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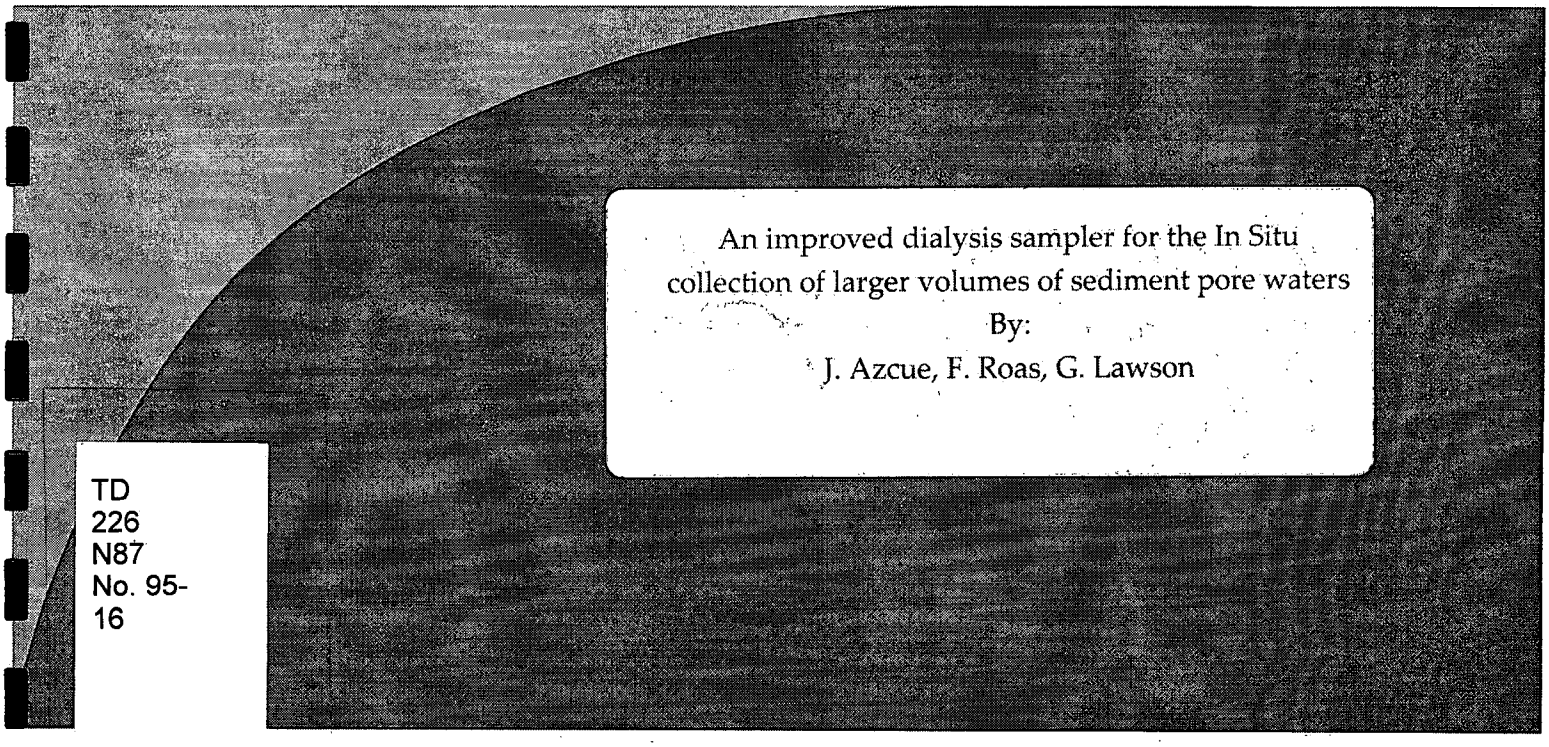

An improved dialysis sampler for the In Situ collection of larger volumes of sediment pore waters

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MANAGEMENT PERSPECTIVE

AN IMPROVED DIALYSIS SAMPLER FOR THE *IN SITU* COLLECTION OF LARGER VOLUMES OF SEDIMENT PORE WATERS

Sampling of sediment pore water has become a very important tool in environmental studies. Pore water is the linkage agent between bottom sediment and overlying water. Pore water has been collected and analyzed to determine the diffusion of contaminants and nutrients into the water column, and/or their precipitation in the solid phase. Knowledge of pore water concentrations is critical in dredging operations, underwater disposal of mine wastes, and to assess the toxicity of sediments to local biota. Selection of the method for pore water sampling is usually affected by the objectives of the study. There is no particular method for pore water sampling that can be considered ideal for all objectives, and is problem free. The *in situ* dialysis ("peeper") technique has been recognized as one of the most accurate methods. Recently, it has been suggested that sediment pore water may be used for the determination and assessment of sediment quality criteria and toxicity testing. However, the limited sample volume (3-5 ml) of the conventional peeper is its major drawback. In this manuscript we describe a new Volume Enhanced Sediment Porewater Sampler (VESPOS) for *in situ* separation of pore water from aquatic sediments. The main advantages of the VESPOS sampler are: larger sample volume (30 ml); simplification of the assembly and recovery; and minimization of risks of sample contamination. The sampler significantly reduces the labour and handling in sediment pore water sampling.

AN IMPROVED DIALYSIS SAMPLER FOR THE *IN SITU* COLLECTION OF LARGER VOLUMES OF SEDIMENT PORE WATERS

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ABSTRACT

A new Volume Enhanced Sediment Porewater Sampler (VESPOS) for the *in situ* separation of pore water from aquatic sediments is described. This sampler offers several improvements over conventional *in situ* sediment pore water sampling devices, particularly for the collection of a large sample volume (30 ml); simplification in the assembly of the sampler and recovery of the sample; and, consequently, minimizing the risks of sample contamination. The large volume of pore water sampled within a 2-cm interval increases the analytical potential. The sampler significantly reduces the labour and equipment involved in sediment pore water sampling, particularly during retrieval of the samples.

Key words: pore water, sampler, membrane, peeper, dialysis.

INTRODUCTION

Relatively small changes in the geochemical composition of aquatic sediments can cause considerable variations in the quality of sediment pore water. The sediment pore water geochemistry can help to explain many diagenetic processes occurring in the sediments. However, the technique involved in the collection of sediment pore water plays an important role in investigating the quality of the pore water. Selection of a proper method for sediment pore water sampling is usually affected by the objective(s) of the study. However, there is no particular method for pore water sampling that can be considered ideal for all objectives, and is problem-free.

The maintenance of an oxygen-free atmosphere and the avoidance of sample contamination are critical factors in sediment pore water sampling. Many methods have been developed to collect sediment pore water *in situ* to minimize sampling artifacts. Several sampling systems have been proposed utilizing *in situ* sediment pore water suction and filtration (1-6). Samplers based on diffusion-controlled transport were first developed by Hesslein (7) and Mayer (8). The principle of operation of these samplers is the equilibration between oxygen-free de-ionized water contained in the sampler and sediment pore water through a dialysis membrane. Hesslein's dialysis sampler (7), also called a peeper, consisted of individual compartments machined into two sheets of acrylic with a dialysis membrane placed between the sheets. The dialysis sampler

developed by Hesslein and its modifications are one of the most common sampling techniques for *in situ* sediment pore water collection.

Although the principle of Hesslein's *in situ* pore water sampler remained the same, many scientists have modified the design of the sampler to suit their specific needs. The use of different membranes and covers allows for the discrimination of particles or molecules of variable sizes to enter the sampling chamber (9-11). Kepkay *et al.* (12) designed another pore water sampler with shutters positioned over the dialysis membrane. Bottomley and Bayly (13) designed a cylindrical sampler with a non-degradable membrane, sampling at 4-cm intervals and emptied by hypodermic syringes. Recently, Davison *et al.* (14) and Davison and Zhang (15) described a new technique of diffusive equilibration to study the distribution of trace components in sediment pore water at sub-millimetre resolution. This technique relies on the equilibration principle, similar to the peeper but rather than confining the solution to compartments, it uses a thin film of gel to provide the medium for solution equilibration.

In this manuscript we describe a new *in situ* Volume Enhanced Sediment Porewater Sampler (VESPOS). The sampler is an intensively modified design of the conventional "peeper", featuring enhanced sample volumes, 30 ml compared to 3-5 ml for a conventional peeper, and simpler assembly and quick, contamination-free retrieval of the samples. The reliability of the VESPOS sampler was compared by

chemical composition of pore water collected in Lake Erie by the VESPOS and that collected by the conventional dialysis sampler design similar to Hesslein's (7).

MATERIALS AND METHODS

Description of the sampler:

The sampler is a modified version of Hesslein's (7) design and works on the same equilibration principle. The sampler (Figure 1) consists of two sheets of acrylic (one, 0.3 cm thick cover and the other, a 1.3 cm thick body), the acrylic bottle attachment blocks, and 30 ml HDPE (high density polyethylene) sample bottles. The membrane holder is a dialysis sampler with compartments vertically placed at 2-cm intervals. The compartment (or cell) opening is approximately 2 cm x 6 cm offering an equilibration surface area of about 12 cm^2. The compartments are covered by 0.45 μm pore size cellulose acetate membrane. The body of the sampler and the cover are attached by stainless steel screws. Acrylic bottle blocks are glued to each side of the samplers' body. Threaded bottle holder openings are 4 cm apart on each side of the sampler, alternating every second compartment to maintain the 2-cm intervals (Figure 1). Each compartment is joined to the bottle block by a 0.5-cm opening, from the side of the compartment to the threaded bottle holder (Figure 1).

The blocks can incorporate an optional valve mechanism, preset at deployment and then remotely triggered by a timer or electronic messenger to seal *in situ* the bottles before retrieval of the sampler (16). This should be suitable, particularly when retrieving the sampler from deep water environment. The pore water sample integrity is altered during a long ascent through the water column to the surface when using the original peeper design (17).

The new design incorporates 30-ml high density polyethylene bottles which are screwed to the threaded bottle blocks (Figure 1). Upon retrieval of the sampler, the bottles are simply unscrewed from the blocks and capped for transport back to the laboratory. Comparing the bottles to the compartments of the original peeper, they are easier to clean, and the sample can be acidified directly in each of the bottles, eliminating the use of hypodermic needles (or pipette tips) to collect the samples from the compartments. In addition, it provides a larger volume of sample. The new design may also incorporate other bottle sizes and different materials, although the bottle block would need to be modified accordingly, based on the bottle's cap and appropriate thread.

Assembly:

To remove any O_2 stored in the samplers acrylic material, the peepers were bubbled with N_2 for two days before assembling (18). Each peeper has a sequence of 30 compartments (optional) which, a few days prior to sampling, were filled with oxygen-free deionized, doubly distilled water (DDW) and covered the open side with a 0.45

μm cellulose membrane (Gelman Scientific, Inc.) (19). The new design does not require the membrane to be mounted to the peeper underwater. The sampling bottles are filled with oxygen-free DDW and attached to the sampler underwater. Subsamples of the DDW water used in the assembling and storage of the dialysis samplers were kept for further analysis to monitor any possible contamination.

Field work:

The samples for the comparative study of the two designs of the *in situ* sediment pore water samplers were collected from the central basin of Lake Erie (41°56′06"N, 81°39′30"W). The samplers were kept in oxygen-free DDW until divers deployed them vertically in relatively flat areas on the lake bottom. The samplers were left from August 6 to September 7, 1994, to allow the chambers to equilibrate with the sediment pore water. At retrieval time, the bottles on the side of the sampler with collected pore water were removed, acidified with 50 μl of Ultrapure Seastar HNO_3 (conc.), capped, and stored at 4°C until analysis. All materials were previously acid washed following the method recommended by Nriagu *et al.* (20). For comparison purposes, three conventional dialyzer samplers (peepers) were used simultaneously in this study to recover *in situ* pore water in the same location. These peepers were assembled following standards procedures (19).

Analysis:

All samples were analyzed for 18 trace elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Jobin Ivon Model 74. The standard solutions consisted of high purity concentrations of the trace elements in a solution of 2% HNO_3 (Delta Scientific Laboratory Products, Canada).

RESULTS AND DISCUSSION

The conventional dialysis sampler in sediments (4-6°C) requires 20 days for equilibration for major ions (21). The equilibration time had to be determined for the VESPOS sampler because the sample volume increased to 30 ml from conventional sampler compartments. It is well known that the most important factors controlling equilibration time are the diffusion coefficient of the substance of interest, its degree of adsorption to the solid phase, the temperature, and the porosity of the sediment (21). Porosity of the sediment of the study location decreased from about 0.86 at the sediment surface to about 0.74 at 30 cm sediment depth. The equilibration time for the new sampler was tested in two laboratory experiments using sediments from the study location in the Central Basin of Lake Erie. In the first experiment, eight samplers were placed approximately 30 cm below the sediment-water interface in a box core and kept at room temperature (±20°C). Every week, two samplers were retrieved and analyzed. By the first week the majority of the elements were already equilibrated. Two weeks

appeared to be an adequate equilibration period for all the trace elements analyzed (Figure 2). In the second experiment, the sediments were kept at ±4°C. Under this condition, the equilibration of some elements required up to three weeks (Figure 2). The concentrations shown in Figure 2 represent the average results obtained by separate determination in pore water collected by two different samplers. The results were consistent with the equilibration times reported by Carignan (21) for the conventional dialysis sampler.

The reliability of the VESPOS sampler was tested by comparing the concentration profiles of elements in sediment pore water with those obtained by using the conventional peeper sampler. Examples of the concentration profiles of selected elements obtained with the VESPOS sampler after an equilibration period of four weeks in Lake Erie, are presented in Figure 3. Potential heterogeneity of sediments at the sampling location, even within a few meters, makes the comparison of the concentration profiles from different samplers difficult. However, trends and concentrations in the profiles were similar in the pore water collected by both samplers (conventional/VESPOS). The observed differences were consistent with the natural variation of sediment geochemistry in the Central Basin of Lake Erie (22). The only exception was the concentration profile of Mg. Trends in the concentration profiles were similar for both samplers, however, Mg concentrations were 28% lower in the pore water collected with the VESPOS. Contamination from the conventional dialyser sampler equipment or assembling process can

be ruled out due to concentrations of Mg below the detection limit in sample blanks. The concentrations of some trace elements, such as Be, Cd, Pb and V, in collected pore water samples were below the detection limit of the analytical instrument employed in this study. Therefore, we were not able to compare the efficiency of the two sampling techniques for these elements.

Simon *et al.* (10) showed that when diffusion-controlled samplers were exposed to air for 5 min, as much as 0.5 $mg.L^{-1}$ of oxygen diffused into the sampler compartment solutions. The concentration profiles of Fe and Mn show reduction of these two elements without any indication of oxidation artifacts. When sampling pore water in deep water, the VESPOS sampling bottles can be capped in the sediments by a remotely operated valve system attached to the sampler (16), therefore, the pore water is never exposed to oxygen. Similar concentration profiles of Fe, Mn, and Si in sediment pore water obtained by both methods indicated that 2-cm sampling intervals (rather than 1-cm in the conventional sampler) were adequate to describe the concentration profiles in pore water and to evaluate diagenetic changes in the sediments.

The test of the two pore water samplers in Lake Erie demonstrated that uncontaminated samples can be collected on a routine basis. Further, since the retrieval of the samples from the VESPOS did not require additional manipulation, except capping the sampling bottles, a single person can process several VESPOS samplers simultaneously. It appears that this technique

considerably reduces the labour, retrieval time and handling involved in sediment pore water sampling.

CONCLUSIONS

The VESPOS sampler, like any other sampler for sediment pore water, unavoidably suffers from certain limitations. In this case they are the sampler dimensions, only feasible for soft sediments, and the limitations of depth resolution of sampling (2 cm). However, when compared with many currently available sampling methods, the advantages of this sampler are considerable. The main benefits are logistics. The large volume of pore water sampled within a 2-cm interval increased the analytical potential. Assembly of the sampler and the recovery of the samples are much simpler, minimizing the risks of contamination. This sampler considerably simplifies the sampling procedure eliminating the need for several people, glove box, and disposable syringes to be used in the field. Also, because the sampling bottles can be capped in the sediment, this sampler can be used for collecting sediment pore water in deep waters where the time for retrieval from the bottom sediments and sampling become a critical factor.

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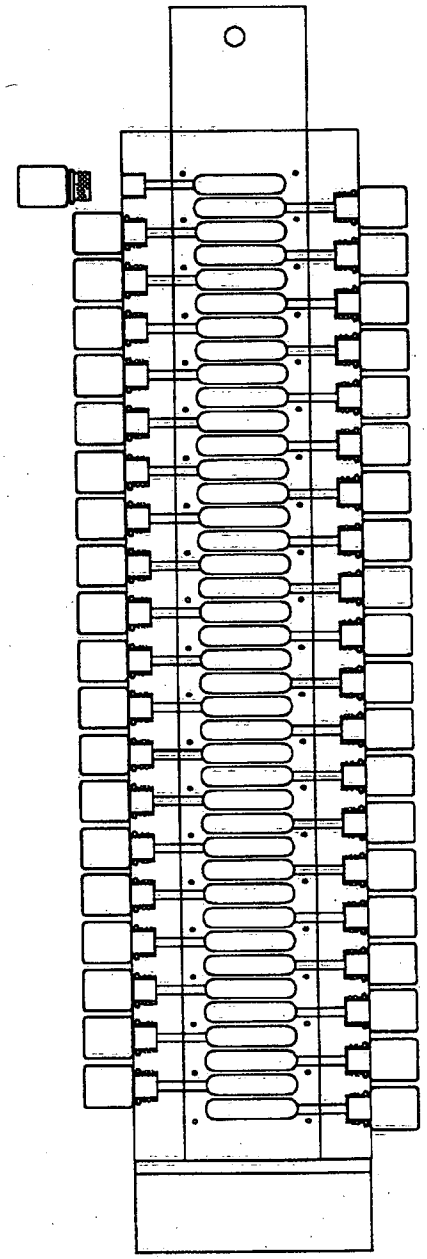
Figure 1.

VESPOS
(Volume Enhanced Sediment Porewater Sampler)

Front view



3-D view

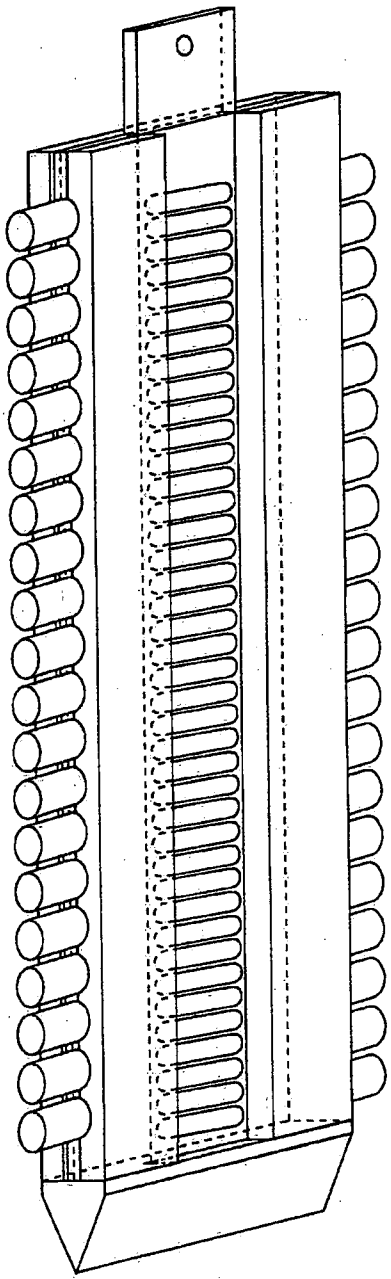


Figure 2. VESPOS Equilibration with Porewater at 20C and 4C 20 cm Below the Sediment-Water Interface

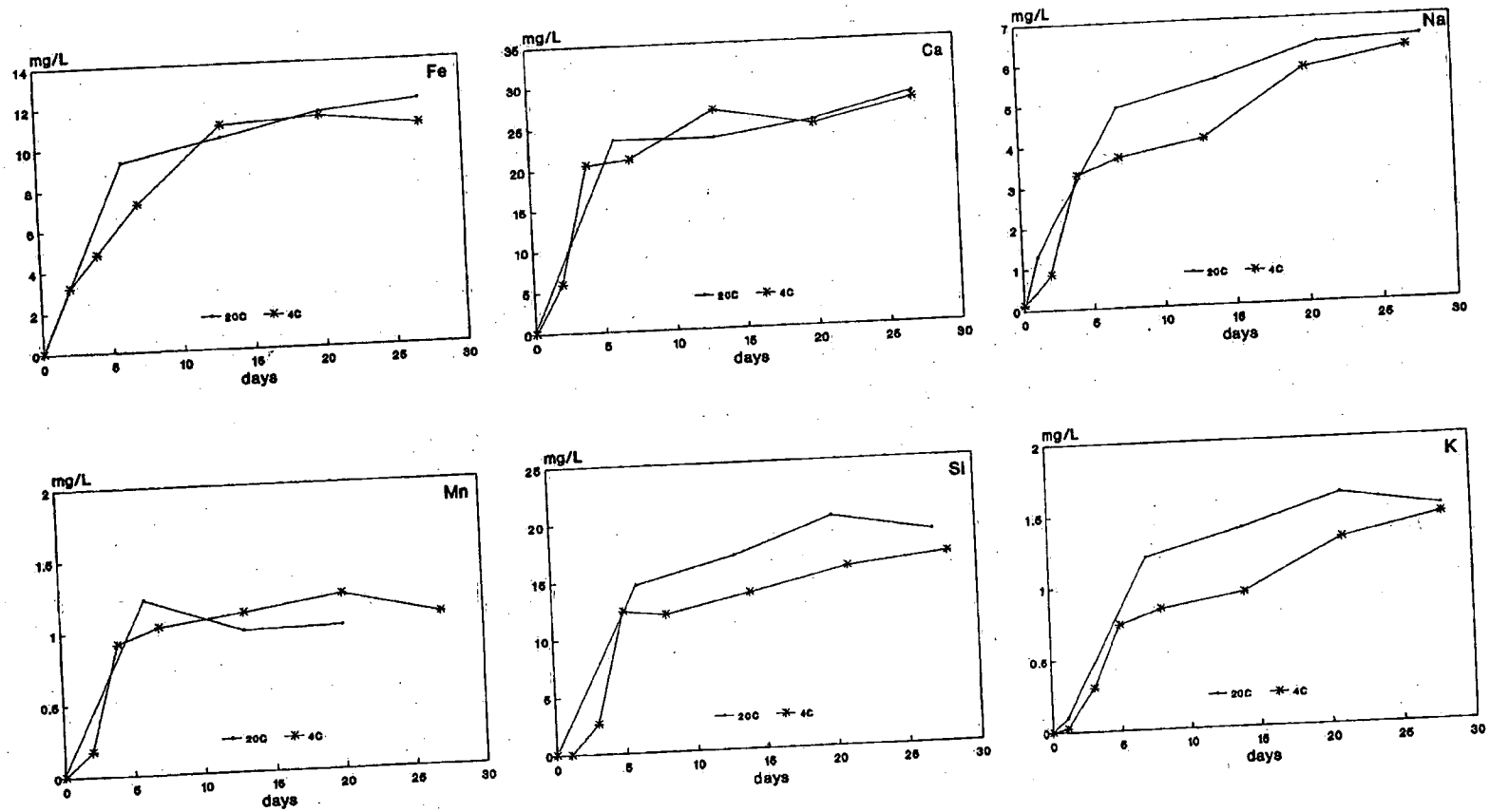
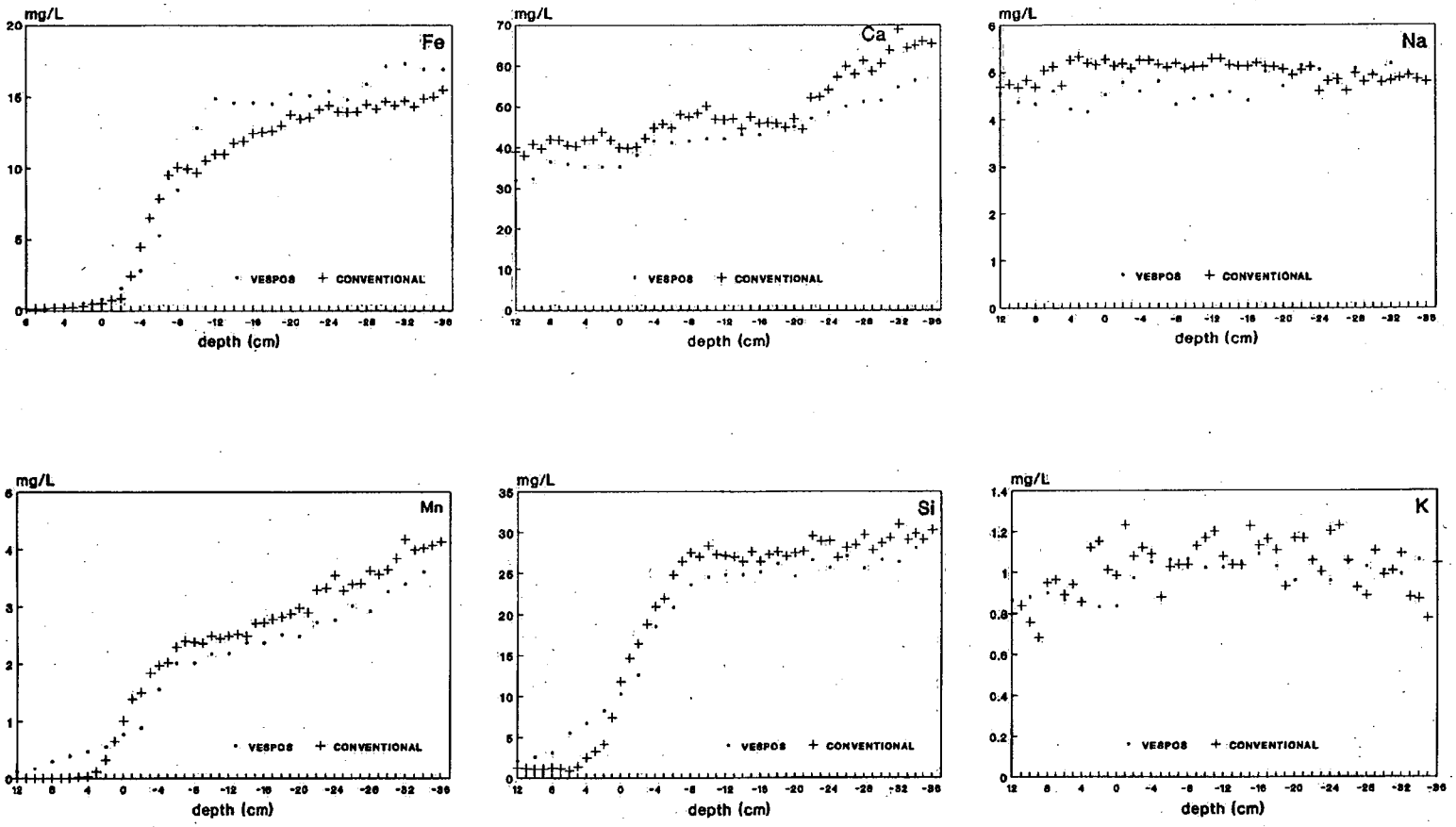


Figure 3. Lake Erie Porewater Concentration Profile Obtained with Conventional Peeper and VESPOS



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