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Effects of Centrifugation Speed on Measurements of Thallium in Sediment Porewater By: Jose M. Azcue, Venghout Cheam and Josef Lechner NWRI Contribution # 96-58

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Abstract

Pore water recovery increases directly with the speed of centrifugation. After centrifugation at 1,000 rpm a range of 36-17% of total pore water was recovered from the surface and at 20 cm sediment depth. However, even after centrifugation at 20,000 rpm about 30% of pore water remained unrecovered due to sediment compaction and pore size reduction. The results of this study indicated that sediment pore water can be divided in three fractions, free-, trapped-, and bound-pore water. The concentration of thallium (Tl) is significantly different in each pore water fraction and increases with increasing centrifugation speed. Centrifugation of the sediments at low speed (<4,000 rpm) and in situ dialysis yield similar concentrations of Tl in sediment porewater, corresponding to the free-fraction. Pore water data obtained by different centrifugation speeds may be significantly different with serious environmental consequences when studying fluxes and transport of trace elements.

Introduction

Sediment pore water plays an important role in the cycling of trace elements in the aquatic environment. Recent studies have shown that pore water directly affects many processes such as the toxicity of contaminants to aquatic organisms (Ankley and Schubauer-Berigan, 1994; Carr and Chapman, 1995; Reynoldson, 1987); diagenetic reactions of chemical species (Carignan and Lean, 1991; Sherman et al., 1994; Tessier et al., 1989); and the diffusion of trace elements into the water column (Azcue et al., 1994; Pedersen et al., 1993; Rivera-Duarte and Flegal, 1994). Several methods have been developed and are currently used to collect sediment pore water (Mudroch and Azcue, 1995). Centrifuge extraction of sediment pore water is one of the most prevailing methods employed in geochemical studies. Some of the limitations of the first centrifugation methods, such as chemical artifacts from oxidation and temperature variations as a result of sample processing, have been successfully addressed and improved by several groups (Fanning and Pilson, 1971; Bray et al., 1973; Troup et al., 1974; Emerson, 1976; Lyons et al., 1976; Engler et al., 1977; Elderfield et al., 1981; Bauer et al., 1988;).

The trace elements in sediment pore water may be dissolved (free), or held to the solid phase by different degrees of physical or chemical bounding. Carignan et al. (1985) suggested that the measurements of parameters in collected pore water should be regarded as operationally defined (i.e., method-dependent) until it is shown that independent procedures consistently yield similar results. Centrifuge extraction, like other methods, will only yield a fraction of the total sediment pore water. An assumption is usually made that the fraction obtained at the centrifugation speed used in the extraction procedure is representative of the total sediment fluid.

The scientific interest to measure water bound to solid surfaces in larger pores in soils goes back to the beginning of the century. In 1907, Briggs and McLane developed a method to measure the "moisture equivalent" which was defined as the ability of the soil to hold water under centrifugal force 1000 times that of the force of gravity. The large diversity of centrifugation procedures to extract sediment pore water reported in recent literature makes comparison of results from different studies difficult. Centrifugation speed, ranging from <1,000 rpm to >20,000 rpm, is the most common variable described in the literature. However, limited research (Adams et al., 1980; Carignan et al., 1985; Schults et al., 1992; Ankley and Schubauer-Berigan, 1994) has been carried out to evaluate the effects of these variables on the concentrations of trace elements in sediment pore water. There is a definitive need of standardization of the extraction methods of pore water to be able to compare results of concentration of trace elements in pore water from different studies.

Thallium (T1) was selected for this test for three reasons: (i) while being a highly toxic element very little has been studied of its geochemical behavior, most likely due to the scarcity of data as conventional instruments lack the necessary sensitivity for Tl detection; (ii) the ultrasensitivity of the laser-excited atomic fluorescence spectrometric method, requiring only 3-10 μ L of untreated sample for direct determination of Tl, made possible the detection of very low level of Tl in aquatic media; (iii) the determination of Tl is less susceptible to contamination than other trace elements (only 0.2 ng Tl/L in blanks without clean room practices reported by Cheam et.al., 1995) and thus should provide information on geochemical behavior unstained by contamination. The objective of this research was to study the effect of the centrifugation speed on the extraction of Tl in sediment pore water. This work provides an insight on the quantities of trace elements associated with different "fractions" of the pore water.

Material and Methods

Centrifugation followed by filtration

All the samples discussed in this study were collected in July, 1995 at the Central Basin of Lake Erie (41°56′06"N, 81°39′30"W). Figure 1 shows schematically the different samples and procedures carried out in this study. Sediment cores were collected by divers using Plexiglass tubes of 6.6 cm inner diameter. The cores were kept upright and tightly closed with nylon stoppers to minimize perturbation of the sediment during transport to the ship. The cores were kept upright and at 4°C until processed in the field. The extractions of the pore water were made in the field within few hours of sampling and in a refrigerated centrifuge to minimize temperature-related changes. Before centrifugation each sediment core was sectioned into 2 cm subsamples using an hydraulic extruder (Mudroch and Azcue, 1995). Complete details of the sediment preparation used in this study were described elsewhere (Azcue et al., 1996).

Sediment cores were extruded directly into a nitrogen-filled The 2-cm subsamples were placed Plexiglass glovebox. into preweighed 50 mL nitrogen=filled centrifuge bottles, and sealed. The samples were removed from the glovebox, and centrifuged at 1,000 rpm for 30 min. After centrifugation the supernatant water was collected with plastic syringes and filtered through a Millipore 0.45 μ m HA membrane. The filters were soaked in a 0.2% HNO3 solution for about three days prior to the filtration. The filtrates were collected in polystyrene vials pre-acidified with 50 μ l of Ultrapure Seastar concentrated HNO₃ and stored at 4°C until analyzed. The remaining sediment was sequentially centrifuged at 4,000; 10,000; and 20,000 rpm for 30 minutes at each speed. The supernatant from each centrifugation step was processed as previously indicated (Figure 1). All manipulations were carried out under a nitrogen atmosphere to avoid oxidation artifacts. Once the samples were centrifuged at 20,000 rpm and supernatant water was collected, the remaining sediment was oven dried at 60°C for 48 hours to determine total water content.

In situ dialysis ("peepers")

Three dialysis samplers ("peepers", Hesslein, 1976) were used in this study to recover in situ sediment pore water at 1 cm intervals. To remove any oxygen stored in the samplers' acrylic material, the peepers were placed in containers with doubly distilled water (DDW) and the containers were bubbled with nitrogen for two days before assembling the peepers (Carignan et al., 1994). Each peeper had a sequence of 60 compartments which a few days prior to deployment, were filled with oxygen-free deionized DDW and assembled by covering the open side with a 0.45 μ m cellulose (Gelman Scientific, membrane Inc.) (Rosa and Azcue, 1993). Subsamples of the water used in the assembling and storage of the peepers were kept for further analysis to monitor any possible contamination. The peepers were kept in oxygen-free DDW until divers installed them vertically in flat areas of the lake bottom. The peepers were left for three weeks on the lake bottom to allow the chambers to equilibrate with the sediment pore water. Upon retrieval the peepers were quickly rinsed with lake water to dislodge adhering sediment particles. The pore water from each compartment was immediately removed using disposable syringes. The samples were stored in polystyrene vials which were pre-acidified with 50 µl of Ultrapure Seastar concentrated HNO3 and stored at 4°C until analyzed. All materials used in the collection of the pore water were previously acid washed following the method recommended by Nriagu et al. (1993).

Analytical

Laser-Excited Atomic Fluorescence Spectrometer The details of the copper vapour Laser Excited Atomic Fluorescence Spectrometer (LEAFS) have been previously described (Cheam et.al., 1992). For T1, the 511 nm line was used to optically pump a Rhodamine 575 dye laser. The dye laser output (553.58 nm) was then frequency-doubled by a second harmonic generator to give the 276.79 nm UV light, which excites T1 atoms generated in the graphite furnace. The resulting fluorescence light (352.94 nm) was collected and measured via a narrow bandpass filter (1 nm) - monochromatorphotomultiplier- boxcar system.

LEAFS method

Thallium concentrations were determined using a recently developed LEAFS method having a detection limit of 0.03 ng/L of Tl (Cheam et. al., 1995). Five microliters of porewater was analyzed directly (without any preconcentration) via an in situ known addition technique (Cheam et. al., 1994), which was shown to nullify interference effects caused by sample matrices and to compensate instrumental drifts more effectively than the standard the calibration curve. The method accuracy was demonstrated by successfully recovering more than 50 spikes made on six different water samples. In addition, a Reference Material (NIST 1643c) was analyzed undiluted and 2000-times diluted and was found to contain 7.8 \pm 0.5 μ g/l and 4.18 \pm 0.36 ng/l of Tl, which agree with the recommended values of 7.9 μ g/l and 3.95 ng/l, respectively. The precision of 19 groups of replicate analyses showed a median relative standard deviation of 4.7 %.

Results and Discussion

The average content of organic matter in sediments ranged from 13.4% at the surface to 11.6% at 20 cm sediment depth. The water content of the sediment decreased from approximately 90% at the surface to approximately 70% at 20 cm sediment depth. The concentration profiles of major and trace elements in the sediment were discussed elsewhere (Azcue et al., 1996).

Table 1 shows the cumulative amount of pore water, determined by weight loss, extracted from each sample at the different speeds of centrifugation. The decrease in the amount of pore water recovered from the sediment water interface, for each of the ascending centrifugation speeds, reflected the increasing compaction of the sediment with depth of burial. The pore water recovered after centrifugation at 1,000 rpm ranged from 36% at the sediment surface to 17% at 20 cm sediment depth. The centrifugation at 4,000 rpm yielded 73 to 48% of total pore water. When the centrifugation speed was 10,000 rpm the recovered cumulative water ranged from 81 to 65% of the total pore water. The total pore water recovered at 20,000 rpm amounted 93% in the surficial 2 cm of the sediment. However, even at this speed approximately 30% of pore water remained unrecovered at 20 cm sediment depth. Edmunds and Bath (1976) showed that significantly high rotation speeds are required to drain sediment pores of 0.1 μ m radius or less. Therefore, sediment compaction, specially in the deeper sections of the sediment, and pore size reduction during spinning explain the incomplete pore water recovery.

Based on previous classifications of water found in soils or sludges (Bouyoucos, 1921; Vesilind and Martel, 1990) the different volumes of pore water extracted at the four centrifugation speeds were interpreted as different fractions of sediment pore water. The sediment pore water extracted at the low speed can be defined as "free pore water" fraction and represents free water that surrounds the sediment particles and is not associated with the solid phase. This water can be displaced by gravity or pressure gradients (de Marsily, 1986). The fractions of pore water extracted at 10,000 and 20,000 rpm, can be defined as "trapped water" and represent water that is trapped between the sediment particles and held by forces of molecular attraction. These forces decrease with the distance of the water molecule to the sediment particle (de Marsily, 1986). The unrecovered fraction can be referred as "bound water" and represents water that is constituent part within the sediment particle structure and can be released only by thermochemical destruction of the particles (Vesilind and Martel, 1990).

The concentration of Tl in sediment pore water obtained by in situ dialysis is shown in Table 2. The peeper sampler is based on the passive equilibration and is only a function of the diffusion coefficient and the equilibration time. Therefore, it seems that the pore water sampled with the peepers corresponds only to the fraction previously defined as "free pore water". The concentration of T1 in the pore water peaked (30 ng/1) just below the sedimentwater interface, then decreased with increasing sediment depth to approximately 1 ng/l. This profile indicated precipitation of T1(III) in the oxic surface sediment layer. Thallium forms the most stable of the complexes of trivalent cations (Korenman, 1963). The effects of diagenetic processes in the pore water profiles for Tl in Lake Erie has been discussed elsewhere (Cheam et al., 1996). The concentrations of Tl obtained after centrifuging the sediment at 1,000 and 4,000 rpm were similar to those obtained by in situ dialysis. These results suggested that Tl extracted from sediment pore water by centrifugation speeds up to 4,000 rpm and by dialysis methods are of comparable nature, originating from the free porewater. Different scientists reported previously similar results of trace elements for both methods, i.e., in situ dialysis and low speed centrifugation (<5,000 rpm) (Bufflap and Allen, 1995).

The concentrations of Tl in the fractions extracted by centrifuging the sediment at 10,000 and 20,000 rpm were significantly greater than in the rest of the extractions. The

concentrations in the pore water in the surface 2 cm were 95 and 113 ng/l. On the other hand at 18 to 20 cm sediment depth the concentration of Tl averaged only 7 and 34 ng/l, at 10,000 and 20,000 rpm, respectively (Table 2). The forces of molecular attraction between pore water and solid phase can reach forces of >10¹² Pa, decreasing rapidly with increasing distance of the water molecule to the grain. When the applied forces due to centrifugation at a high speed is greater than those attracting the molecules and the solid phase they will separate. For instance, pore water will displace Tl⁺ ions from exchange sites in the geological material (Table 3). Other process which may affect the release of pore water is sediment compaction due to high speed centrifugation. Thallium compounds have a wide range of densities varying from 2.32 g/cm³ for thallium aluminum to 10.2 g/cm³ for thallium oxide (Tl₂O₃) (Korenman, 1963). Sediment compaction during spinning may release pore water fluids trapped in unconnected and dead-end-pores (Table 3). These pores are like "bubbles" of fluid occurring in the sediment solid phase and are very important to study mechanisms of sediment compressibility and total concentration of trace elements in porous media (de Marsily, 1986).

Similar differences were observed in recent data on mercury concentrations in sediment pore water of the Great Lakes. Mercury concentrations were approximately one order of magnitude greater when the sediments were centrifuged at 15,000 rpm (Matty and Long, 1995) than those obtained at 4,000 rpm centrifugation speed (Gobeil and Cossa, 1993). Although, part of the reported concentration differences may be site-related, the speed of centrifugation may play an important role in the reported concentrations. Further, it is interesting to note that the concentrations of trace elements, such as Cu, Pb, and Zn, in pore water extracted by low speed centrifugation were reported to be greater than those obtained by high speed extraction (Ankley and Schubauer-Berigan, 1994). Therefore, it is important to review the environmental implications of comparing pore water data obtained by different centrifugation speeds and by other methods.

Conclusions

There have been relatively few studies to determine the effects of centrifugation speed on the extraction of trace elements in sediment pore water (Carignan et al., 1985). As far as we are aware this is the first study comparing sequential extraction of pore water from the same sediment sample, with gradually increasing centrifugation speeds up to 20,000 rpm. The results of this study indicated that the speed of centrifugation plays a critical role in the extraction of sediment pore water. The different methods tested in this study showed that the sediment pore water can be divided into three fractions: free-, trapped-, and bound-pore water. In the first fraction, TI was not associated with the sediment particles and could be extracted by passive methods, such as peepers, based or gravity methods, such as concentration gradients on centrifugation (<4,000 rpm). Thallium included in the fraction defined as "trapped-pore water" was held by forces of molecular attraction or trapped within the sediment particles. The high centrifugation speeds tested in this study extracted significantly different concentrations of Tl. Even at speeds of 20,000 rpm some 7 to 30% of pore water remained unrecovered. This fraction, called "bound-pore water", included Tl linked to water that is an integral part of the sediment particle structure. This fraction is not available by conventional sampling techniques and requires thermochemical destruction of sediment particles.

The results of this study confirmed that the term "pore water" is very ambiguous. The different methods commonly used for the extraction of sediment pore water remove different fractions. The concentration of Tl was significantly different in each pore water fraction. Therefore, the measurement of Tl and trace elements in general, in sediment pore water should be further defined based on the specific method employed. There is a definitive need for standardization of the methods for extracting sediment pore water. Each scientific publication dealing with the quantification of trace elements in sediment pore water should include details of the extraction method used, water recoveries, and, if possible, characterization of the sediments. This will enable comparison of results of trace element concentration in sediment pore water from different environments.

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Zimmermann, C.F., Price, M.T., and Montgomery, J.R., A comparison of ceramic and teflon *in situ* samplers for nutrient pore water determinations, *Estuarine Coastal Mar. Sci.*, 7, 93, 1978. Table 1. Cumulative amount of pore water extracted from sediment core sections at four different centrifugation speeds and expressed as percentage of total fluids in sediments

Sediment depth	1,000 rpm	4000 rpm	10,000 rpm	20,000 rpm	un- extractable
(cm)	(sd)	% (sd)	% (sd)	% (sd)	%
0-2	36 (±4)	73 (±3)	81 (±1)	93 (±3)	2
2-4	30 (±2)	63 (±3)	79 (±8.)	89 (±6)	11
4 ⊢6	26 (±5)	64 (±2)	77 (±4)	86 (±2)	14
8 9	29 (±4)	63 (±2)	74 (±5)	84 (±3)	16
8 - 1 0	27 (±3)	58 (±1)	71, (±2),	83 (±4)	17
10-12	26 (±4)	59 (±4)	74 (±2)	85 (±6)	15
12-14	27 (±1)	59 (±1)	70 (±2)	81 (±3)	61
14-16	23 (±1)	55 (±1)	73 (±1)	84 (±2)	16
16-18	21 (±4)	55 (±4)	60 (±2)	77 (±3)	23
18-20	17 (±1)	48 (±1)	65 (±6)	(11 (11)	29

Table 2. Concentration of Tl in sediment pore water extracted at different centrifuged speeds and by *in situ* dialysis (peeper). (All concentrations expressed in ng.l⁻¹).

Centrifuged at 20,000 rpm	113 ± 36	85 ± 37	70.9 ± 27	19.4 ± 0.4	8.6±1.1	11.7 ± 2.7	35.3 ± 12	40.9 ± 13	38.7 ± 3.6	34.4 ± 14
Centrifuged at 10,000 rpm	94.5 ± 26	17.2 ± 7.8	14.7 ± 7.9	11.6 ± 6.2	11.6 ± 1.0	16.5 ± 4.0	7.8 ± 1.5	7.3 ± 1.5	11.9 ± 2.3	7.4 ± 1.9
Centrifuged at 4,000 rpm	40.5 ± 22	4.9 ± 0.4	8.3 ± 1.7	10.6 ± 1.1	2.6 ± 0.7	2.9 ± 0.8	3.5±0.2	3.5 ± 0.1	3.4 ± 0.5	4.0±0.9
Centrifuged at 1,000 rpm	27.1 ± 4.9	3.3 ± 1.7	3.9 ± 2.4	1.9 ± 0.4	2.1 ± 0.6	2.7 ± 1.6	5.2 ± 2.4	4.2 ± 2.1	1.9 ± 0.7	1.6 ± 0.3
In Situ Dialysis (peepers)	30.0 ± 5.7	10.4 ± 6.9	1.6±0.2	0.7 ± 0.4	1.1 ± 0.3	1.3 ± 0.4	0.9 ± 0.2	1.3 ± 0.3	1.2 ± 0.4	2.0 ± 0.4
Sediment Depth (cm)	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16	16-18	18-20

Table 3. Characteristics of thallium species in the three different fractions of sediment pore water

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	Free-Pore Water	Trapped-Pore Water	Bound-Pore Water
Extraction methods:	 concentration gradients (dialysis) gravimetry methods (centrifugation low speeds <4,000 rpm) 	- gravimetry methods (high speed centrifugation)	- Thermochemical destruction of the particles
Examples:	Tl ⁺ (1.49Å) Tl ³⁺ (1.05Å)	T1 ⁺ , T1 ³⁺ T1 ₂ SO ₄ T1 ₂ O ₃	Tl4Fe(CN)6.2H2O Tl(OH)3 TlASS2
	T1+000 000-1	Jo- Tet Jo- Tet	





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