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Review of Techniques Available for the Isolation of
Sediment Pore Water in Mining Areas

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Management Perspective

The sampling and analysis of sediment pore water can provide valuable information on chemical changes occurring in the sediment, on the equilibrium reactions between minerals and water, on the transport and fluxes of contaminants into the sediment/water interface and overlying water. The concentration of trace elements in sediment pore water at mining areas has already been proved to be a very useful tool to several mining-related studies, such as the suitability of disposal of tailings and waste rock permanently underwater; the composition of tailing pore water; and the effects of abandoned tailings disposed in lakes. However, the extreme variety of mining environments, such as tropical, arctic, lacustrine or marine areas, makes the choice of the sampling technique case-specific. The objective(s) of the study will define the proper method for sediment pore water sampling. There is no particular method for pore water sampling that can be considered ideal for all objectives or that is problem-free. This paper reviews the main techniques for sampling pore water in mining areas. These techniques are divided in two broad categories: 1) indirect methods and 2) in situ methods. Advantages and drawbacks of centrifugation, squeezing, and dialysis methods are discussed. Collection and analysis of pore water has proved to be a very important tool to study environmental impact in mining areas. However, we emphasize that due to its complexity, sediment pore water sampling is not suitable in any monitoring program, and should only be carried out by personnel experienced with the sampling methods.

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REVIEW OF TECHNIQUES AVAILABLE FOR THE ISOLATION OF SEDIMENT PORE WATER IN MINING AREAS

Jose M. Azcue and Fernando Rosa^{1,2}

Abstract

Negligible chemical changes in sediments or tailings often cause variations in the quality of the sediment pore water. Sediment pore water chemistry can help to explain and predict many diagenetic processes in sediments. However, the technique involved in the collection of the pore water can affect the interpretation of redox processes, and concentration profiles and fluxes of contaminants at the sediment/water interface. Many factors, such as objectives of the study, requirements of special equipment, and time and cost constraints, should be considered before selecting the technique for the sampling of sediment pore water. The different techniques for separation of pore water from sediments, such as centrifugation, squeezing, dialysis, direct suction, and equipment available for in situ pore water sampling will be discussed in this paper. We emphasize that due to its complexity, sampling of sediment pore water is not suitable in monitoring programs, and should only be carried out by personnel experienced with the sampling methods.

Key Words: mining, sediment, pore water, sampling, techniques.

Introduction

Sediment pore water, also referred as interstitial water, acts as a linking agent between the bottom sediments and the overlying water. Negligible changes in sediment composition often cause noticeable variations in the quality of sediment pore water. The sediment pore water chemistry can help to explain many diagenetic processes. The sampling and analysis of sediment pore water can provide valuable information on chemical changes occurring in the sediment, on the equilibrium reactions between minerals and water, on the transport and fluxes of contaminants into the sediment/water interface and overlying water. These processes will affect the availability of nutrients and toxic chemicals to the biota. Pore water is also important in geophysical, sedimentological, and geotechnical studies of sediments. The composition and mobility of pore fluids are critical factors in determining sediment's strength, bearing capacity, and their ability to conduct heat, sound and electricity (Manheim, 1976).

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The concentration of trace elements in sediment pore water at mining areas has already been proved to be a very useful tool to study the suitability of disposal of tailings and waste rock permanently underwater (Pedersen et al., 1993); the composition of tailing pore water (Al et al., 1994); and the effects of abandoned tailings disposed in lakes (Azcue et al., 1994; Tessier et al., 1989). However, the extreme variety of mining environments, such as tropical, arctic, lacustrine or marine areas, makes the choice of the sampling technique case-specific. The objective(s) of the study will define the proper method for sediment pore water sampling. There is no particular method for pore water sampling that can be considered ideal for all objectives or that is problem-free. However, we emphasize that due to its complexity, sediment pore water sampling is not suitable in any monitoring program, and should only be carried out by personnel experienced with the sampling methods.

With the exception of the sediment/water interface, sediments are generally anoxic, and become rapidly oxidized upon exposure to air. The oxidation of the sediments induce immediate changes of the redox-sensitive chemical species of different dissolved elements in the pore water usually with their subsequent precipitation. Several studies have shown that maintenance of an oxygen-free atmosphere and the avoidance of contamination are the critical factors in the sampling of pore water (Azcue and Rosa, 1995; Bolliger et al., 1992; Carignan et al., 1985). As previously mentioned, in no other environmental compartment the technique involved in sample collection plays such an important role as in pore water sampling. This manuscript summarizes some of the available techniques for sampling pore water that can be used at different mining areas. Detailed reviews of pore water sampling can be found, for example, in Adams (1994), and Mudroch and Azcue (1995). Therefore, no attempt was made to describe the sampling devices in this paper.

PORE WATER SAMPLING - GENERAL CONCEPTS

The techniques for sampling sediment pore water can be divided in two broad categories: 1) indirect methods, and 2) in situ methods. Centrifugation and squeezing of the sediments are the most feasible indirect techniques. Other typical indirect sampling methods are leaching (Glass and Poldoski, 1975; Kriukov and Manheim, 1982), desiccation (School, 1963), and displacement techniques (Kinniburgh and Miles, 1983). There are two main in situ techniques, dialysis (Hesslein, 1976; Mayer, 1976) and direct suction (Brinkman et al., 1982; Sayles et al., 1973). Although, many in situ samplers have been developed to fulfil different study objectives, all of them are based on the dialysis or direct suction principles. The only common factor among all these sampling techniques is that the risks of contamination are considerable when sampling sediment pore water, due to lower concentrations of elements in the pore water than those in the sediments. Although, not discussed in this manuscript, we would like to emphasize that to avoid contamination, the handling and cleaning of all sampling equipment and containers for collection of the pore water need special attention, see Rosa and Azcue (1993).

1) INDIRECT METHODS

In these methods, the sediment pore water is recovered from sediments previously collected. The common advantage of these methods is the simultaneous collection of sediment and pore water which allows to compare the concentrations of analyzed parameters in the pore water to those in the sediment. The drawback of the indirect methods is the difficulty to achieve the rapid sampling to maintain the sediments in the laboratory under their *in situ* conditions. Consequently, there is an increasing risk of changes in the geochemical character of the sediment induced by exposure to the atmosphere. During sampling in deep waters the differences in pressure and temperature between the bottom sediments and the water surface inevitably affect the distribution of some chemical constituents in the pore water. The change in the pressure affects the carbonate equilibria, and may lead to exsolution of methane gas which will result in the formation of gas pockets in the sediments (Manheim, 1976). Changes in sediment temperature from 1 to 2°C to the room temperature of 20 to 22°C leads to changes in the distribution of cations in pore water (Fanning and Pilson, 1971; Mangelsdorf and Wilson, 1969).

Centrifugation

Centrifugation has been used for fluid removal, from various saturated or partly saturated geological materials since the 1940's. The specific problems of this technique are the speed and time of centrifugation, and the contamination from the equipment. The speed of centrifugation has to be high enough to separate the pore water from the sediments without heating the centrifuged samples which may cause physico-chemical changes. It is well known that to obtain representative pore water samples centrifugation has to be carried out as soon as possible, after sample collection under anaerobic conditions in a refrigerated centrifuge. Pore water samples obtained by centrifugation should be filtered. Several researchers addressed and tried to minimize these problems (Adams et al., 1980; Emerson, 1976; Engler et al., 1977; Saager et al., 1990).

Centrifugation technique has been used by Pedersen et al. (1993) to study the early diagenesis of submerged sulphide-rich mine tailings in Anderson Lake, Manitoba. Despite high metal levels in the lake water, the concentrations of Zn, Cu, Pb, and Cd in pore water in both tailings and natural sediments were low. Based on the pore water profiles, the authors suggested that the tailings in Anderson Lake were consuming metals rather than releasing them to the overlying lake waters. Recently, Azcue and Rosa (1995) have shown that immediate centrifugation under anaerobic conditions followed by filtration yield results for trace elements similar than *in situ* techniques. However, this technique is not suitable for determining concentrations of Na and K in pore water (Figure 1). Carignan et al. (1985) suggested that due to the elevated number of variables involved in the centrifugation of sediment for pore water measurements of parameters should be regarded as operationally defined, i.e., method dependent, until it is shown

that independent procedures consistently yield similar results.

Squeezing of sediments

Squeezing of sediments for extraction of pore fluids was first carried out in 1895 by the British oceanographer Sir. John Murray (Manheim, 1976). Since then, modified filter presses have been used by workers in the petroleum exploration for extraction of pore water from drilled mud. In the 1960's, the squeezing methods were adapted for extracting pore water from sediments (Hartmann, 1965; Reeburgh and Erickson, 1982; Siever, 1962). The designs were usually based on the principles of low or high-pressure mechanical squeezing, or low-pressure gas-mechanical squeezing, followed by filtration. The principal potential artifacts during extraction of pore water by squeezing are: oxygen contamination; effects of high pressure in sediment particles; temperature of squeezing; and contamination from equipment. A great deal of effort has been devoted to correct and improve the squeezing technique (Bender et al., 1987; Kalil and Goldhaber, 1973; Matisoff et al., 1980; Robins and Gustins, 1976; Sasseville et al., 1974).

Pore water was one of the compartments studied in a multidisciplinary investigation to evaluate the effects of effluent discharges from a gold mine on the ecosystem of Larder Lake in Northern Ontario (Mudroch et al., 1994). Sediment cores were extruded under nitrogen atmosphere of nitrogen and c sediment sections were squeezed to collect the pore water. The concentrations of trace elements in pore water were 10 times greater in Larder Lake, compared to other studied lakes, such as Jack of Clubs, British Columbia, which also has been contaminated by effluents from gold mining (Figure 2) (Mudroch et al., 1992). Arsenic and Pb had the greatest "Mobility Index", defined as the ratio of pore water concentration divided by the total metal content in the surficial sediments, followed by Ni, Zn and Cu. The results of the study indicated that the trace elements in lake water were not being regenerated from the lake sediments. The same technique was used to study the effects of sand-capping and bioturbation on release of contaminants from sediment to water (Rosa et al., 1994). Preliminary results showed that the sand cap was an efficient way to reduce chemical exchange of trace elements between the sediment and water column. We can conclude that squeezing is not a suitable method for quantitative extraction of pore water, but when properly employed it is a feasible way to obtain representative samples of pore water for chemical analysis.

2) IN SITU TECHNIQUES

Up to 1970, pore water was extracted from sediments only by indirect methods, such as squeezing, centrifugation, leaching, and successive dilution. However, several researchers showed significant concentration changes mainly due to temperature- and pressure-related changes during the recovery of the pore water. It has been shown that the major problem during sediment pore water sampling is the potential for oxidation of different elements in the samples. Therefore many methods have been developed to collect pore water *in situ* to minimize these sampling artifacts.

Dialysis

Samplers based on diffusion-controlled transport were first developed by Mayer (1976) and Hesslein (1976). The principle of operation of these samplers is the equilibration between de-oxygenated water contained in the sampler and sediment pore water through a dialysis membrane. Many scientists have designed new samplers based on the same equilibration principle, (Azcue et al., 1995; Bottomley and Bayley, 1984; Höpner, 1981; Simon et al., 1985; van Eck and Smits, 1986;).

The peeper sampler developed by Hesslein (1976) and its modifications are one of the most common sampling techniques for *in situ* sediment pore water sampling (Figure 2). Azcue et al. (1994) used peepers to study the role of pore water in the cycling of As in a mine-polluted lake. The concentrations of total As in pore water were characterized by subsurface maxima, with concentrations four to six times greater than those in the lake water (Figure 3). In all the sediment profiles examined, inorganic As [III+V] comprised most of the As. The concentration gradient of total dissolved As indicated that an upward diffusion of As towards the lake water column with the estimated annual fluxes being $0.8-3.8 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$. Therefore, the elevated As concentrations in bottom sediments represented a "continuous mining" of As towards the sediment/water interface during the whole year.

Since the early 70's, several sampling systems have been proposed utilizing *in situ* sediment pore water suction (Bauer et al., 1988; Howes et al., 1985; Hursthouse et al., 1993; Montgomery et al., 1981; Rey et al., 1992). However, there is a need of comparative studies to ensure these methods yield similar results than the well studied techniques of sediment pore water sampling.

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Fig. 1. Larder Lake As

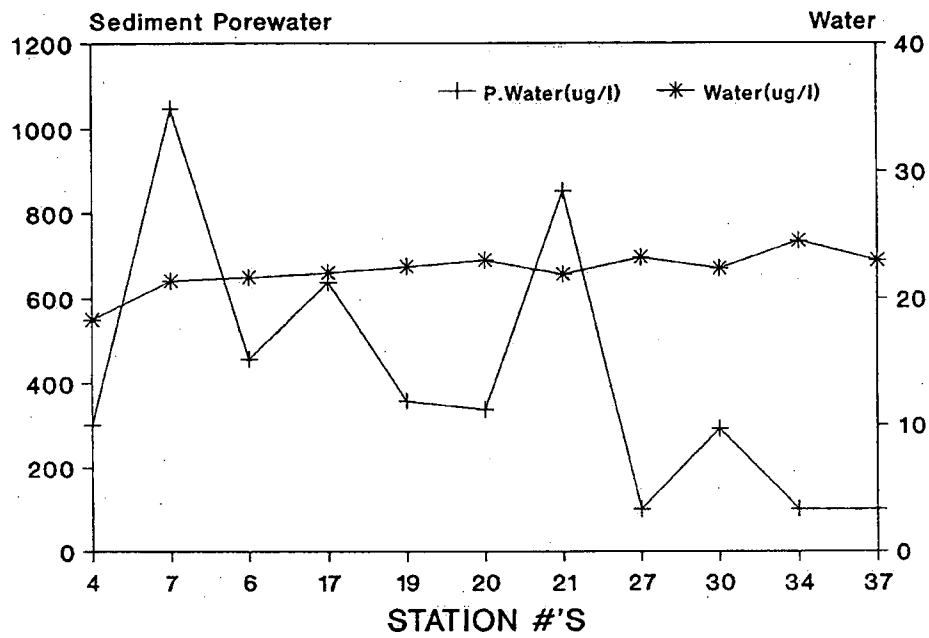


Fig. 3. Moira Lake As

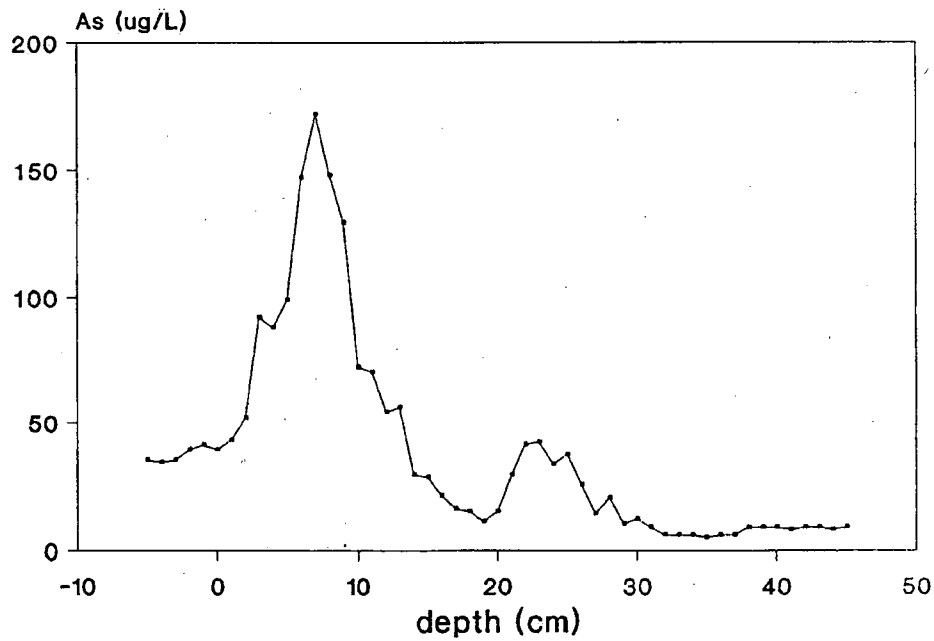
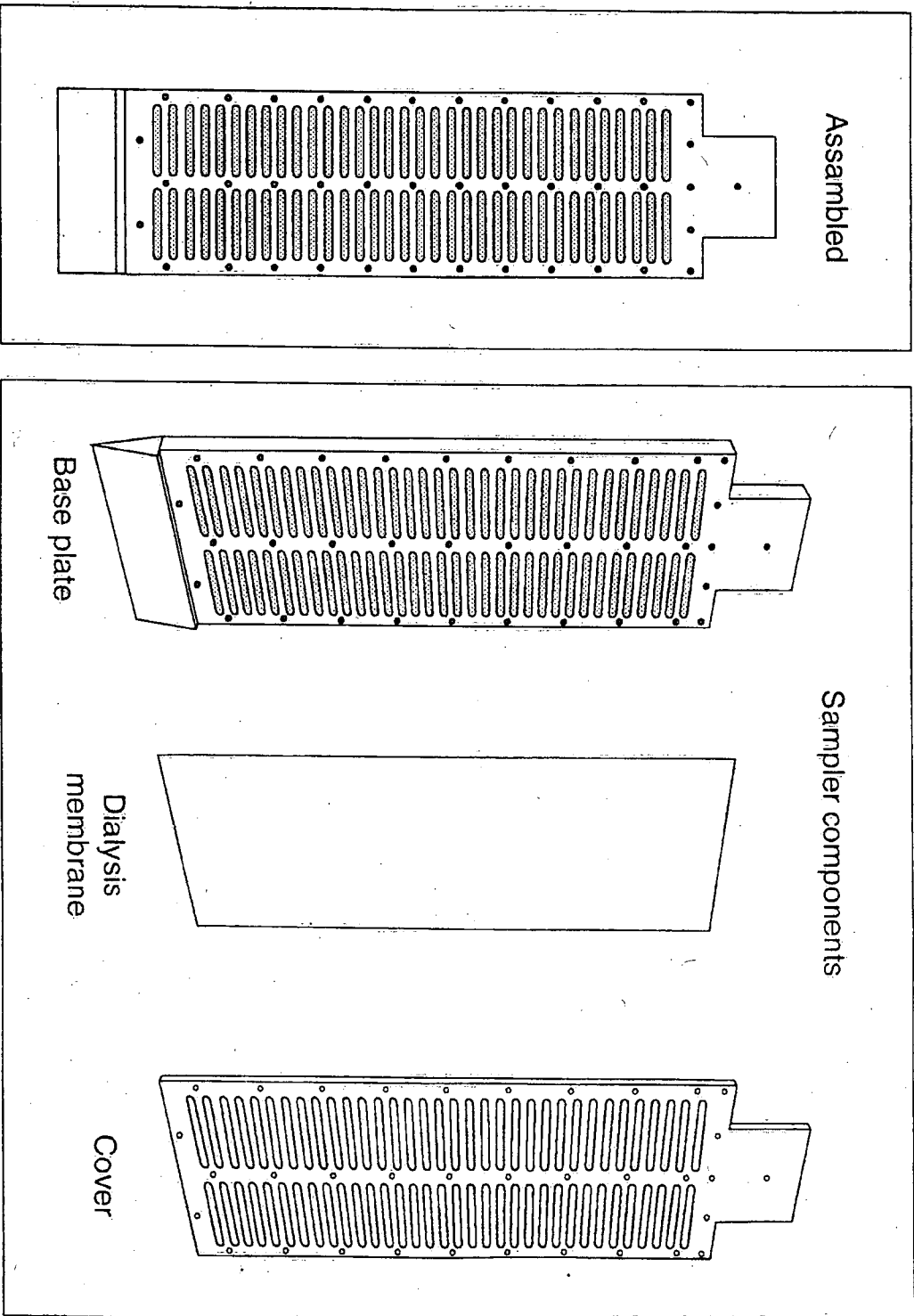


Figure 2

Dialyzer Sampler or "Peeper"





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