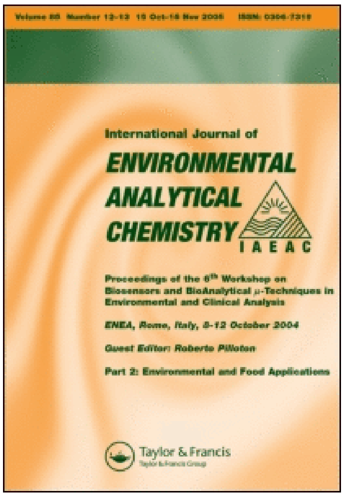

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EFFECTS OF CENTRIFUGATION SPEED ON MEASUREMENTS OF THALLIUM IN SEDIMENT PORE WATER

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Pore water recovery increases directly with the speed of centrifugation. After centrifugation at 1,000 rpm, a range of 36 to 17% of total pore water was recovered from the surface and at 20 cm sediment depth. 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 indicate 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 pore water, 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.

Keywords: Pore water; thallium; centrifugation; dialysis

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[1–3]; diagenetic reactions of chemical species[4–5]; and the diffusion of trace elements into the water column[6–8]. Several methods have been developed and are currently used to collect sediment pore water[9]. Centrifuge extraction of sediment pore water is one of the most prevailing methods employed in

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geochemical studies. Some of the limitations of early 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[10–17].

The trace elements in sediment pore water may be dissolved (free), or held to the solid phase by different degrees of physical or chemical binding. Carignan et al.[18] 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 1,000 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 has been carried out to evaluate the effects of these variables on the concentrations of trace elements in sediment pore water[1,18,20,21]. There is a need for standardization of the extraction methods for pore water to be able to compare results of the concentration of trace elements in pore water from different studies.

Thallium (Tl) was selected for this study for three reasons: (i) while being a highly toxic element very little has been studied on its geochemical behaviour, 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 to 10 μL of untreated sample for direct determination of Tl, made possible the detection of very low concentrations of Tl in aquatic media; and (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[22], and thus should provide information on geochemical behaviour unstained by contamination. The objective of this research was to study the effect of centrifugation speed on the extraction of Tl in sediment pore water. This work provides insight of the quantities of trace elements associated with different "fractions" of the pore water.

EXPERIMENTAL

Centrifugation Followed by Filtration

All the samples discussed in this study were collected in July, 1995 from 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, stored at 4°C until processed in the field. The extractions of the pore water were made in the field within a few hours of sampling and in a refrigerated centrifuge to minimize

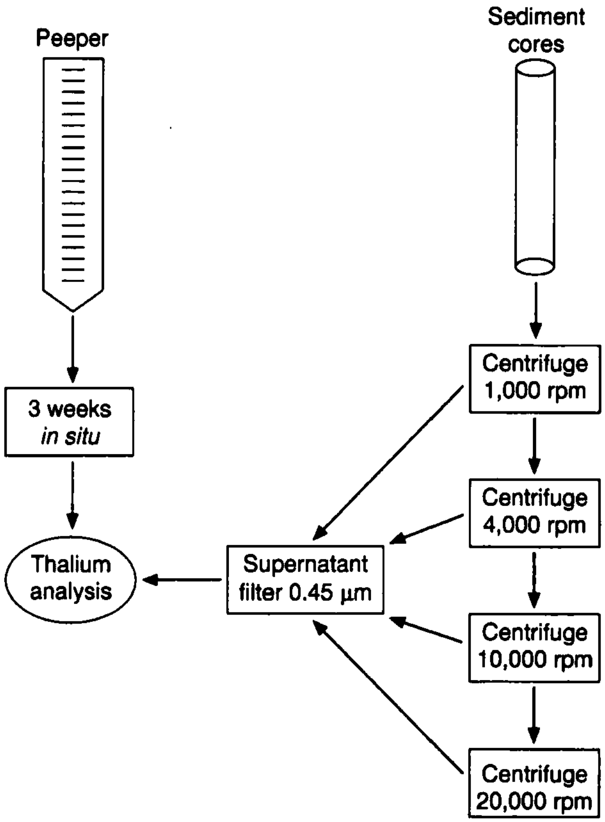

FIGURE 1.

temperature-related changes. Before centrifugation, each sediment core was sectioned into 2-cm subsamples using an hydraulic extruder[9]. Complete details of the sediment preparation used in this study are described elsewhere[23].

Sediment cores were extruded directly into a nitrogen-filled Plexiglass glovebox. The 2-cm subsamples were placed 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 minutes. After centrifugation, the supernatant water was collected using plastic syringes and filtered through a Millipore 0.45 μm HA membrane. The filters were soaked in a 0.2% HNO_3 solution for about three days prior to filtration. The filtrates were collected in polystyrene vials, pre-acidified with 50 μl of Ultrapure Seastar concentrated HNO_3, 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 the supernatant water was collected, the remaining sediment was oven-dried at 60°C for 48 hours to determine the total water content.

In Situ Dialysis ("peepers")

In this study, three dialysis samplers ("peepers")[24] were used to recover *in situ* sediment pore water at 1 cm intervals. To remove any oxygen stored in the acrylic material used to construct the samplers, the peepers were placed in containers with double distilled water (DDW) and the containers were bubbled with nitrogen for two days before assembling the peepers[25]. Each peeper had a sequence of 60 compartments which were filled, a few days prior to deployment, with oxygen-free deionized DDW and assembled by covering the open side with a 0.45 μm cellulose membrane (Gelman Scientific, Inc.)[26]. Subsamples of the water used in the assembly 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 on 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 HNO_3 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.*[27].

Analytical

Laser-excited atomic fluorescence spectrometer

The details of the copper vapour Laser Excited Atomic Fluorescence Spectrometer (LEAFS) have been previously described[28]. For Tl, 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 Tl atoms generated in the graphite furnace. The resulting fluorescence light (352.94 nm) was collected and measured via a narrow bandpass filter (1 nm)—monochromator- photomultiplier 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[22]. Five microliters of pore water were analyzed directly (without any preconcentration) via an *in situ* known addition technique[29], which was shown to nullify interference effects caused by sample matrices and to compensate the instrumental drifts more effectively than the standard 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 ± 0.5 μg/l and 4.18 ± 0.36 ng/l of Tl, which agree with the recommended values of 7.9 μg/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 the 20 cm sediment depth. The water content of the sediment decreased from approximately 90% at the surface to approximately 70% at the 20 cm sediment depth. The concentration profiles of major and trace elements in the sediment are discussed elsewhere[23].

Table I 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 the 20 cm sediment depth. The centrifugation at 4,000 rpm yielded 73 to 48% of total pore water. When the centrifugation speed was increased to 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 to 93% in the surficial 2 cm of the sediment. However, even at this speed, approximately 30% of pore water remained unrecovered at the 20 cm sediment depth. Edmunds and Bath[30] showed that significantly high rotation speeds are required to drain sediment pores of 0.1 μm radius or less. Therefore, sediment compaction, especially 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[31,32], 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 low centrifugation 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[33]. 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 par-

TABLE I 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 (cm)	*1,000 rpm % (sd)*	*4000 rpm % (sd)*	*10,000 rpm % (sd)*	*20,000 rpm % (sd)*	*unextractable %*
0–2	36 (±4)	73 (±3)	81 (±1)	93 (±3)	7
2–4	30 (±2)	63 (±3)	79 (±8)	89 (±6)	11
4–6	26 (±5)	64 (±2)	77 (±4)	86 (±2)	14
6–8	29 (±4)	63 (±2)	74 (±5)	84 (±3)	16
8–10	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)	19
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)	71 (±7)	29

ticle[33]. The unrecovered fraction can be referred to as "bound water" and represents water that is a constituent part within the sediment particle structure and can be released only by thermochemical destruction of the particles[32].

The concentration of Tl in sediment pore water obtained by *in situ* dialysis is shown in Table II. The peeper sampler is based on the passive equilibration and is a function only 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 Tl in the pore water reached a maximum (30 ng/l) just below the sediment-water interface, then decreased with increasing sediment depth to approximately 1 ng/l. This profile indicated precipitation of Tl(III) in the oxic surface sediment layer. Thallium forms the most stable of the complexes of trivalent cations[34]. The effects of diagenetic processes in the pore water profiles for Tl in Lake Erie has been discussed elsewhere[35]. The concentrations of Tl obtained after centrifuging the sediment at 1,000 and 4,000 rpm were 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 pore water. Different scientists previously reported similar results of trace elements for both methods, i.e., in situ dialysis and low speed centrifugation (<5,000 rpm)[36].

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; respectively. On the other hand, at the 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 II). The forces of molecular attraction between pore water

TABLE II 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})

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

and solid phase can reach forces of $>10^{12}$ Pa, decreasing rapidly with increasing distance of the water molecule to the grain. When the applied forces due to centrifugation at a high speed are 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 III). Another 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/cm^3 for thallium aluminum to 10.2 g/cm^3 for thallium oxide (Tl_2O_3)[34]. Sediment compaction during spinning may release pore water fluids trapped in unconnected and dead-end pores (Table III). 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[33].

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[37] than those obtained at 4,000 rpm centrifugation speed[38]. 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[1]. 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[18]. As far as we

TABLE III Characteristics of thallium species in the three different fractions of sediment pore water

	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^+(1.49A) Tl^{3+}(1.05A)	Tl^+, Tl^{3+} Tl_2SO_4 Tl_2O_3	$Tl_4Fe(CN)_6 \cdot 2H_2O$ $Tl(OH)_3$ $TlAsS_2$

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 show that the sediment pore water can be divided into three fractions: free-, trapped-, and bound-pore water. In the first fraction, Tl was not associated with the sediment particles and could be extracted by passive methods, such as peepers, based on concentration gradients or gravity methods, such as 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, 7 to 30% of pore water remains 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 concentrations in sediment pore water from different environments.

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