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A New Method for Determining the Concentrations of Volatile Organic Compounds in Sediment Interstitial Water

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The bioaccumulation of sediment-sorbed organic contaminants is likely to be mediated by the transfer of chemicals through interstitial water. Unfortunately, laboratory studies of sediment-sorbed chemical bioavailability have either not assessed chemical concentrations in interstitial water or have utilized methods that require disruption of the sediment layers. We report here a simple method for the removal of interstitial water samples with an in situ technique. This method can be used to determine relevant exposure concentrations in laboratory studies of sediment-sorbed chemical bioavailability and toxicity.

MATERIALS AND METHODS

Chlorobenzene (CB) was used as the test compound in all studies. Unlabeled (Aldrich Chemical Co., Milwaukee, WI) and uniformly ring-labeled ^{14}C-CB (Pathfinder Laboratories, Inc., St. Louis, MO) were used as received and were reported by the manufacturers to be at least 98% pure. A natural sediment that has a high organic carbon content (14.5%) was used as a sorptive test substrate, and acid-washed and combusted sea sand was used as a nonsorptive substrate for control experiments.

The in situ sampling device consisted of a 5-mL plastic syringe that was fitted with a conical sampler (Fig. 1). The sampler was fabricated from the tip of a 30-mL plastic syringe that was cut off behind the point where the syringe walls begin to taper. The resultant cone had an inner diameter of 18 mm, a height of 13 mm, and an internal volume of 2.2 mL. The male end of the cone was attached to the syringe with a 50-mm long section of polyethylene tubing (3.0-mm i.d.). A steel screen (18-mm o.d., #20 mesh) was inserted in the cone and served as a support for a 0.45-µm pore-size membrane filter (Nuclepore Corp., Pleasanton, CA) and was held in place by a retaining collar that was fabricated from a polypropylene tube (18-mm o.d.). Only Nuclepore filters were used in these experiments because other membrane or glass-fiber filters (e.g., Millipore, Whatman, or Gelman) were found to sorb CB. Accordingly, the use of this

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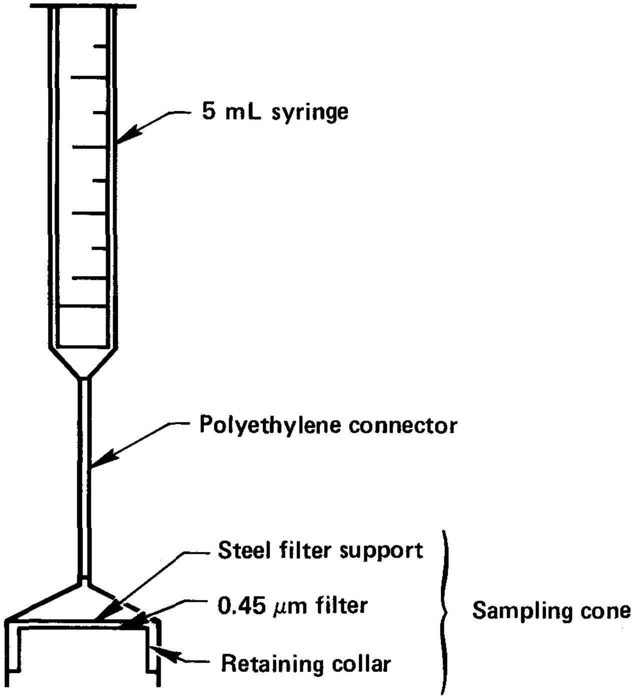

Figure 1. Diagram of the in situ interstitial water-sampling device.

system for any compound other than CB must be accompanied by tests for compound sorption to the filters, sampling device, and labware.

Interstitial water samples were obtained by inserting the sampling device through the overlying water and directly into the sediment to a depth of approximately 8 mm. Water samples (up to 350 µL) were effectively removed from the sediment by the vacuum created in the syringe when the plunger was withdrawn; the sampling cone was then disconnected. Each water sample was added directly to a tared scintillation vial that contained 15 mL of scintillation cocktail (Instagel, Packard Instrument Co., Downers Grove, IL). The concentration of chemical in the interstitial water was determined subsequently by weighing the vial to determine water content and then by quantifying the radiolabel by liquid scintillation counting.

Control experiments were conducted to verify that water above the sediment surface was not being drawn up with the interstitial water samples obtained by the in situ method. A series of five nonradiolabeled sediment solutions were prepared as before, and tritiated water (Amersham Corp., Arlington Heights, IL) was added to the overlying water (final specific activity = 2 μCi/L). Interstitial water samples (100-500 μL) were removed and analyzed as before, and the volume at which ^3H appeared in the interstitial water was determined. The effectiveness of the *in situ* method was investigated by comparing it to conventional centrifugation and compression techniques (Adams et al. 1980; Edmunds and Bath 1976). Three replicate, 200-mL radioactive solutions of CB (1 μg/L; 1 μCi/L) were mixed with 10 g of each test sediment in 250-mL glass centrifuge jars and equilibrated for 48 hr on a mechanical shaker. Sediments were precipitated from solution by centrifugation at 400 x g for 30 min, and overlying water samples (1 mL) were subsequently withdrawn and counted. Samples for isolation of interstitial water by centrifugation were obtained by decanting the overlying water, scooping out approximately 5 cc of sediment that was immediately placed in a 40-mL glass tube and centrifuged at 1,300 x g for 30 min. After the sample was centrifuged, the overlying water was pipetted directly into a tared scintillation vial that was subsequently weighed and counted. Sediment aliquots for isolation of interstitial water by compression were obtained in an identical manner except that the sediment was placed directly into a Reeburgh-type squeezer (Reeburgh, 1967) and was compressed under 80 lb of pressure. *In situ* samples were obtained and analyzed as described above, and three replicate analyses were conducted for each method of extraction.

RESULTS AND DISCUSSION

The results of the comparative interstitial water analyses (Table 1) indicate that the *in situ* extraction method greatly reduced the loss of the volatile test compound when compared to conventional methods. Quantitative recoveries of tritium and CB were achieved with the *in situ* method, whereas significant losses of CB were observed with the centrifugation and squeezing methods.

Table 1. The percent recovery of tritium and chlorobenzene in interstitial-water samples.

	% Recovery[a]			
	Sand		Organic Sediment	
Method	Tritium	Chlorobenzene	Tritium	Chlorobenzene
Compression	91(8)[b]	73(15)	94(6)	67(15)
Centrifugation	104(4)	33(9)	95(5)	49(1)
In-Situ Extraction	100(6)	101(3)	96(6)	95(2)

[a] 100 x (cpm/mL interstitial water)/(cpm/mL overlying water)
[b] (Standard deviation)

Control experiments conducted with tritiated surface water confirmed that only interstitial water was withdrawn by the *in situ* method, as no surface water was drawn into samples less than 350 µL. Such overlying-water-breakthrough experiments must be conducted for individual sediments due to differences in compaction and porosity. The interstitial-water-sampling method described in this paper can be used to determine the interstitial water concentrations of other contaminants in laboratory sediment assays. Although radiochemical detection was used in these experiments, modifications in this basic technique should permit sample quantitation by conventional analytical methods.

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