Sampling riverine sediments impacted by acid mine drainage: problems and solutions

C. Herr · N. F. Gray

Abstract Sampling acid mine drainage (AMD) or natural acid rock drainage (ARD)-impacted sediments is complex, requiring appropriate field sampling techniques to ensure representative samples that are both repeatable and reproducible. The important factors affecting sampling of riverine sediments are examined. These include sample site location, field observations, representative sampling, sample collection techniques, and sample preservation. A recommended sampling and processing protocol is presented for AMD- and ARD-impacted riverine sediments, which includes sediment sampling, Fe hydroxide floc sampling, chemical analysis, interstitial (pore) water collection, sediment elutriates, sediment fractionation, and physical analysis. The importance of bioassay testing is discussed, as is quality assurance and assessment approaches to define sediment quality criteria.

Key words Acid mine drainage · Acid rock drainage · Riverine sediments · Sediment sampling

Introduction

Metals in streams may occur as individual fragmented mineral particles or in chemical phases including oxides/hydroxides of Fe, Mn, and carbonate (Mantei and others 1993). For the quantification of metals in stream sediments, it is important to obtain an indication of the variation within a specific location of the river reach, as well as the variation of metal content of an individual sample. Higher quantities of metals generally accumulate on smaller sediment grain fractions because of the higher surface area-to-grain size ratio (Gibbs 1973). The discharge of acid mine drainage (AMD) and acid rock drainage (ARD) not only introduces large quantities of metals that will become associated with the sediment, but also results in the formation of ochreous precipitate consisting largely of Fe. For example, it has been shown that Cu is highly concentrated in ochreous surface depositional material, which is mainly due to accumulation by coprecipitation of Cu with Fe oxyhydroxides (Chapman and others 1983; Herr and Gray 1995). The concentration of elements such as Zn, with high solubility in acidic waters, depend primarily on the pH of the surface waters (Herr and Gray 1995).

The objective of any sampling protocol should be the quantification of the pollution input and the potential risk posed onto the ecosystem. The basic requirements of a sampling protocol should be rapid, inexpensive, easy to apply in the field throughout the year (different seasons), and standardized to allow for comparison with other surveys. The basic tests in current use to characterize the pollution of bottom sediments include: *field observations:* at sampling sites – color of sediment, accumulation of floc material, presence of periphyton; *chemical analyses:* total metal concentration of bulk sediment and/or clay/silt fraction; *physical analyses:* physical characteristics such as grain size, organic carbon; *biological analyses:* benthic macroinvertebrate community structure; and *bioassay testing:* toxicity testing to examine the bioavailability of contaminants.

The impact of AMD and ARD on the biota also depends on the buffering capacity of the receiving river system, resulting in a faster recovery of biota downstream of the outfall due to neutralization of the acidic waters. Because solubility of metals depends strongly on pH and mixing of acid mine water, river water results in heavy Fe hydroxide precipitation and high pollution impact on sediments at the point source.

Sampling considerations

The pattern of metal distribution in sediments downstream from mine wastes depends to a great extent on the characteristics of the particular stream (Lewin and others 1977). The application of appropriate field sampling techniques is critical to the collection of high quality data, i.e., accuracy of results (repeatability and reproducibility) and representative samples. Important considerations that may influence sediment test results and in-

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terpretations include loss of sediment integrity and depth profile, disruption of chemical equilibrium resulting in sorption and desorption, completeness of mixing, and sampling container contamination (Burton 1992). The main objective of field data collection is to ensure that the site is adequately characterized. This can be addressed by: (1) collecting representative samples, (2) using appropriate handling techniques, and (3) proper storage of the sample prior to analysis.

Sample site location

Sites selected for sediment sampling should be easily accessible throughout the year and, if possible, cover areas of already existing water quality data. Higher metal concentrations are detected in the finer sediment usually found in the inside edge of a river bend or channel, in pool habitats, or trapped behind large rocks or by macrophytes. Therefore an attempt should be made to sample similar substrate types. In riverine systems gravelly type substrates (i.e., riffles) only should be sampled (Herr and Gray 1995). These substrates provide a variety of niches for freshwater organisms (i.e., invertebrates, periphyton) and are important for fish spawning. The number of sampling sites depend on the length of the river and affected river stretch, the number of tributaries, and also on the rate at which the river system recovers from pollution. Sampling sites should represent different parts of the course of a river that may induce a change in water quality of the river system (e.g., distance from AMD outfall, wide/narrow floodplains, additional point source discharge, changes in geochemical composition of the bedrock resulting in a low or high buffering capacity). Additional sampling sites may be located in depositional zones, i.e., areas of low water flow, as contaminants tend to become concentrated in such areas due to the higher sediment fraction of fine material (clay or fine silt) with greater surface area per unit weight (Plumb 1981). Sample sites should be located about one third of the total width of the river from the nearest bank, which is thought sufficient to minimize the risk that samples could contain materials from the adjacent river bank (Moriaty and Hanson 1988). An additional factor to include in establishing a sampling program is the selection of reference sites or control stations. These sediments should be subjected to the same heterogeneity as for contaminated sites. If a reference site upstream of the discharge point is not accessible, a site in the headwater area of the catchment with similar geology may be selected.

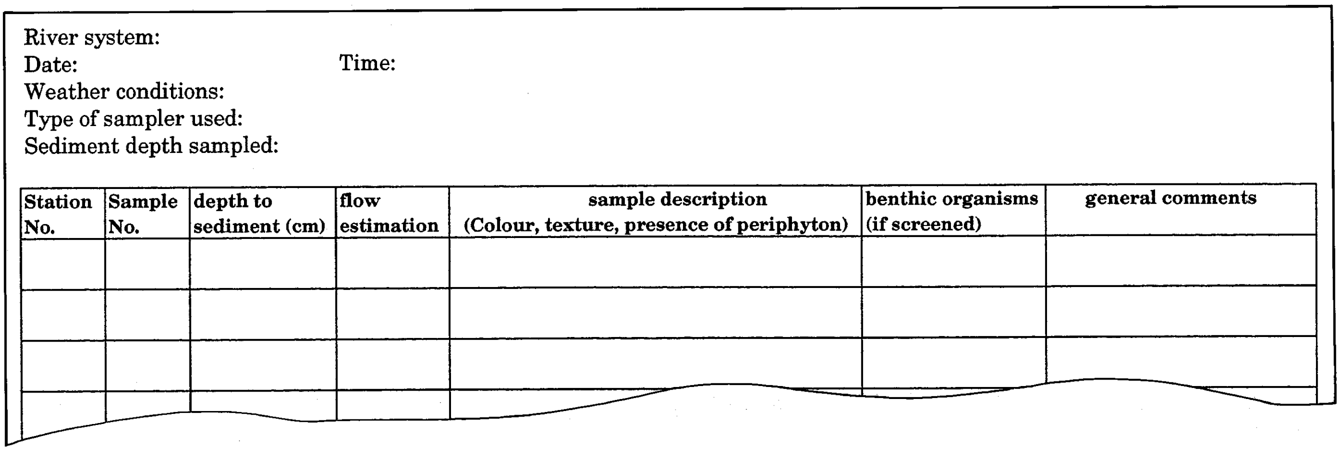
Field observations

Observations on general features in the area or characteristics of the water and sediment samples at a particular sampling site forms an important part of the pollution evaluation. Visual characterization, including photographs, provides valuable information for future reference and data interpretation. Field observations that should be recorded include sampling date and time, sampling site significance and location, sampling depth, estimation in measurement of flow, color of water and sediment, texture, visual characterization of substrate, weather observations, periphyton biomass, presence of ochre, turbidity of water, absence or presence of benthic organisms, and also a sketch of the sampling location for future reference (Fig. 1). The use of a standard substrate classification index such as the one described by Gray (1995a) allows a semiquantitative comparison of the riverine substrate both spatially and temporally. At sites where standard macroinvertebrate sampling will not be carried out, it is useful to sieve a portion of the sediment sample through standard mesh and record any benthic organisms on a field observation sheet. The pH of the streamwater should also be taken to determine if and to what extent the pH may influence variation of metal quantities in the sediments, while the conductivity will indicate dilution of impact (Gray 1995b).

Representative sample

To define the representative nature of a sample, the following criteria need to be considered: (1) clear definition of project area, (2) distribution of sampling locations, and (3) collection of subsite samples from each sampling

Fig. 1
Sample of field observation data sheet



River system:
Date: Time:
Weather conditions:
Type of sampler used:
Sediment depth sampled:

Station No.	Sample No.	depth to sediment (cm)	flow estimation	sample description (Colour, texture, presence of periphyton)	benthic organisms (if screened)	general comments

location unless sample variability has been established. To obtain a range of chemical concentrations or characteristics for the project area, sampling sites should be located over the whole length of the affected river system. The collection of representative samples is largely dependent on sample site location, the number of subsites sampled, and the sampling depth. In rivers contaminated by AMD or ARD, the collection of representative samples for a single location presents a major problem. Due to continuous precipitation of Fe hydroxyoxides and changes in hydrological characteristics of the river over time, restricted areas with increased metal accumulation may occur, resulting in very high metal concentrations of some subsites and introducing bias to the sampling protocol. Certain characteristics of the sediments, such as coloration or texture will provide an indication of patchiness. The greater the patchiness, the larger the number of samples that will be required to define the project area. Assessment of metal contamination of the sediment in the Avoca River (Ireland), showed significant variation for analysed Zn, Cu, and Fe concentrations among subsites and subsite replicates (Table 1) at a confidence level $P < 0.05$ (areas of visual differences, i.e., intensive orange coloration not included) (Herr and Gray 1995). It can be seen from this example that subsite sampling is vital to obtain a reasonably accurate estimate of the metal concentration of a specific location. The condition of representativeness is essential to most statistical tests. However, the only practical recommendation that can be given is to be aware of the possible introduction of bias during sampling (Plumb 1981). Bias can also be introduced through variation in numbers of subsite samples due to equipment, time, or financial restrictions. Therefore, before setting up a sampling program one should be familiar with experimental constraints within the project framework.

Table 1
Example of variation occurring within subsites and replicates for Zn (μg/g), Cu (μg/g), and Fe (%)

Substite	Replicate		
	Zn-1	Zn-2	Zn-3
1	519	521	463
2	465	507	463
3	368	411	382
	Cu-1	Cu-2	Cu-3
1	1004	765	885
2	714	634	695
3	514	468	534
	Fe-1	Fe-2	Fe-3
1	9.10	7.26	8.28
2	9.24	8.75	8.34
3	7.72	7.46	7.89

Table 2
Average metal concentration as a function of dredge penetration (Plumb 1981)

Depth of sample collected (cm)	Calculated average concentration (mg/kg)
1	10
2	7
3	5.6
4	4.7
5	4.0
6	3.5
7	3.1
8	2.9
9	2.7
10	2.5

Sampling technique selection

Sediments are frequently stratified vertically as well as horizontally. This should be considered when establishing a sampling program. For river systems contaminated by AMD or ARD this is an important consideration owing to continuous sedimentation of Fe hydroxides due to high dissolved Fe concentration in AMD and ARD leachate water. Therefore, a sample should be obtained from the ochreous surface layer (2 mm) as well as from the whole sediment (top 30 mm). In fast flowing rivers with high turbulence, such as the Avoca River, the ochreous sediment, which is the precipitate that has settled on large stones or small boulders, can be sampled. Even in less turbulent streams the surface sediment layer (< 10 mm) is generally very difficult to collect as it is very loosely bound and of high water content ($> 90\%$) (Håkanson 1980). Comparison of the metal concentration in the < 63 μm fraction collected from the top 30 mm of sediment with orange surface layer (ochreous precipitate) in the Avoca River, showed that Fe and Cu concentrations in the precipitate was approximately two- to fourfold greater at contaminated sites (Herr and Gray 1995).

Plumb (1981) calculated for a hypothetical situation an average metal concentration as a function of dredge penetration (Table 2). A difference in penetration of 1 cm could produce analytical variability of between 7–43%. The actual variation will depend on the site-specific depth profile and the differential depth of penetration. The choice of sample equipment will depend on the known or suspected characteristics of an area to be sampled, the volume and efficiency required, and the objective of the study. For the collection of sediments, three broad types of sediment collection devices are commonly used: corers, grabs, and dredges. Corers, generally used for lake sediment sampling, produce the least disturbance in the riverbed and are considered to be a quantitative measure. However, they do not work well in sandy or stony sediments and collect only small quantities of sediment, which may not be sufficient for many studies. For metal analysis a core sampler with plastic liner should be used whenever possible (Palmer 1984). Historical pollution studies to obtain information of vertical stratification sometimes require cores of up to several meters depth. This may be done by freeze coring. A hollow probe is driven into the stream bed and is subsequently filled with a cryogenic medium such as liquid nitrogen or liquid carbon dioxide to retrieve a frozen sediment. After thawing, the sample has to be segmented instantly to avoid dissolved metals from migrating (Gordon and others 1992). However, because of the large amount of equipment required and the time-consuming application, sampling may become quite expensive.

Surface grab and dredge samples are collected when the coring devices are ineffective or large quantities of material are required. The advantages and disadvantages of the most commonly used sediment sampler have been reviewed by Burton (1992) and summarised in Table 3. For monitoring purposes, the surface layer of the sediment provides the most valuable information because it represents the most recent metal accumulation, interacts with the surface water, and is in direct contact with the biota. In erosional river systems that have a very stony substrate, such as the Avoca River, corer or mechanical grab sampling devices such as the Eckman grab or dredge sampler are virtually ineffective. They cannot penetrate the substrate and cause most of the fine material to be lost during the sampling process. Therefore, alternative manual collection techniques such as grab sampling by hand or with a plastic scoop must be employed as discussed below. However, these methods restrict surveys to those times when the river is easily and safely accessible, whereas mechanical equipment could be lowered from a boat at all water levels. Grab sampling in a given project area does not provide a quantitative measure and only gives an estimation of the contamination concentration of substances for pollution load assessments. To minimize variation, it is important that samples are taken from the same depth profile throughout the whole program.

Sediment traps are used to provide information on sediment accumulation processes. The general principle is that these traps collect settling particles from the water column and are generally designed for measuring in situ flux of particulate suspended matter. It is important to keep in mind that samples collected by sediment traps do not accurately reflect the bottom sediment composition. However, it was shown by Vernet and others (1991) that

Table 3
Comparison of most widely used sediment samplers (Burton 1992)

Sampler	Advantages	Disadvantages
Hand and gravity corer	Maintains sediment layering of inner core. Fine surficial sediments retained. Replicate samples efficiently obtained. Removable liners. Inert liners may be used. Quantitative sampling.	Small sample volume. Liner removal required for repetitive sampling. Not suitable in large grain or consolidated sediments.
Box corer	Maintains sediment layering of large volume of sediment. Surficial fines retained relatively well. Quantitative sampling allowed.	Size and weight require power winch; difficult to handle and transport. Not suitable in consolidated sediments.
Vibratory corers	Samples deep sediments for historical analysis. Samples consolidated sediments.	Expensive and require winch. Outer core integrity slightly disrupted.
Ekman and box dredge	Relatively large volume may be obtained. May be subsampled through lid. Lid design reduces loss of surficial sediments as compared to many dredges. Usable in moderately compacted sediments of varying grain sizes.	Loss of fines may occur during sampling. Incomplete jaw closure occurs in large-grain sediments or with large debris. Sediment integrity disrupted. Not an inert surface.
Ponar	Commonly used. Large volume obtained. Adequate on most substrates. Weight allows use in depp waters.	Loss of fines and sediment integrity occurs. Incomplete jaw closure occurs occasinally. Not an inert surface.
Van Veen or Young grab	Useful in deep waters and on most substrates. Young grab coated with inert polymer. Large volume obtained.	Loss of fines and sediment integrity occurs. Incomplete jaw closure possible. Van Veen has metal surface. Young grab is expensive. Both require a winch.
Peterson	Large volume obtained from most substrates in deep waters.	Loss of fines and sediment integrity. Not an inert surface. Incomplete jaw closure may occur. May require a winch.
Orange-peel	Large volume obtained from most substrates. Efficient closure.	Loss of fines and sediment integrity. Not an inert surface. Requires a winch.
Shipek	Adequate on most substrates.	Small volume. Loss of fines and sediment integrity. Not an inert surface.

in depositional zones particle size distribution between sediment traps and bottom sediment was nearly identical. The method of setting sediment traps is simple; however, they need to be positioned at the best river location to collect sufficient settling material. Traps are normally simple PVC cylinders or boxes, ballasted with clean river pebbles, positioned on the bottom of the river, and protected by surrounding pebbles (Vernet and others 1991). The fluctuation of water depth and flow characteristics, as well as the curiosity and carelessness of people are disadvantages with this technique.

Sample preservation

The importance of sampe preservation between time of collection and time of analysis cannot be over-emphasized (Plumb 1981). Proper sampling handling is essential to obtain successful results from any monitoring program. This includes using appropriate clean storage containers, ensuring appropriate preservation, and using reliable sample labelling and identification procedures. In most cases, immediate analysis to prevent sample deterioration is not practical. Preservation methods are relatively limited and are generally intended to retard biological action, hydrolysis, and/or oxidation of chemical constituents (Skoch and Britt 1969). Selection of preservation method should be based on the purpose of the study and the constituents measured. If one is interested in the total concentration of a metal in sediments, either drying, freezing, or refrigeration in an airtight container would be acceptable. However, if mobilization of metals into the water phase is to be examined, only refrigeration at 4 °C would be acceptable. As a result, multiple samples will have to be collected and individually preserved or as single sample split into subsamples. Polyethylene and polypropylene containers are generally considered acceptable for most inorganic material, glass and polyethylene for elutriate water (Palmer 1984).

Recommended sampling and processing

The pollution loading in a river system contaminated by AMD or ARD is difficult to quantify. The use of the <63 μm fraction for chemical characterization provides a base to normalize data from different locations and proves to be a good method that is easy to apply to compare sediment pollution loads. The clay fraction of <2 μm also has been widely used for chemical characterization of sediments; however, the extraction procedure is more time consuming. For bioassays, the use of the <63 μm fraction would not be appropriate as the normalized data do not reflect the real situation in the field and cannot be directly related to the impact on the biota. Therefore chemical analysis on sediments used for sediment toxicity investigations should be performed on bulk sediments (<2 mm fraction), while for quantification purposes of the pollution load, the fine sediment fraction (<63 μm) should be considered.

To assess the overall impact of AMD or ARD on sediments, various sediment types may be analyzed including the deposited surface ochreous sediment Fe(III) precipitate, the <63 μm fraction in the top 0–30 mm of sediment, and the accumulated Fe(III) hydroxide floc at the river bank and in depositional zones. Ramezani (1994), working on a river contaminated by AMD, reported that the highest concentrations of Fe were found in the sediment consisting of the largest proportion of silt. Mantei and others (1993) found higher metal homogeneity in the coarse silt size sediment compared to very fine sand size sediment. They also showed that sediments need not be quartered to obtain a better homogeneity because field sieving appeared to give a uniform sample.

With regard to physicochemical analysis of sediments, sample handling techniques depend on the type of test to be performed on the sediment. This includes specific bulk sediment analysis (<63 mm fraction for chemical numerical assessment; <2 mm fraction in toxicity studies), elutriate test, sediment fractionation procedures, and analysis of interstitial (pore) water. The type of test selected for physicochemical analysis depends largely on the nature of the assessment (e.g., toxicity, chemical speciation). Elutriate tests simulate the potential mobility of metals from the sediment to the soluble phase after disturbance; the sediment fractionation test (sequential extraction) and examination of interstitial water provide information regarding the bioavailability of contaminants (Plumb 1981).

Sediment sampling

Approximately 3 kg of the sediment should be collected with a plastic scoop at all sampling sites along the river from the top 30 mm of the oxidized layer. Presieving in the field through 2 mm mesh using river water is a quick and efficient method of particle size separation, easing subsequent work in the laboratory (Herr and Gray 1995). The <2 mm fraction should then be retained and stored in polyethylene containers. The light unconsolidated sediments will be easily washed away when grab samples are collected in a fast flowing river, and therefore special care needs to be taken during collection. Because of high variation within a single location, it is important to take at least 3 to 5 subsite samples (number of subsamples taken should also be standardized for all sampling sites). Although there are no set guidelines on the number of samples that need to be taken, number and location of subsite samples should reflect the natural river flow, i.e., depositional/erosional zones. This can be easily assessed by visual characterization of the substrate prior to the sampling survey. In the laboratory, samples are wet sieved using river water through a set of sieves and the <63 μm fraction retained and dried for subsequent analysis. Subsamples of the sediments will be digested using concentrated HNO_3 and organic matter determined (Fig. 2). To predict the buffering capacity of the sediment, the carbonate content should be measured on a dried and

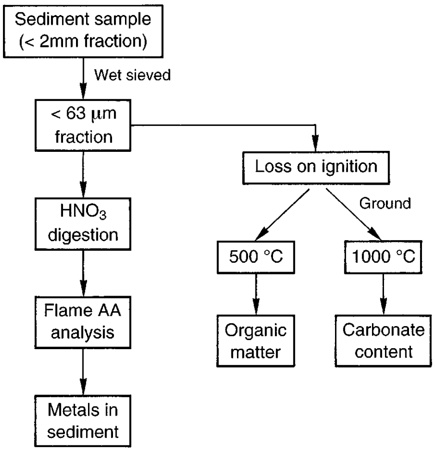


Fig. 2
Flow diagram showing main steps in sediment analysis procedure

finely ground sample. For analysis of the chemical composition of the ochre, the orange precipitate is washed of large stones or small boulders of approximately 20 cm in diameter. Three stones of equivalent size should be treated as one replicate sample. A minimum of three replicate samples should be taken at each location.

Fe hydroxide floc sampling

Floc samples can be collected in several ways: (1) if floc accumulates in pools, it can be taken up with a wide-bore syringe and stored in a polyethylene bottle; (2) floc samples can be carefully scraped from dry or almost dried out pools and stored in polyethylene bags; (3) and finally floc samples can be collected in sediment traps. Sediment traps (e.g., 3-l volume; 250 × 250 × 450 mm) are securely buried in the riverbed and left for a standard period of several days to one week and brought back to the laboratory in polyethylene containers where the floc is separated from the water phase and dried. If traps are left submerged for prolonged periods, then deposited material may be resuspended and lost.

Chemical analysis

Various digestion procedures have been used to dissolve the total metals contained in sediment samples. Dissolution of metals of a sediment sample can be performed using a combination of HNO_3 and HCl or HNO_3 and HF (total digestion) or concentrated HNO_3 or HCl (strong acid digestion) or diluted acids (E.V.S. consultants 1990). The silicate minerals are completely dissolved when total dissolution is used, whereas almost all metals (including Cd, Cu, Zn, Pb, Hg, and Ag) except for some minerals are dissolved by strong acid digestion. A concentration of 6 N HNO_3 will separate chemical phases and speciated metals form the sediment but will not affect metals in silicate lattices (Axtman and Luoma 1991). Metals are analyzed using spectroscopy techniques.

Interstitial (pore) water

Pore water is in dynamic equilibrium with the particulate phase and is the most sensitive indicator of the reactions on particles and the aqueous phase that contacts them (Krebs 1992). Collection of sediment pore water has been accomplished by several methods: centrifugation and squeezing (ex situ), suction and equilibrium dialysis (in situ). In general, methods for recovery of relatively large volumes are limited to either centrifugation and squeezing; however, these methods require removal from the natural environment, whereas in situ techniques have less potential for producing sampling artifacts (Bufflap and Allen 1995).

Sediment elutriates

An elutriate test is a short-term, sediment-leaching procedure. The test is an indicator of the chemical constituents likely to be released to the water column during a dredge/disposal or filling operation (E.V.S. Consultants 1990). It can also be used to assess the maximum amount of metals that are likely to be released from a sediment contaminated with AMD or ARD. The test consists of agitating a known volume of sediment with a known volume of site water. Vigorous agitation of a 4:1 site water to sediment mixture is commonly used for this test (Plumb 1981). The water phase may then be separated from the sediment by centrifugation.

Sediment fractionation (sequential extraction)

These tests provide more detailed information on the distribution of chemical constituents within the sediments by subjecting the sample to a series of extraction solutions. These methods make use of relatively mild reagents selected to attack particular nondetrital solid phases. The reagents may be used singly or in sequence (weak to strong) (Luoma 1983). It should be kept in mind, however, that sequential extraction only describes operational steps and no chemical or mineral phases. The operation procedure is time consuming and requires strict sample storage. Examples for application procedures of sequential leaching techniques and limitation of the methods are given by Tessier and Campbell (1987). An example for sequential extraction for the determination of heavy metals bound to sediments is shown in Table 4.

Physical analysis

Physical characterization of sediments is described by total carbon contents and carbonate fraction and particle size distribution. In sediments that are likely to be anoxic, Eh (redox potential) also provides valuable information. Carbon fractions may be of importance in determining toxicant fate and bioavailability. A commonly used method is to determine total organic carbon content by combustion (loss on ignition) at 500 °C and carbonate content at 1000 °C. A more sophisticated method for organic carbon analysis would be using a carbon analyzer (e.g., CNS-1000 Elementar Analyzer) controlled a microprocessor. The method of particle size analysis should be chosen based on the type and size of material being analyzed and the accuracy required (Gordon and others 1992). However, standardization of the sieving method is important to ensure reproducibility and comparability.

Table 4
Sequential extraction procedure to determine availability of heavy metals (Calmano and others 1993)

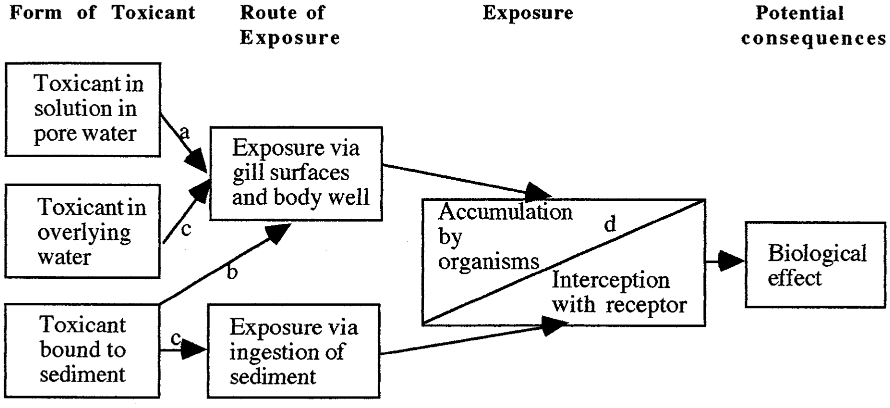
Fraction	Extraction reagent	Extracted sediment phase
Exchangeable	1 M NH_4OAc (pH 7)	exchangeable cations
Carbonatic	1 M NaOAc (pH 5)	carbonates
Easily reducible	0.1 M $NH_2OH \cdot HCl$ (pH 2)	Mn oxides
Moderatley reducible	0.1 N oxalate buffer (pH 3)	amorphous Fe oxides
Sulfidic/organic	30% H_2O_2 + 0.1 M HNO_3, extracted with 1 M NH_4OAc in 6% HNO_3	sulfides and organic materials

Common particle size fractionation techniques are wet or dry sieving (Allan 1989) or settling techniques (Müller 1967). Redox measurements provide information of the oxidation–reduction status of sediments, which is a particularly important factor controlling metal speciation and determining the extent of sediment oxidation. The measurements are carried out with a platinum electrode relative to a standard hydrogen electrode (Plumb 1981).

Bioassay testing

The quantification of contaminant concentration cannot provide enough information to adequately evaluate potential adverse effects, interaction to chemicals, or the time-dependent availability of contaminants to aquatic organisms. Chemical fractionation procedures describe bioavailability of substances by evaluating substances using mild or harsh extractants. However, the impact of the contaminants directly affecting benthic organisms through resuspension, remobilization, or sediment ingestion of substances sorbed onto sediment particulate cannot be evaluated using these techniques. Sediment bioassays provide information on toxicity and bioavailability that cannot be provided by chemical analysis alone (E.V.S. Consultants 1990). Because the exposure route of contaminants (Fig. 3) is an important consideration, tests should be directed towards a particular phase of the sediment, i.e., direct contact with bulk sediment, exposure to pore water, exposure to overlying water, and ingestion of sediments. The main route of contaminant uptake and exposure of toxicants in solution to aquatic organisms is via pore water (Giesy and others 1990; Power and Chapman 1992). Toxicity of sediments can be evaluated both in laboratory experiments and field investigations. In the laboratory, acute or chronic effects are determined by direct exposure of benthic organisms to sediments, while a dose–response relationship (i.e., lowest observed effect concentration LOEC) can be determined for single toxicants or mixtures by dilution of the contaminated sediment with uncontaminated sediment or by spiking of sediments with a known concentration of a pollutant. The use of sediment pore water and elutriates for toxicity tests facilitates not only dilution to determine the dose–response relationship, but also permits the use of standard, nonbenthic bioassay organisms (Giesy and others 1990).

Bioassay tests vary with respect to bioassay type (lethal, sublethal, genotoxic, and bacterial) and to bioassay organisms (bacteria, algae, daphnia, and fish) (Kilroy and Gray 1995). Methods range in complexity from short-



a Expected major route of uptake
b Not a major route for direct uptake; often estimated by normalisation of bulk sediment contamination (e.g. total organic carbon (TOC) and acid volatile sulphides (AVS))
c Route of exposure; relative importance subject to debate
d Biological effects only occur through entry of toxicants into biological systems; accumulation alone is a phenomenon, not an effect.

Fig. 3
Interactions of contaminated toxic sediments with benthic organisms (Power and Chapman 1992)

term acute tests of the effects of individual contaminants on single species to long-term tests of the effects of chemical mixtures on the function of benthic mesocosms. Because different bioassays can produce different results, it is recommended that toxicity assessments incorporate more than one end point, and tests should incorporate various trophic levels. At least three tests are recommended in order to describe sediment toxicity adequately (E.V.S. Consultants 1990). Sediment bioassay techniques have not been widely applied to acid mine drainage problems in freshwater systems to date. Most approaches have documented the degree and distribution of contaminants without addressing the significance of toxicity. Field investigations of algae, fishes, and invertebrates provide an essential component of biological assessments of toxicity associated with contaminated sediments. Advantages of field surveys include that indigenous organisms complete all or most of their life cycle and field assessment of natural populations can be used to screen potential zones of sediment contamination.

Quality assurance

Quality assurance (QA) is essential for any monitoring program. It provides a set of operating principles that will produce data of known and defensible quality, so that the accuracy of analytical results can be stated with a high level of confidence. The generation of quality data begins with the collection of the sample. Therefore, the integrity of the sample collection process is of importance to analytical laboratories and for success of the investigation. Quality control guidelines should be issued with regard to: (1) sampling and sample handling (minimization of contamination, collection of appropriate sample volume, insurance of proper transport, i.e., cooling of samples) and (2) definition and accuracy of the analytical method (method blanks, replicates to provide an indication of reproducibility – at least 15–20% or one sample batch, check standards that are prepared independently of calibration standards, certified standard reference material). With regard to bioassay quality control, procedures may include test organisms (e.g., health, similar size and life stages), negative controls, use of reference toxicants (positive controls), blind testing and monitoring of water quality if organisms are kept in aqueous media to ensure survival and to avoid additional stress to the organism.

Assessment approaches to define sediment quality criteria

Determination of sediment quality criteria is an immensely difficult task because such factors as partitioning of sediment contaminants into the dissolved phase (i.e., interstitial water) and adsorption of contaminants to particulate material, determine the availability of contaminants to the biota. Various approaches to quantify metal pollution have been suggested, including the geoaccumulation index (Müller 1979), the ecological risk index (Håkanson 1980), and the sediment quality triad (Chapman 1986). Whereas the geoaccumulation index is based entirely on a chemical numerical approach, the ecological risk index and the sediment quality triad also take biological criteria into consideration.

The geoaccumulation index (I_{geo}) introduced by Müller (1979) is a quantitative measure to assess metal enrichment of aquatic sediments:

$$I_{geo} = \log_2 C_n / 1.5\, B_n$$

The concentration of a substance (C_n) in the pelitic sediment fraction (<2 μm) is compared to the geochemical background (B_n) value in fossil argillaceous sediments (average shale). To include natural variation of background concentrations and already existing low anthropogenic contamination, the background concentration is multiplied by a factor of 1.5. The index consists of 7 grades (0–6), where the highest grade (grade 6) reflects a 100-fold enrichment above the background value.

The basic working hypothesis of the ecological risk index (RI value) proposed by Håkanson (1980) may be expressed on following four premises: (1) the concentration of substances, which emphasizes that the RI value should increase when the sediment contamination increases; (2) the number of substances contaminating the area, which states that a waterbody polluted by numerous substances should have a higher RI value than an area contaminated by only a few substances; (3) a toxicity factor, which should account for the fact that various substances have different toxicological effects (the RI value should differentiate between mildly, moderately and very toxic substances); and (4) a sensitivity factor, which means that the risk index should account for the fact that various water systems do not have the same sensitivity to toxic substances (i.e., buffering capacity).

The sediment quality triad proposed by Chapman (1986) takes the approach of using toxicological data derived directly from sediments to develop the necessary sediment quality criteria. The approach is based on the assumption that the biological responses observed in sediment bioassays and in situ studies are a function of the concentration of certain chemicals sorbed to the sediments in the study area. Sediment chemistry and sediment bioassay measures are combined with in situ studies. Chemistry and bioassay estimates are based on laboratory measurements using sediments collected in the field, while in situ studies include analysis of resident organism histopathology, benthic community structure, and bioaccumulation. Figure 4 shows a conceptual model of the sediment quality triad (Chapman 1986). The information provided by each component is unique and complementary. All three components provide the strongest evidence presently available for determining pollution induced degradation. The combined information obtained by the sediment

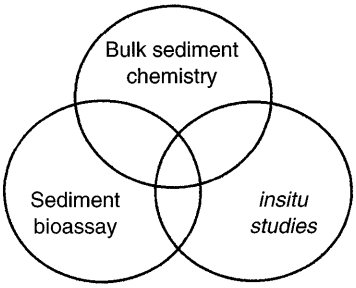


Fig. 4
A conceptual model of the sediment quality triad (Chapman 1986)

quality triad can be utilized to determine problem areas of sediment contamination, to priotize degraded areas and their environmental significance, and to predict occurrence of degradation based on levels of contamination and toxicity (E.V.S. Consultants 1990).

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