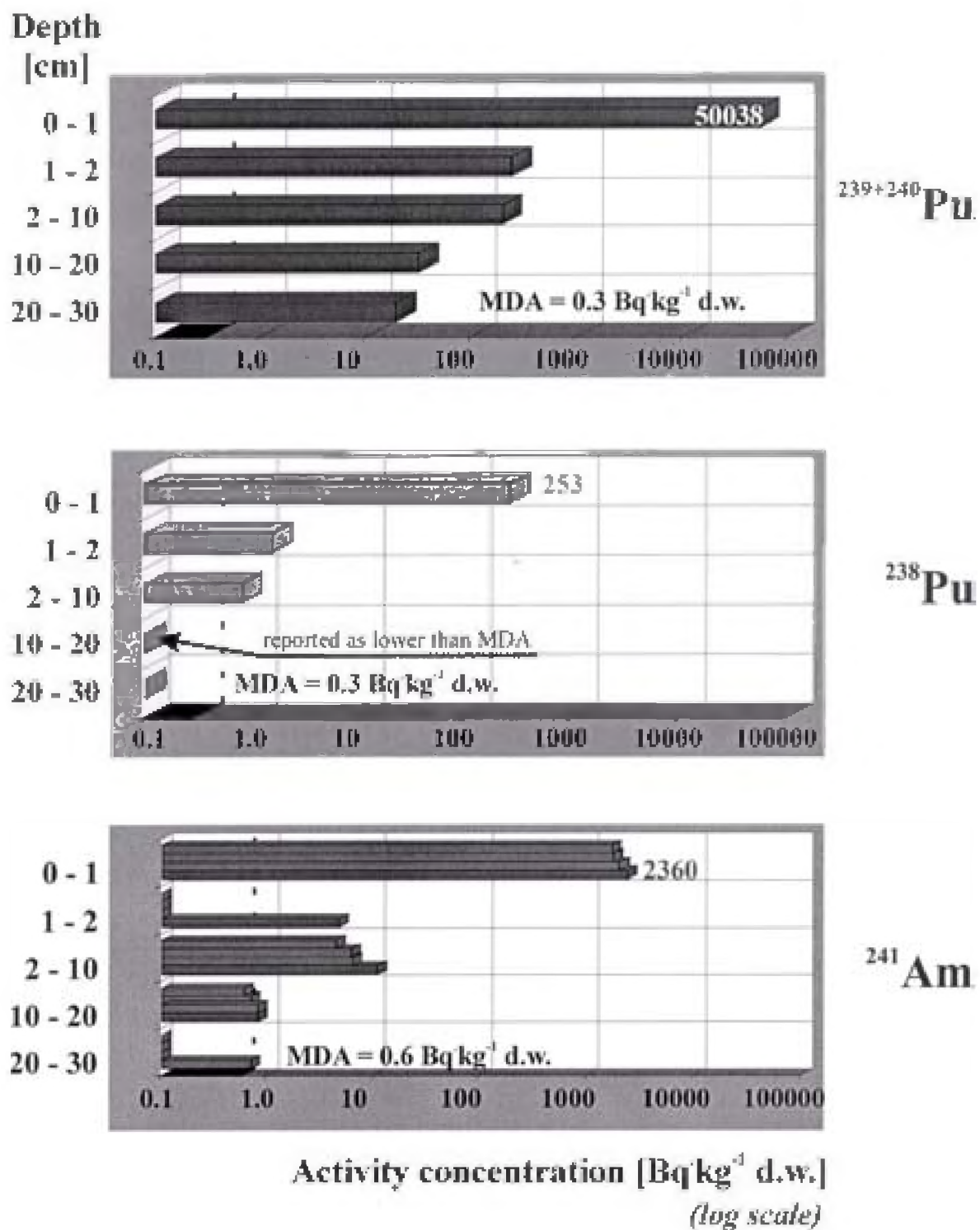


FIG 12: Activity concentrations of ²³⁹⁺²⁴⁰Pu, ²³⁸Pu and ²⁴¹Am versus depth in the Colette area bedrock (location 7.2.1.1-5).

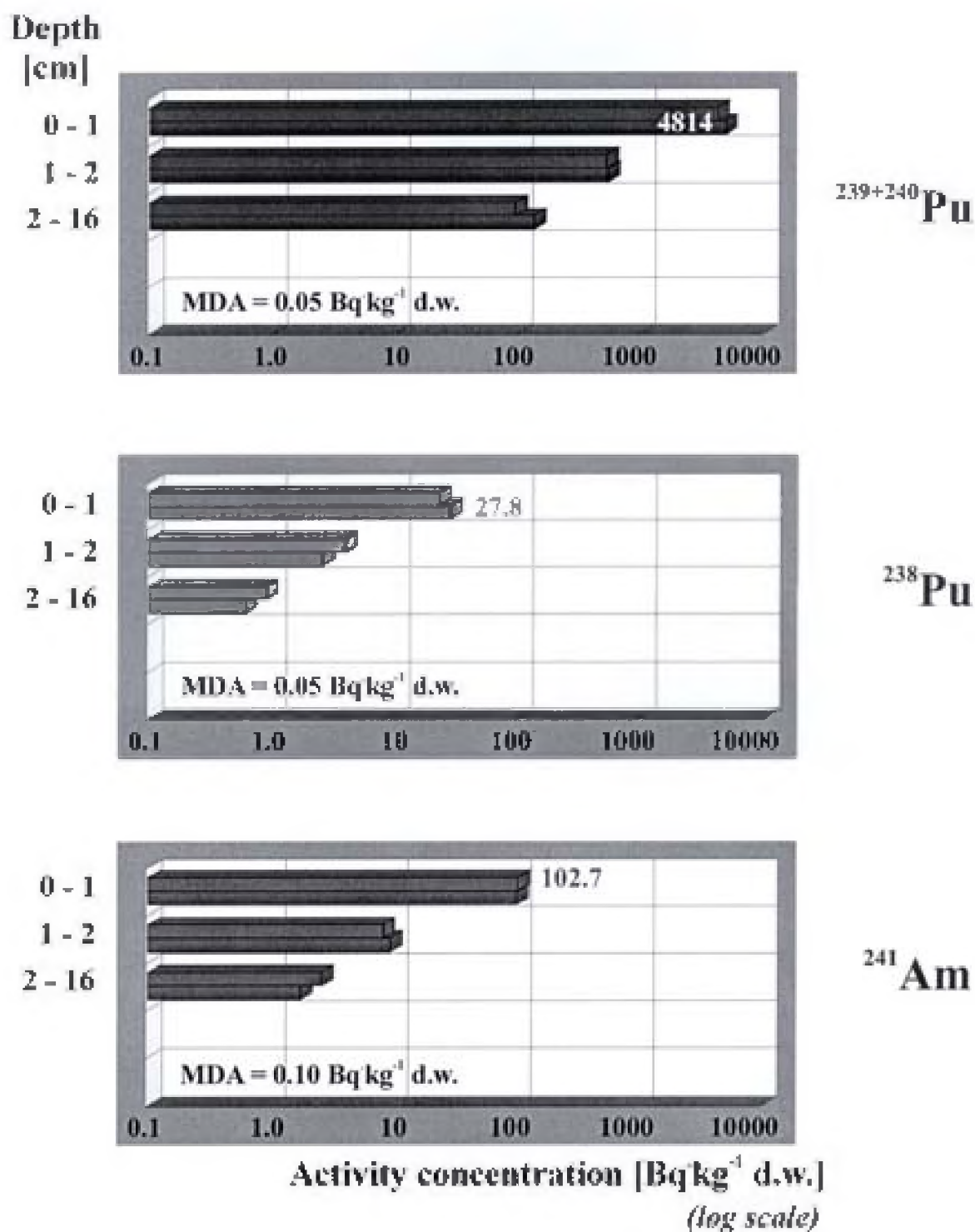


FIG 13: Activity concentrations of ²³⁹⁺²⁴⁰Pu, ²³⁸Pu and ²⁴¹Am versus depth in the Colette area bedrock location (7.2.1.1-3).

It is interesting to note that the consistency can be verified between the surface contamination values determined by in-situ gamma-spectrometry and those evaluated from the three core samples (activity profiles are shown in Figures 11, 12, 13), where the activity was determined in the laboratory by alpha-spectrometry after radiochemical separation. Considering that the diameter of the corer was 14 cm (area 154 cm²) and assuming that the activity was confined to the surface of the bedrock, the surface concentrations of ²³⁹Pu could be calculated.

Result: Histogram Report

User Name: Ben

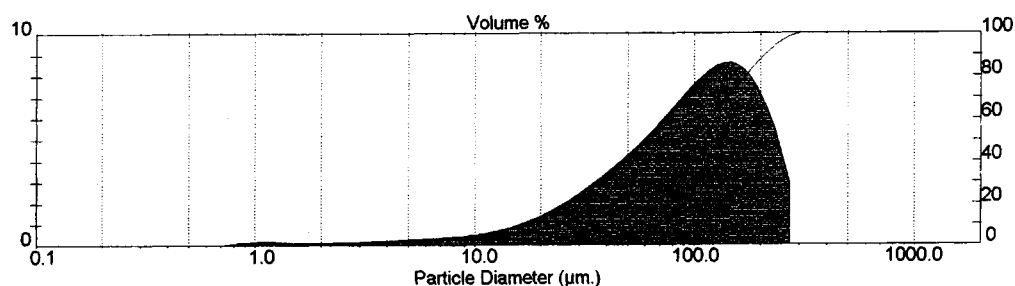
Security Level: 1

Sample Details		
Sample ID: 201904	Run Number: 9	Measured: Fri 11 Apr 1997 11:16
Sample File: MURU	Record Number: 16	Analysed: Fri 11 Apr 1997 11:21
Sample Path: C:\SIZERMUDATA\		Result Source: Analysed
Sample Notes: Site 33 Core 1		

System Details		
Sampler: Internal	Measured Beam Obscuration: 14.0 %	
Presentation: 4OHD	[Particle R.I. = (1.5295, 0.1000); Dispersant R.I. = 1.3300]	
Analysis Model: Polydisperse	Residual: 0.867 %	
Modifications: None		

Result Statistics			
Distribution Type: Volume	Concentration = 0.0829 %Vol	Density = 2.560 g / cub. cm	Specific S.A. = 0.0689 sq. m / g
Mean Diameters:	D (v, 0.1) = 24.53 um	D (v, 0.5) = 98.91 um	D (v, 0.9) = 210.15 um
D [4, 3] = 108.86 um	D [3, 2] = 34.03 um	Span = 1.877E+00	Uniformity = 5.799E-01

Size (um)	Volume Under %	Size (um)	Volume Under %	Size (um)	Volume Under %	Size (um)	Volume Under %
0.335	0.00	1.87	0.97	10.40	4.07	57.97	28.36
0.359	0.00	2.00	1.04	11.14	4.32	62.10	30.63
0.384	0.00	2.14	1.10	11.93	4.59	66.51	33.04
0.411	0.00	2.29	1.17	12.78	4.89	71.25	35.60
0.441	0.00	2.46	1.25	13.69	5.22	76.31	38.31
0.472	0.00	2.63	1.32	14.66	5.58	81.74	41.19
0.506	0.00	2.82	1.40	15.71	5.99	87.56	44.22
0.541	0.00	3.02	1.48	16.83	6.45	93.79	47.42
0.580	0.00	3.23	1.56	18.02	6.95	100.5	50.77
0.621	0.00	3.46	1.66	19.30	7.51	107.6	54.27
0.665	0.00	3.71	1.75	20.68	8.14	115.3	57.89
0.713	0.01	3.97	1.86	22.15	8.83	123.5	61.63
0.764	0.03	4.26	1.97	23.73	9.60	132.2	65.46
0.818	0.07	4.56	2.08	25.41	10.45	141.7	69.32
0.876	0.13	4.88	2.20	27.22	11.38	151.7	73.20
0.938	0.20	5.23	2.33	29.16	12.39	162.5	77.02
1.01	0.29	5.60	2.47	31.23	13.50	174.1	80.76
1.08	0.38	6.00	2.61	33.45	14.72	186.5	84.35
1.15	0.46	6.43	2.76	35.83	16.03	199.7	87.70
1.24	0.55	6.89	2.91	38.38	17.44	213.9	90.77
1.32	0.63	7.38	3.08	41.11	18.97	229.2	93.53
1.42	0.71	7.90	3.25	44.04	20.61	245.5	95.90
1.52	0.78	8.46	3.43	47.17	22.36	262.9	97.72
1.63	0.84	9.06	3.63	50.53	24.23	281.6	99.01
1.74	0.91	9.71	3.84	54.12	26.23	301.7	100.00



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FIG 14: Particle size distribution of some Mururoa sediment (site 33)

5. SAMPLE TREATMENT AND ANALYSIS

5.1. Marine sediment samples

The sediment samples were pretreated on site; core sample slices were extruded and individually sealed in plastic bags as were the grab samples. The samples were packed in leak-proof containers and sent to the network laboratories for analysis. All laboratories handled the samples in a similar manner: recording the wet weight, freeze-drying or oven drying, recording the dry weight, crushing by ball-milling or hammer-milling and homogenising. For some sediment samples a particle size analysis was made using a laser mastersizer. A typical particle sample size distribution of a surface sediment sample taken in the Mururoa lagoon is shown in Figure 14. Only about 30 % of the particles were less than 64 μm . The particle size distribution maximum is 150 μm . The deeper layers contain larger particles, even stones of centimeter scale. Open sea sediments usually have much finer particles. As lagoon sediments are composed of coral sand (almost 100% calcium carbonate), their particle size distribution is different.

Gamma-emitting isotopes were determined using HPGe detectors in a calibrated geometrical set-up. Anthropogenic isotopes ^{60}Co , ^{125}Sb , ^{126}Sb , ^{137}Cs , ^{155}Eu and ^{241}Am were usually identified as well as natural ^{210}Pb and ^{226}Ra used for sediment dating purposes.

Different methods were used for radiochemical analysis by the different laboratories. After adding chemical or isotopic yield determinants, the samples were digested, homogenized, checked for any undissolved residues and subjected to a redox treatment to ensure isotopic exchange with the yield determinant prior to chemical separation procedures. The laboratories of the MARINALABS network participating in the project were selected for their capability of providing high precision data in a short time with a minimum of financial requirements. Although they participate regularly in intercomparison exercises, all laboratories participated in proficiency tests organized by IAEA-MEL to ensure correct analytical quality management throughout the project.

^{210}Pb measurements were made in sediment cores to estimate sedimentation rates and the time history of the sediments. ^{210}Pb and ^{226}Ra (for the calculation of the excess ^{210}Pb in sediment profiles) were measured by alpha (^{210}Pb) and gamma-spectrometry on sections of selected sediment cores. The ^{210}Pb profiles with depth have shown heavy mixing of surface sediments. The sedimentation rates estimated for depths below 10 cm were between 1 and 2 mm per year.

The dominant activity in the sediment was due to $^{239+240}\text{Pu}$ (up to 1 MBq/kg dry weight). Depth profiles showed that actinides are well mixed down to 15 cm, but in some areas, even down to 2 meters. Cumulative inventories of radionuclides have shown that saturated values were not reached at almost all sites and therefore, the inventories were underestimated.

5.2. Terrestrial soil, debris and core samples

The initial sample preparation was carried out on site in order to categorize the samples and to facilitate identification, packaging and shipment. Topsoil samples of about one kg were sieved to remove debris larger than 5 mm and dried for 24 hours at 110°C to constant weight. The dry samples were then milled to a particle size of 0.5 mm and homogenized. A similar procedure was used for exposed sediment and sand samples and for the individual layers obtained from the soil cores. Bedrock cores were sliced with a water cooled band saw before

crushing and milling. Bulk materials to serve as potential future reference and quality control materials for soil radionuclide analysis were also collected.

Gamma-spectrometry was carried out by using HPGe detectors in a calibrated high efficiency counting geometry. The same isotopes observed in the marine sediment samples were identified. Duplicate or triplicate measurements were usually carried out as part of the validation and quality control measures.

The moisture content was determined on 1 to 3 g samples dried at 105°C until constant weight. This usually took about four hours with a weight loss of less than 0.5 % as the samples had already been dried on-site. The processed and homogenized samples (200 to 300 g) were subsequently ashed in a large porcelain dish in an electric muffle oven. The temperature was raised gradually from 25°C to 300°C over six hours, then rapidly raised to 600°C and maintained at 600°C for six hours.

Rather than the standard 10 g sample size for environmental samples, only 2 g samples were used for the following reasons:

- a) activity concentrations were expected to be larger than in usual environmental samples;
- b) smaller samples allow faster digestion and shorter dissolution times;
- c) the low amount of rare earth elements expected in the samples would not cause interference with Am separations (usually reducing the Am yield in lengthy procedures);
- d) the natural Sr content being quite large would not fit to the standard ^{90}Sr separation procedure, which was optimized for 10 mg of natural Sr carrier.

The smaller sample size raised the minimum detectable activity levels and adversely affected the sampling error because of the greater sensitivity to sample heterogeneity.

Before starting the sample digestion procedure yield determinants for the different isotopes of interest were added: ^{236}Pu for plutonium isotopes and ^{243}Am for Am and Cm isotopes, as the separation procedure does not fractionate these elements; natural Sr in the samples was determined and used as a yield determinant for the separation of ^{90}Sr . The use of ^{243}Am also introduces also the daughter isotope ^{239}Np in equilibrium into the sample, which can be used as a yield determinant for measurements of ^{237}Np .

The 2 g ash samples were weighed and transferred with 1 M nitric acid into a 250 ml PTFE beaker. Yield determinants were added to the slurries using calibrated pipettes. The sample was dissolved in 20 mL of 65 % nitric acid. 20 mL of 40 % hydrofluoric acid were then added to increase the efficiency for dissolving plutonium bearing particles. A precipitate of calcium fluoride usually formed and the slurry was boiled for about three hours and then evaporated to a thick paste. A second portion of 20 mL 40 % hydrofluoric acid was added and evaporated. Hydrofluoric acid was then removed by three successive evaporations of 20 mL 65 % nitric acid. Usually the black undissolved particles in the initial solution had disappeared and possibly some white particles remained. After evaporation of the third nitric acid addition to near dryness, 30 mL of 32 % hydrochloric acid 1 g of boric acid were added. The mixture was digested for several hours resulting in almost all cases in a clear solution. The solution was then again converted to nitrate by adding 50 mL of 65 % nitric acid and evaporation. A final addition of 50 mL of 0.1 N nitric acid and evaporation to less about 10 mL resulted in a sample solution which was invariably clear. The solution was then filtered through a 25 mm diameter 0.2 micron polysulfone membrane filter and rinsed with 1 N nitric acid. To the

filtrate of about 100 mL 1 N nitric acid about 10 mg of iron carrier was added and 0.5 mL of 100 % hydrazinium hydrate, which reduced Fe (III) to Fe(II). Reduction usually took about 10 to 20 minutes and could be tested with a spot test using 1 M ammonium rhodanide, which should have turned pale pink (deep-red before reduction). The Fe(II) in turn reduced all soluble plutonium species to the trivalent state, thereby ensuring isotopic exchange with the isotopic yield determinant ^{236}Pu . This solution was reserved for subsequent radiochemical separations [4] of the radionuclides of interest. The loaded filter was rinsed with 80 % ethanol and air-dried. The filters did not usually have any insoluble matter. Nevertheless they were measured with a low background gas-flow proportional counter to check for undissolved hot particles. In two out of about 40 samples plutonium could be measured despite the aggressive digestion procedure. The spectral degradation indicated a probable particle size below 0.2 micron. The total activity could therefore be estimated with an acceptable uncertainty. The correction made to the bulk quantity in the filtrate due to this undissolved fraction was usually less than 10 %.

6. DETECTION OF HOT SPOTS AND ISOLATION AND MEASUREMENTS OF HOT PARTICLES

6.1. Marine sediments

Hot particle analysis was confined to the sediment samples collected from the Colette sandbank. To obtain hot particles from the coral sand, it was digested in 1 M HCl and the resulting residue filtered off using a 50 mm diameter and 0.45 μm membrane filter. A scan of samples on a filter paper with a thin window GM counter indicated the presence of significant alpha activity (2-220 counts per second). This information was used to determine an initial exposure (1-5 min) for the assay of hot particles by CR39 plastic sheet (polyallyl diglycol carbonate) detectors. Track concentrations from individual hot particles, as recorded on the plastic sheet, were captured with a combined microscope-image analysis system and the digitised image stored on a hard disc. A graticule image was similarly stored to provide a calibration scale. The actual dimensions of the rectangular field captured in the image was 1.05 x 0.78 mm. The hard copy image (Figure 15) used to assess the activity and size of the individual active particles was 229 x 171 mm (an overall linear magnification of 218x). The total particle activities in the two samples.

Aliquots might be in the ranges 210-280 Bq and 2400-3200 Bq, corresponding to concentrations in the raw sediment samples of $(1.8-2.5) \times 10^5$ and $(7.2-9.6) \times 10^5 \text{ Bq kg}^{-1}$ respectively. These estimates may be compared with the activity concentrations of 6.4×10^5 and $5.9 \times 10^5 \text{ Bq kg}^{-1}$ estimated on the basis of radiochemical separation. Given the evident inhomogeneity of the particle activities, the fact that longer exposure periods would probably have revealed lower activity hot particles and the uncertainties in the estimation of the activities in the hot particles by the track etch method, this level of agreement may be considered satisfactory.

Spherical particles of pure plutonium with activities of 10 and 500 Bq would have diameters of 8 μm and 29 μm respectively. The apparent sizes (radius from approx. 10 to 100 μm) and estimated activities (from approx. 1 to 500 Bq) of the investigated hot particles, indicated that these particles were not pure plutonium; it was considered more likely that the plutonium had been mixed with an inactive matrix and that the carrier particles had a larger size.

Overall, it may be concluded that the sediment on the Colette sandbank contained up to 10^4 hot particles per kg with activities in the range of 10-2000 Bq and sizes less than approximately 0.5 mm.

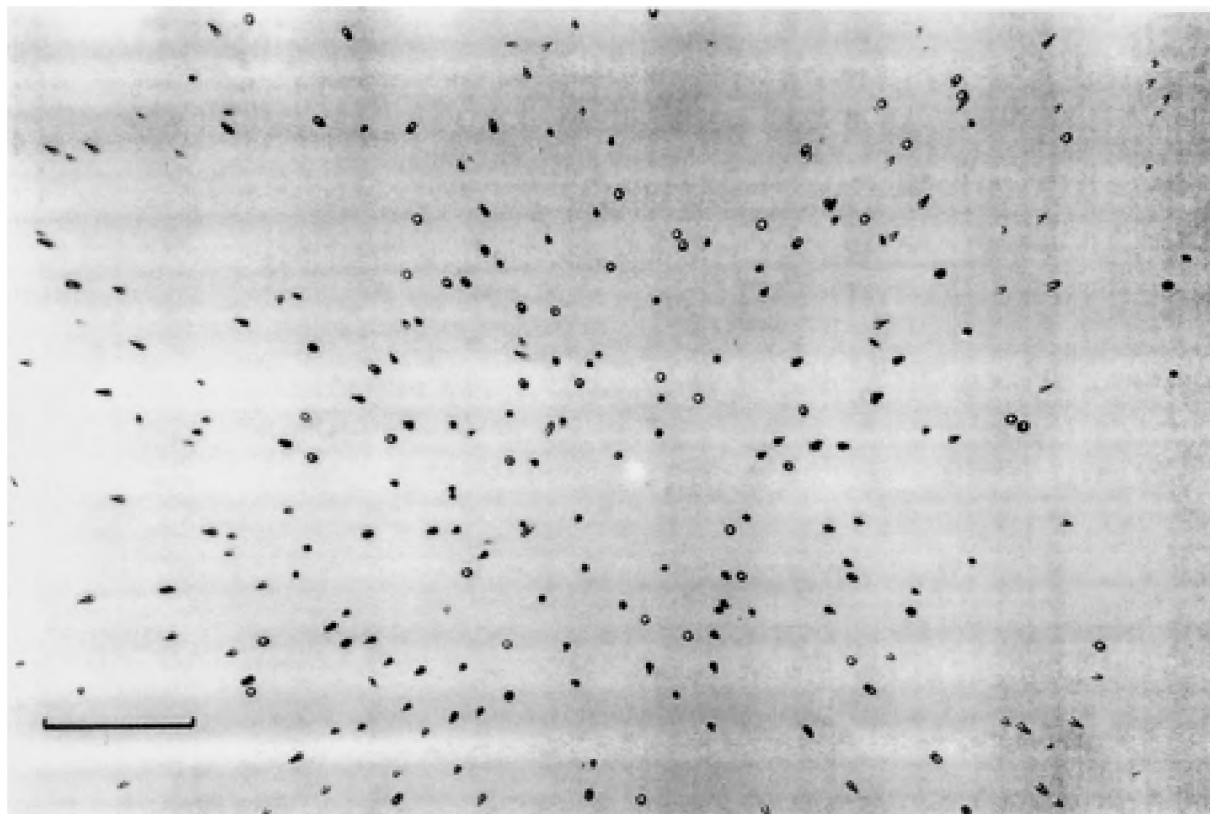


FIG 15: Hot particles (2-3 centres of activity with 15-20 μm particles in the radius), radius of the spot $\sim 65 \mu\text{m}$, activity $\sim 30 \text{ bq}$ (sample 204302-C). Scale bar 100 μm

6.2. Terrestrial soils and corals

Hot Spots

To learn more about the spatial distribution of hot-spots the IAEA team also conducted a survey of a 10 m x 10 m (100 m^2) area, chosen arbitrarily in the center of a contaminated site. The 10 m x 10 m square was marked at one meter intervals. The area was thus divided into 100 squares of 1 m^2 . Each square was then scanned along 5 to 6 cm wide adjacent strips using a NaI detector of 5 cm in diameter. For this exercise hot spots were defined as areas smaller than 20 cm^2 with ^{241}Am activity exceeding 50 Bq. They were measured by an NaI detector suitably calibrated. Activities lower than 50 Bq were neglected. Two in-situ gamma-ray spectra were also measured in the center of this 10m x 10m area.

Hot-spots (as previously defined) located over this area were very unevenly distributed. The ^{241}Am activities in each square meter were converted into ^{239}Pu activities by multiplying them by 50, which was arbitrarily assumed to be a representative constant value of the $^{239}\text{Pu}/^{241}\text{Am}$ ratio. ^{239}Pu activities in the 1 m^2 squares containing hot spots falling in the range of 1 up to 83 MBq/ 100 m^2 were obtained. When the activities of all the hot spots were added and averaged over the entire 100 m^2 , a ^{239}Pu activity of 5 MBq/ 100 m^2 was found. However it must be pointed out that in this investigation a hot spot was defined as an area of not more than 20 cm^2

with ^{241}Am activity exceeding approximately 50 Bq (this corresponds to having set the threshold of the probe reading at 100 counts in 30 s). Therefore all readings lower than this threshold were considered as “background”. This “background” may have contributed to ^{241}Am activities of up to 24.1 kBq/m² corresponding to ^{239}Pu activities of up to 120 MBq/100 m². This result was confirmed by the two in-situ gamma-spectrometry measurements performed in the center of this 10 m x 10 m square, which gave ^{241}Am concentrations of 22.4 kBq/m² and 22.0 kBq/m², corresponding to a ^{239}Pu concentration of 110 MBq/100 m². It would appear that the hot spots contribute to less than 5% of the overall ^{239}Pu activity in the upper soil layers. The frequency distribution of the hot spots shows that 50 % of them have an activity below 30 Bq/cm², 75 % are below 60 Bq/cm², 90 % are below 120 Bq/cm² and 95 % are below 180 Bq/cm². A few spots with up to 400 Bq/cm² were identified.

These data do not give any information on whether the residual Pu contamination was fixed to the coral bedrock or was present in an easily removable form.

Hot Particles

Information on the presence of relatively large (visible to the naked eye) particles containing Pu was been obtained by the IAEA from the analysis samples of fine coral debris, samples of loose coral pieces and single hot-particles identified on site. Some particles were directly identified and collected for further analysis. A few particles with lower radioactivity were later isolated from the sand samples in the IAEA's Seibersdorf laboratories.



FIG 16: Screening corals looking for "hot" particles.

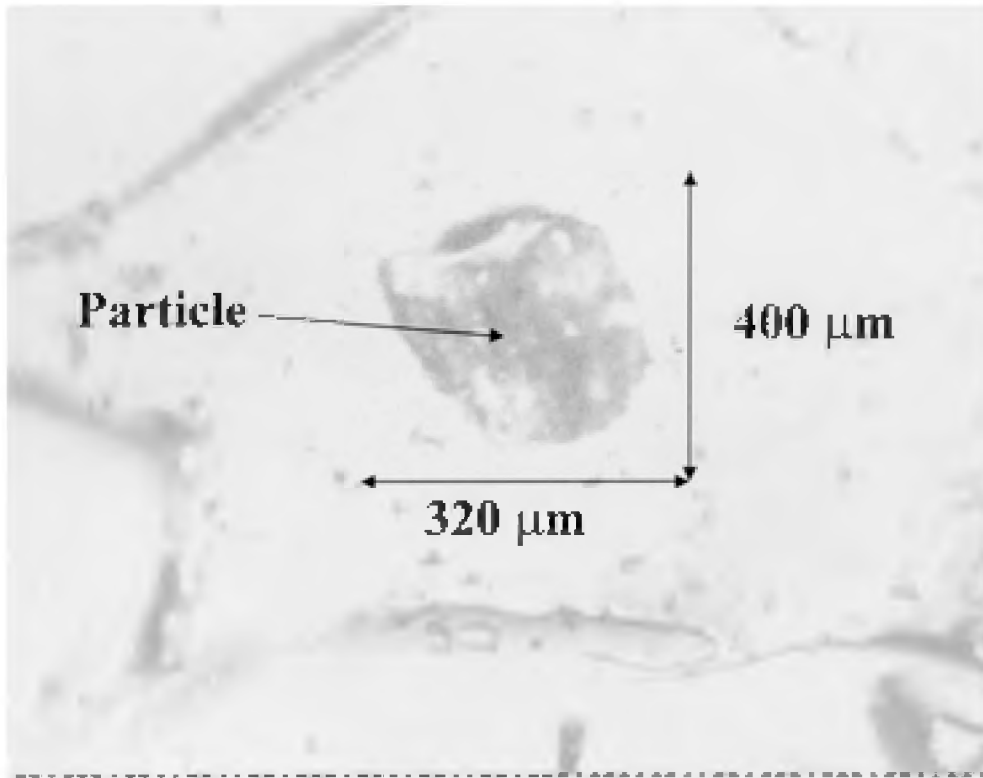


FIG 17: Optical image of hot particle nr 4 (different scales for horizontal and vertical axis).

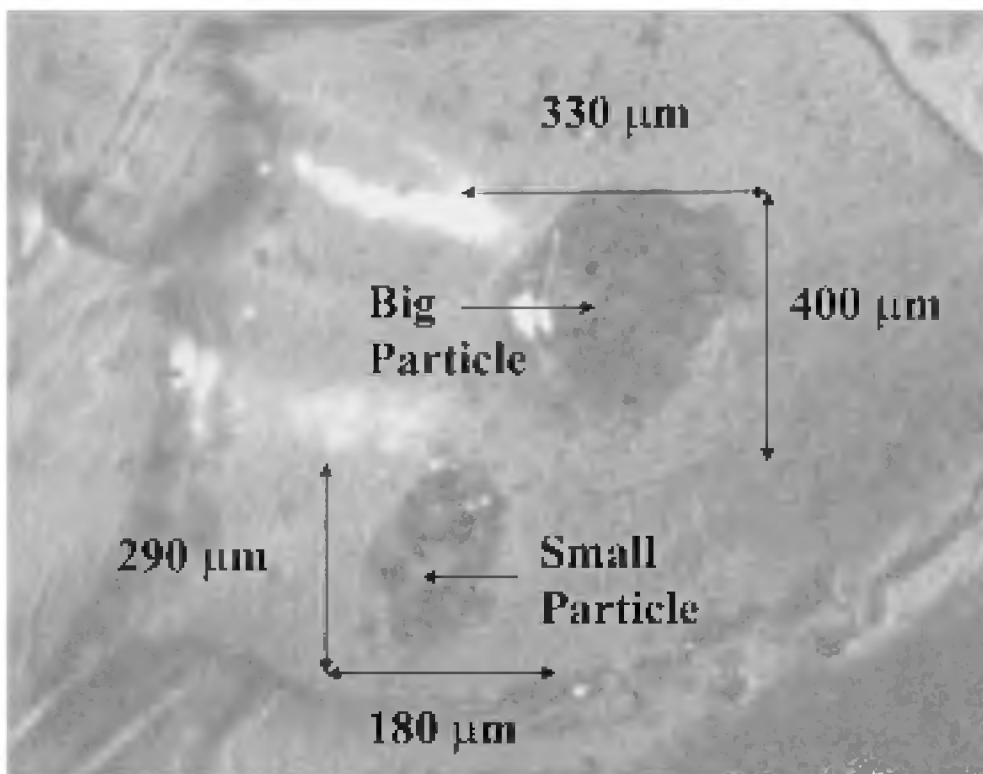


FIG 18: Optical image of hot particle nr 5 (different scales for horizontal and vertical axis).

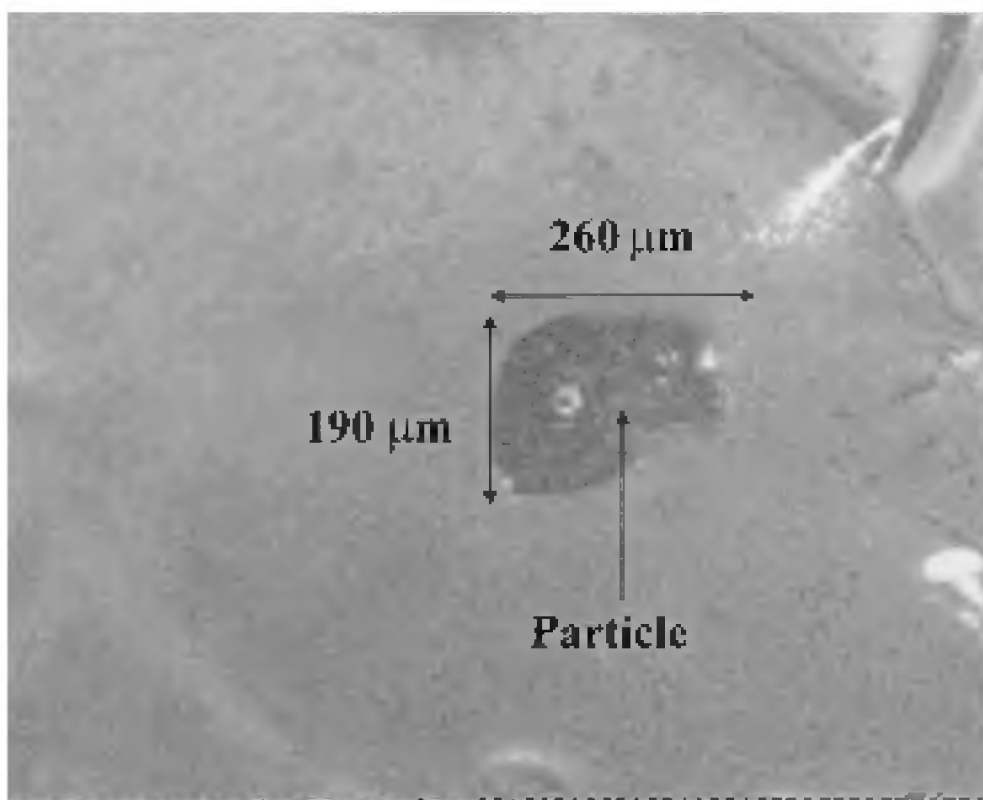


FIG 19: Optical image of hot particle nr 8 (different scales for horizontal and vertical axis).

Samples from the test sites thought to contain hot particles (sand, loose coral rock etc.) were carefully screened in the IAEA laboratories (Fig. 16). The lower detection limit of the screening technique was approximately 70 Bq for ^{241}Am , which was taken as an indicator for plutonium contamination. The hot particles identified were separately investigated by special methods.

Radioactive particles were identified in five samples at the Seibersdorf Laboratory by distributing 5 to 7 mm of debris on a sheet of glossy paper. This layer of debris was scanned by a probe (Ratemeter ROTEM, model RAM-A, S/N 0182094 with a low-energy photon probe based on a thin NaI scintillation crystal, model No. 1173057, S/N PM-10) at a distance of 5 to 10 mm. The probe was protected against possible contamination by a thin sheet of polyethylene. This procedure gave a detection limit of about 70 Bq of ^{241}Am (evaluated experimentally in a simulated screening experiment) corresponding to about 3500 Bq of ^{239}Pu . Once a hot-particle was identified, it was collected on a small piece of adhesive tape and placed on a Petri dish. Often the adhesive tape collected not only the hot particles but also a number of other adjacent (not necessarily radioactive) particles. The debris layer was then screened a second time to search for particles which could have been missed during the first scan. The hot-particles were then measured for ^{239}Pu and ^{241}Am by gamma-ray spectrometry. Nine hot-particles were identified in the first sample (3.6 kg), three in the second sample (3.2 kg), and one in the third and the fifth sample (none in the fourth sample).

In another series of samples, each weighing about 4.0 kg and consisting of several loose coral rocks, hot-particles were searched for on the surface of the rocks (approximately 5 to 15 cm in diameter) using the probe described above. The rocks were turned one by one around the probe at a distance of 5 to 10 mm. Once a hot-particle was found, the rock was broken, the

particle isolated and then measured by gamma-spectroscopy. Four hot particles found in one sample were thus identified.

All particles, including the two single particles, directly identified and isolated on the test site, were analysed by gamma-spectrometry.

The measurements, corrected for counting geometry, allowed the determination of the ^{239}Pu and ^{241}Am activities of the twenty “hot-particles”. The data could not be corrected for gamma-ray self-attenuation due to the present limited knowledge of the chemical composition of these particles. Therefore, the real activity values may be underestimated.

The lower $^{239}\text{Pu}/^{241}\text{Am}$ ratio shown in the particles compared to that measured by in-situ gamma-spectrometry could be due to the different age and purity of the Pu “seen” by this method.

In order to obtain information on the size, shape and composition of the particles, optical microscopy and X-ray fluorescence (XRF) were used. The results of this investigation are reported in detail in Appendix II of the Mururoa Technical Report [1] [5].

Compositional analysis of the particles was performed by XRF (a non destructive microanalytical technique) to permit further investigations on the particles (for examples solubility studies) and in consideration of the expected microscopic heterogeneity of particle composition. The limited number of particles investigated shows considerable heterogeneity in composition. Interpretation and extrapolation of the data to characterize site contamination is hampered by the specific collection/identification methodology which restricted the activity and size of the particles examined, by the limited fraction of the particle area which was explored in the XRF study (it ranged from 5% to 37% of the cross-sectional area), some of the assumptions which had to be made for the interpretation of the XRF spectra, and finally by the intrinsic limitation of the XRF technique which does not permit the identification of light elements (atomic number < 13) and by some heavy elements when present at low concentration together with other more abundant ones.

The optical images (Fig 17, 18, 19) showed that the particles had diameters ranging between ~200 and ~500 μm , i.e. sizes which are of minor concern as an inhalation hazard. Half of the particles showed a relatively smooth surface and appeared as compact, single entities. The remaining ones appeared to have a rougher surface and could be a conglomerate of smaller particles.

The results show that Ca and Fe were present in all particles, indicating a CaCO_3 matrix (as expected) and that the particles also had a metallic component (Fe). The presence of Mn, Ni, Cr, Co and Ti in many particles probably originated from the steel containers of the fissile material used for the tests. The presence of Cl most likely arose from sea salt. The presence of U (in all particles) and Np (in six out of seven), at concentrations always 10 to 100 times lower than Pu, probably reflected the initial presence of actinide impurities in the plutonium used for the tests.

The results of semi-quantitative analysis showed large variations in concentration for the same element from particle to particle and within the same particle, pointing to a considerable compositional heterogeneity.

7. SIZE FRACTIONATION

Information on the distribution of the ^{239}Pu and ^{241}Am activities among the various particles of fine coral debris was obtained by sieving. This was done after a single large radioactive particle with an activity of 6,700 Bq had been removed. The sieved sample had a total weight of 1053 g. The following fractions were separated:

> 2 mm, between 1 mm and 2 mm, between 250 μm and 1 mm, between 125 μm and 250 μm , between 71 μm and 125 μm , between 50 μm and 71 μm and < 50 μm .

The various fractions were measured by gamma-spectrometry. The data show that 99.85% of the mass and 95.8 % of the activity was contained in particles larger than 250 μm . On the other hand, the highest activity per unit mass (Bq/g) was measured in particle size fractions of less than 125 μm . It is worth noting that ^{239}Pu activity concentration in particles of less than 50 μm , a size fraction of some concern with respect to the risk of inhalation or incorporation in wounds, represented only 1 % of the total activity in the sample. The specific activity of this fraction was around 240 Bq/g.

8. QUALITY ASSURANCE AND QUALITY CONTROL

8.1. Sample collection, pretreatment and distribution

The entire sampling procedure itself as well as the preparation, storage and distribution of the samples was carried out using stringent quality assurance measures in order to maintain sample identity and integrity throughout the study.

The sampling sites were photographed with a table showing the sample code and the date and time of sampling. Sampling operations were recorded using video cameras. The data were transferred daily to a personal computer and for security reasons copied on floppy disks. During sample collection and on site preparation, special care was taken not to contaminate or cross-contaminate the samples and all sample collection and preparation details were documented.

On Mururoa, samples were prepared in different laboratories, according to the expected activity level. In the Agency's Laboratories in Seibersdorf the samples were treated in the order of expected increasing activity. Whenever possible, the samples, distributed to the ALMERA Network laboratories for analysis, were selected from samples having a similar activity level in order to avoid cross-contamination during analysis.

A major point of concern was the homogeneity of the processed samples before distribution to the different laboratories for analysis. Sample homogeneity is important in order to assure the comparability of results. Special care was therefore taken in the final homogenization. Homogeneity was verified by gamma-spectrometry of several sub-samples before shipment to the ALMERA Network laboratories. In general the homogeneity was satisfactory.

The presence of hot particles was expected in samples taken at the test sites. Therefore, all laboratories were requested to perform double determinations and to check any undissolved part of the samples, which could contain hot particles.

8.2. In-situ Measurements

Each measurement was documented and the spectra and measurement locations clearly coded. The locations were photographed for future reference and inspection. The energy calibration

of the detector was checked daily. All recorded spectra were evaluated on site, inspected for anomalies and saved in duplicate on floppy-disks.

The in situ efficiency response of the gamma-spectrometer was modeled for a standard soil matrix using a Monte Carlo approach according to Briesmeister [6]. The accuracy of this calculated efficiency curve was checked via a series of measurements with calibrated point sources containing ^{241}Am and ^{152}Eu , which have gamma rays of energy similar to ^{239}Pu . The calculated efficiency agreed with the measured efficiency to within 5 to 7 %, which is of the order of their combined respective uncertainties.

8.3. Sample Measurements

The participating laboratories were requested to fully document their sample measurements and to include systematic measurements on reference materials and report these results together with the results for the samples. Cross-checks between external laboratory results and the Agency's Laboratories in Seibersdorf were carried out.

8.4. Data Reporting and Evaluation

The results provided by the laboratories for the samples and for the reference materials were carefully screened and any discrepancies, ambiguities or doubtful data were investigated and clarified. The activity concentration ranges reported were carefully established from the individual results and independently cross-checked for consistency.

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PRELIMINARY CHARACTERIZATION OF TWO SEDIMENT REFERENCE MATERIALS AT THE IAEA SEIBERSDORF LABORATORIES USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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Abstract. Since 1961, The International Atomic Energy Agency (IAEA) through its Analytical Quality Control Services (AQCS) has been providing reference materials characterized for radionuclides, trace/toxic elements, stable isotopes and organic contaminants for the benefit of the laboratories in its Member States. In the majority of cases, the values for the analytes of interest for a particular AQCS reference material represent consensus values derived from the statistical evaluation of the results from an intercomparison exercise involving a large group of laboratories. However, before a candidate material can be distributed for an intercomparison exercise, the IAEA AQCS must process and check the homogeneity of the material by measuring a number of analytes of interest to determine the minimum sample intake mass that is representative of the bulk material. In the case where the analytes of interest are stable elements, the IAEA has a number of nuclear and non-nuclear analytical techniques which it uses to measure the elements of interest. This paper describes the IAEA AQCS efforts in the preliminary characterisation of one IAEA candidate Baltic Sea sediment reference material and a second New York Harbour sediment reference material where instrumental neutron activation analysis was used to determine the concentrations of approximately twenty elements in each material.

1. INTRODUCTION

The International Atomic Energy Agency (IAEA) has been assisting laboratories in its Member States (MS) to maintain and improve the reliability of their analyses through the distribution of biological, environmental and marine reference materials (RMs) prepared and characterized under its Analytical Quality Control Services (AQCS). Currently there are over 90 RMs in stock which have been characterized for a variety of analytes including: trace and toxic elements (30); anthropogenic and primordial radionuclides (27); stable isotopes (37) and organic/organo-mercury contaminants (8). Prior to characterization, the majority of these materials had to undergo a variety of processing steps (drying, cutting, chopping, blending, sieving, grinding, milling and particle size analysis) to ensure the materials were adequately mixed and homogenized. To evaluate the effectiveness of the mixing/homogenization process, the IAEA Laboratories in Seibersdorf have a variety of nuclear and non-nuclear analytical techniques available. These include in the case of elemental analysis: instrumental neutron activation analysis (INAA), X ray fluorescence (reflective, transmission and micro-XRF), proton induced X ray emission, atomic absorption spectrometry, inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry (ICP-MS). In the case of radionuclide analysis, the analytical techniques include: gamma-spectrometry, alpha-spectrometry, liquid scintillation counting, gas proportional counting, ICP-MS and INAA. INAA is the technique frequently used by Seibersdorf for the preliminary characterization of the element content as it is non-destructive, has excellent sensitivity for a large number of elements and suffers from minimal matrix effects and interferences. As this TEC-DOC is specifically concerned with the topic of sediments, this paper deals with the preliminary elemental characterization of two sediments, a Baltic Sea sediment (IAEA-300) and New York Harbour sediment, using INAA.

2. DESCRIPTION OF MATERIALS

The IAEA-300 Baltic Sea sediment sample was collected by the "Federal Maritime and Hydrographic Agency", Hamburg, Germany, during July 1992 in the Baltic Sea on board of RV VALDIVIA. This material was sampled with a large BSH box corer (500 x 500 mm) and the fraction 0-10 cm top layer was kept for the exercise. This sediment was muddy, clayish and mainly anoxic, except the upper 0-3 cm layer which was oxic. This material was freeze-dried and the final amount obtained was around 39 kg dry weight. This material was ground in a ball mill and further homogenized by mixing in a stainless steel rotating drum for approximately one week. Greater than 99% of the material was in the size fraction below 500 μm . Only 6.7% of the material was below 63 μm and 90.9% between 63 and 250 μm . The moisture content of the sediment was determined by drying several aliquots of the material in an oven at 80°C to constant weight and was found to be 14% at the time of sample preparation.

The New York Harbour sediment sample was collected by the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA, from six contaminated sites in the vicinity of New York Bay and Newark Bay during October 4-5, 1994. A total of approximately 2100 kg (wet weight) sediment was collected by an ACE epoxy-coated modified Van Veen-type grab sampler. Samples from each sampling site were stored separately, freeze dried and kept in the dark before further processing. Samples were then combined, granulized and sieved. The material was sieved into three fractions: coarse (>250 μm) weighing approximately 140 kg which was discarded, medium (between 61 and 250 μm) weighing approximately 180 kg which was taken for further processing, and fines (<61 μm) which was not used in this work but was kept for other purposes. The fraction of the material with a particle size between 61 and 250 μm was then homogenized in a large core blender (double blend, 25 min per blend), stored in polyethylene bags and sterilized to a total dose of 27.5 kGy using a ^{60}Co source. After sterilization the sediment material was bottled and stored at approximately 20°C in the dark. A number of these bottles were received from NIST at the IAEA AQCS to be rebottled as 20 g samples for future intercomparison exercises. After rebottling, the samples were re-sterilized to a total dose of 25 kGy using a ^{60}Co source.

3. ANALYSIS AND RESULTS

For each sediment, a total of 10 sub-samples, each from a different bottle and weighing approximately 50 mg, were sealed in quartz ampoules. These twenty samples were irradiated together with multi-element standards and two 50 mg samples of NIST SRM-1941 marine sediment as a quality control standard, at the nuclear reactor ASTRA in the Austrian Research Center, Seibersdorf. The samples were irradiated at a neutron fluence rate of $7 \times 10^{17} \text{ m}^{-2}\text{s}^{-1}$ for a period of 30 minutes. Standards were prepared by aliquoting 50 μL of a multi-element standard solution onto a 25 mm Whatman filter paper which was allowed to air dry and then sealed in quartz ampoules.

Prior to measurement, the samples were stored for six days to allow activity levels to decay to acceptable levels where dead time losses would typically be less than 20%. All samples, standards and QC standards were measured on a gamma-spectrometry system equipped with a sample changer. The gamma-spectrometry system consisted of an Ortec PopTop GEM-20 170-P-Plus-S (transistor-reset preamplifier) of 20% relative efficiency (FWHM of 1.85 keV at 1.3 MeV), and NIM electronics: Ortec 672 amplifier (pulse shaping time of 3 μs), analogue to

digital converter (model ND 581), loss free counting module (model ND 599), dual counter timer (Canberra model 2071 A) and bias supply (Ortec model 459). The sample-to-detector distance was approximately 1 cm. All samples, standards and QC standards were measured at two separate times: (i) several days after irradiation for a period of one hour to measure short-lived activation products (half-lives of hours to days), and (ii) four weeks after irradiation for a period of four hours to measure long-lived activation products (half-lives of days to months).

TABLE I: CONCENTRATION OF ELEMENTS IN A BALTIC SEA SEDIMENT BY INAA

Baltic Sea Sediment			
Element	Concentration [mg/kg]	Uncertainty [mg/kg] due to counting statistics	Standard deviation [mg/kg] from 10 samples
As	53.6	0.6	7.7
Br	187	19.3	12
Ce	111.4	1.0	1.3
Co	22.11	0.31	0.27
Cr	98.4	1.8	1.2
Cs	8.51	0.18	0.26
Eu	1.46	0.11	0.14
Fe	65561	901	574
La	84.1	0.6	91.4
Mo	4.1	0.5	2.9
Rb	172.9	7.4	5.6
Sb	1.24	0.20	0.17
Sc	16.8	0.22	0.16
Se	2.93	0.6	0.6
Th	17.88	0.26	0.22
U	6	0.22	3.2
Zn	221.2	4.1	4.7

Concentrations were calculated from Canberra GENIE-PC peak search reports using an NAA software package prepared by M. Makarewicz (IAEA staff member responsible for gamma-spectrometry). The concentrations of the elements of interest were calculated by the comparator method based on the induced activities of the activation products in the standards compared to those in the sediments. The results for the two sediments are reported in Tables 1 and 2 and are depicted graphically in Figures 1 and 2. For each sediment, the table of results contains the average measured concentration of each element based on the results from the 10 samples, the uncertainty in a measured value arising from the counting statistics and the standard deviation of the average value arising from the 10 sample measurements. If for a particular element, the standard deviation was significantly greater than the uncertainty due to counting statistics, then the material was considered heterogeneous with respect to this element for sample masses less than or equal to 50 mg. Based on this criterion, the New York Harbour sediment was considered heterogeneous for the following elements: As, Ce, La, Mo, Th and Zn; and the Baltic Sea sediment for the elements As, La and U.

TABLE II: CONCENTRATION OF ELEMENTS IN A NEW YORK HARBOUR SEDIMENT BY INAA

New York Harbour Sediment			
Element	Concentration [mg/kg]	Uncertainty [mg/kg] due to counting statistics	Standard deviation [mg/kg] from 10 samples
Ag	6.38	0.53	0.700
As	18.6	0.19	1.4
Au	0.103	0.003	0.01
Br	123.3	12.6	4.9
Cd	7.4	0.9	1.5
Ce	74	1	44
Co	12.89	0.18	0.44
Cr	247	4	14
Cs	2.8	0.18	0.26
Eu	1.29	0.09	0.37
Fe	35422	495	763
Hg	3.53	0.28	0.28
La	39	0.3	19
Mo	4.9	0.5	3.8
Ni	78	30	11
Rb	67.1	5.5	6.6
Sb	4.39	0.18	0.57
Sc	10.04	0.13	0.14
Se	2.88	0.49	0.36
Th	12.7	0.2	8
U	3.14	0.18	0.51
Zn	633	9	38

The results for the NIST SRM-1941, together with the known NIST values are reported in Table 3. In general, the measured results for the NIST SRM-1941 are approximately 5% lower than the certificate values. The bias could be due to a combination of small differences in the geometry of standards compared to samples (rolled filter paper versus compact powder), and to flux variations (temporal and positional) at the various sample positions. Although the sample holder was designed to rotate during irradiation to average out positional flux variations, it is possible for the container to jam against the irradiation channel preventing its rotation and leading to variations in total neutron exposure of several percent across the sample container.

4. CONCLUSIONS

Instrumental neutron activation analysis has been used successfully to characterise two sediment reference materials for approximately 20 elements covering the range of 0.1 ppm for Au up to 65,000 ppm for Fe. The accuracy of the results has been established through the simultaneous irradiation and analysis of a NIST sediment (SRM-1941) where the analysis results agree with the certificate values within 5%. This work clearly demonstrates the distinct

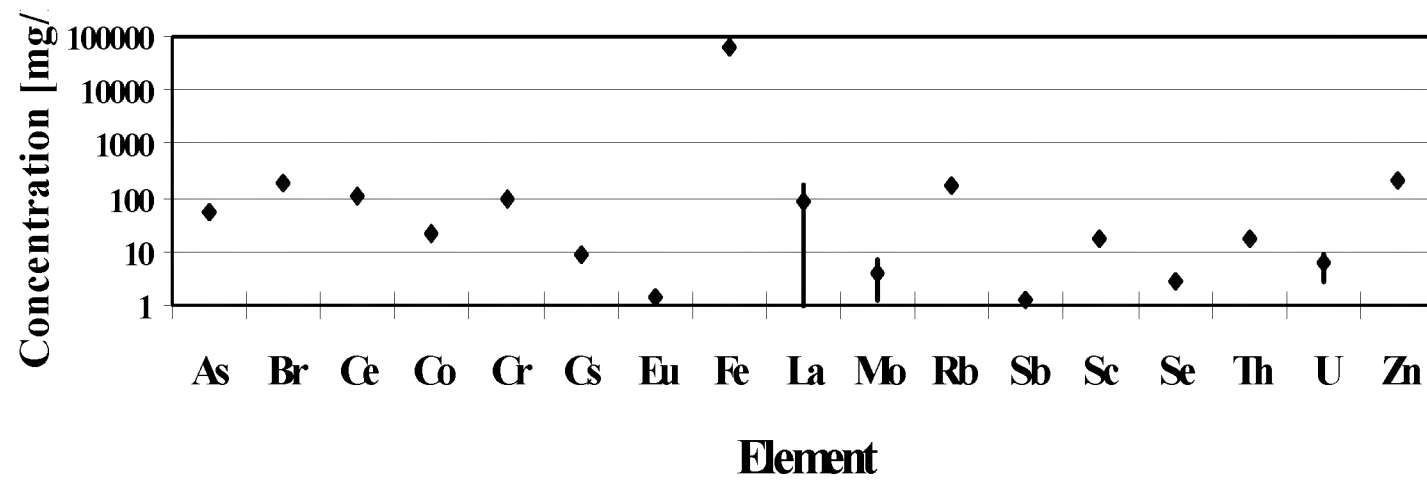


Fig.1: Element concentrations measured in Baltic Sea Sediment by NAA.

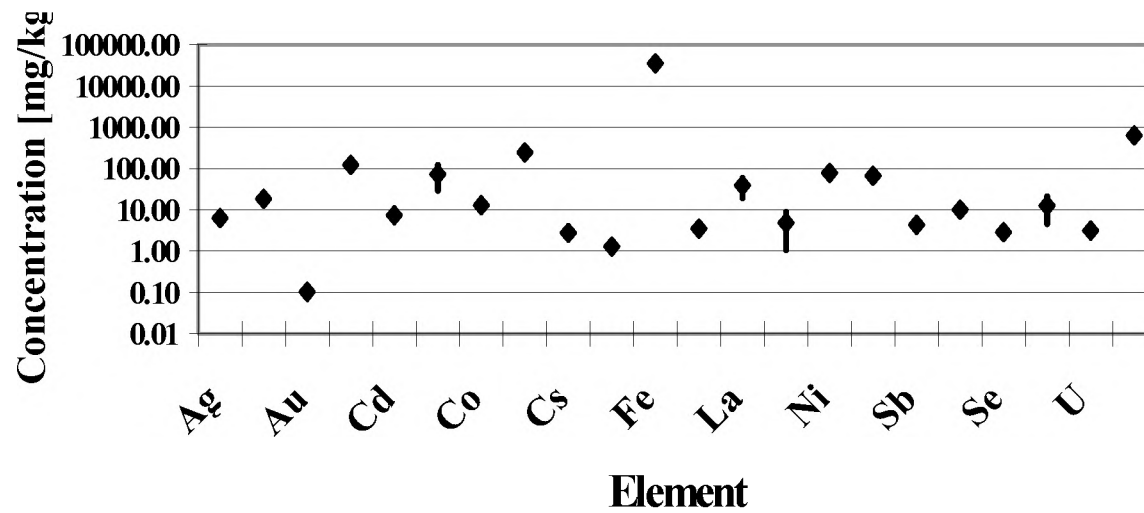


Fig.2: Element concentrations in New York Harbour Sediment by NAA.

TABLE III: CONCENTRATIONS OF ELEMENTS IN NIST SRM-1941 BY INAA

NIST SRM-1941 Marine Sediment			
Element	Concentration [mg/kg]	Standard deviation [mg/kg] from 2 samples	NIST Value [mg/kg]
Ag	1.86	-	1.2 ± 0.5
As	70.9	0.9	75 ± 4
Au	0.014	0.008	-
Br	144	3	-
Cd	<5	-	2.3 ± 0.3
Ce	272	3	272 ± 4
Co	26.1	0.7	27.5 ± 0.1
Cr	608	9	640 ± 10
Cs	4.4	0.3	4.8 ± 0.1
Eu	2.12	0.10	2.19 ± 0.06
Fe	101000	1000	106000 ± 1000
Hg	<5	-	-
La	330.0	4.0	360 ± 10
Mo	10.2	0.3	-
Rb	86	5	92 ± 1
Sb	15.1	0.9	15.2 ± 0.4
Sc	32.4	0.4	34.4 ± 0.4
Se	34.8	0.8	10.1 ± 0.2
Th	25.3	0.3	25.6 ± 0.3
U	15.7	0.7	22 ± 1
Zn	950	10	1010 ± 40

advantages of INAA for multi-element analysis. These advantages include the capability of measuring the concentrations of many elements simultaneously, non-destructively, over a large dynamic range, in very small samples and with minimal interference due to spectral or matrix effects. It should be noted that had a fast pneumatic transfer facility been available, an additional 10-15 elements could have been measured with similar accuracy and precision using short-lived activation products of the elements of interest, leading to a more comprehensive characterisation of the materials.

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