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in Great Lakes Ecosystem

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No. 95-
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LEAFS DETERMINATION AND CONCENTRATION OF METALS IN GREAT LAKES ECOSYSTEM

by

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MANAGEMENT PERSPECTIVE

Under the "Great Lakes Prevention Initiative", which calls for an increase in "Analytical Capabilities", we have developed an ultrasensitive instrument, the Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) which enables direct, accurate trace metals determination in natural waters. The thallium (Tl) method is a recent example. This method has been extended to encompass the direct determination of total lead (Pb) without any preconcentration and acid digestion. The concentration of total Pb was found to be significantly higher than total Tl in Lake Ontario. However, the concentration of dissolved Pb is only about twice as much as dissolved Tl, whose concentration was earlier reported to be higher than that of dissolved cadmium (Cd) in Great Lakes waters. This is an important finding because Tl has been reported to be more toxic than both Pb and Cd. The LEAFS ultrasensitivity also permits the development of a simple, apparently adequate cold dissolution procedure to be used for Tl determination in sediment. The paper further reports for the first time concentration profile of Tl in sediment pore water, which ranges from sub- to 40 ng/l. (The detection limit of the LEAFS method is 0.03 ng/l of Tl). An observed upward diffusive flux of Tl from the sediment into the overlying water may play an important role particularly during processes of hypolimnetic anoxia at the lake bottom. There appears to be a strong similarity between the geochemical transport of Tl and Cd.

Abstract. A Laser-Excited Atomic Fluorescence Spectrometric (LEAFS) method for Tl determination has been extended to investigate the direct determination (without preconcentration and acid digestion) of total Pb, for which the method validation was successfully achieved by using a standard reference material as well as many spike recoveries of digested and undigested unfiltered water samples. The method was applied to study total and dissolved Pb in many water columns collected from different stations in Lake Ontario. Dissolved Pb was found to be about twice as much as dissolved Tl, and total Pb about seven times higher than total Tl. Seventy five percent of Pb is in particulate form versus 11% for Tl. Also, a simple cold dissolution procedure using HNO_3 and HF (not a hot acid digestion) is proposed to "liquefy" sediments in a form suitable for LEAFS analysis. The procedure was used to analyze a sediment core from an area where pore water samples were also collected. The interaction dynamics of Tl within the natural environment of a water / pore water / sediment system from Lake Erie was assessed. The calculations of fluxes suggest a strong similarity between the geochemical transport of Tl and Cd. The paper also presents for the first time a genuine profile of Tl concentration in sediment pore water, which ranged from sub- to 40 ng/l and was directly determined by LEAFS. The detection limit of the LEAFS method is 0.03 ng/l of Tl.

1 INTRODUCTION

Determination of ultratrace levels of metals in environmental samples by conventional methods requires various preconcentration and separation steps, which are complicated, labor intensive, and are prone to accumulating contamination. A Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) makes possible direct analysis of real substrates for various elements [1-7].

Lead is a toxic element and has been possibly the most cited element in the scientific literature along with Cd and Hg. In contrast, thallium (Tl) is the least studied, least cited priority element even though it is next neighbor to the above three elements in the periodic table and is known to be more toxic than Pb and Cd [8-9]. Cheam et. al. [7] attributed this dilemma to the possible historical difficulties with the detection of Tl compared to other toxic metals. They based this hypothesis on their unexpected finding that the concentration of Tl in Great Lakes waters is greater than that of Cd, yet there had been no published Tl data compared to much Cd data reported for this very important ecosystem. Sperling et. al. [10], who recently demonstrated that Tl is a pollutant as they found up to 90 ng/l of Tl in the coastal waters of the German Bight (in Weser estuary at Insum, by the North Sea), attributed the Tl obscurity to the fact that Cd, Hg and others (Tl excluded) were black-listed by the 1972 Oslo-Convention on Environmental Research and hence have received much of the research funding.

This paper deals with two toxic elements, Pb and Tl. As an extension of a recently developed LEAFS method for Tl, the paper validates a method for direct determination of total Pb in lake water and applies it to study seven depth profiles from Lake Ontario. The paper then proposes a simple "cold dissolution" procedure (as opposed to a hot acid digestion of sediment) to be used in a LEAFS method for Tl determination in sediment. The paper finally presents an authentic sediment pore-water profile of Tl concentration and assesses the dynamic geochemical transport of Tl within a natural environment of a water/pore water/sediment system.

2 EXPERIMENTAL

2.1 Laser-Excited Atomic Fluorescence Spectrometer

The Copper Vapor Laser was originally designed to use pure neon as the flowing buffer gas, but we found that a mixture of 0.8 % hydrogen and 99.2 % neon is a much preferred medium. After only 20 minutes of switching from pure Ne to the mixture, the laser power output nearly doubles (Fig.1). The use of the mixture results in better laser stability. The 511 nm line was used to optically pump a Rhodamine 6G dye laser for Pb and a 575 dye laser for Tl. The dye laser output (566 nm for Pb, 554 nm for Tl) was then frequency-doubled by a second harmonic generator to give the 283 nm UV light for Pb and the 277 nm for Tl. The fluorescence light (406 nm for Pb and 353 nm for Tl) emitted by the excited atoms was collected [11-12].

2.2 Sample collection for water, pore water and sediment

Surface water samples were collected using a raft rod sampler whereas the depth samples were collected, using Go-flo bottles, from Lakes Ontario and Erie. Clean room practices were used throughout water collection [13]. The samples were immediately brought to the mobile clean laboratory. A fraction of a lake sample was immediately poured into a clean bottle and acidified to 0.2% HNO_3 (Seastar) for determination of total metals, and the remaining sample was immediately filtered through 0.4 μm filter into a clean bottle and then acidified to 0.2% HNO_3 for determination of dissolved metals.

Sediment pore water was collected using an *in situ* pore water sampler, called a "peeper". It comprises two acrylic plastic sheets (one with sample cells and the other with diffusion windows) which sandwich a dialysis membrane [14]. A peeper was deployed by divers in sediment at one station (Central Basin, 24 m deep) in Lake Erie in August 1994 and was left for three weeks to achieve equilibrium. Sixty five samples (at 1 cm interval) were collected from the peeper.

A mini box corer (25 cm x 25 cm x 50 cm) was used to collect sediment from the same site in Lake Erie. The box corer has been described in detail earlier [15]. A hand-

core was then obtained from the box corer using a clear plastic tube of 10 cm diameter. The core was vertically sectioned at every cm, and each section was freeze-dried, digested, and analyzed by LEAFS.

2.3 In situ Known Addition Analysis

Details of this technique have been described earlier and was used for all analyses [16]. A programmable micropipette was used to carry out *in situ* known addition pick-ups and injections into the graphite furnace. Via matrix matching, this technique was shown to minimize interference effects caused by sample matrices and to compensate instrument drifts more effectively than the standard curve calibration technique. Only 3-10 μ L of aqueous samples was needed for each analysis. Standard concentrations used varied from 0.1 to 100 ng/l and all computations utilized peak heights.

3 RESULTS AND DISCUSSION

3.1 Determination of dissolved and total Pb and Tl in lake water and pore water

A LEAFS method for Tl determination was recently developed [12] in which spike recoveries using lake water samples were successfully made. Also a Reference Material (NIST 1643c) was used to further confirm the accuracy. The precision of 19 groups of replicate analyses ranged from 0.2 to 14 % with a median relative standard deviation of 4.7 %. A detection limit of 0.03 ng/l (0.6 fg) was achieved. The method was used for lake water and pore water analysis.

The Tl method was extended to determination of total Pb in unfiltered water samples. To ensure the analysis of unfiltered samples represents total Pb, a comparison has been made between the results obtained by direct analysis of 3 different undigested unfiltered samples versus those by direct analysis of digested samples. Likewise, a comparison was made involving 2 spiked unfiltered samples. The analysis of both sets of samples (digested and undigested) showed good agreement between the two sets of data. Figure 2 shows replicate analyses of actual samples used; the relative standard deviation for the 18 groups of replicate analyses ranges from 0.3 to 7 %. Also, the analysis of a

diluted Standard Reference Material NIST 1643c gave a value of 18.3 ± 1.2 ng/l ($n = 18$), which agrees with the certified value of 17.7 ± 0.9 . The practical absolute detection limit was 3 fg or 1 ng/l relative. The average concentration of Pb in the blank (0.2 % HNO_3), which was recently monitored over a period of 4 months, was 0.27 ± 0.08 ng/l ($n = 53$ measurements).

3.2 Dissolved and particulate Pb and Tl in Lake Ontario water columns

Table 1 compares the concentrations of Pb and Tl found in Lake Ontario water collected from 8 different water columns across the Lake. Dissolved Pb is about twice as concentrated as Tl, which was reported to be higher than dissolved Cd in Lakes Ontario and Erie [7]. Total Pb is about 7-times more concentrated than total Tl. Seventy five percent of Pb is in particulate form, compared to 11% of particulate Tl. Comparable magnitudes of particulate form for Pb (70%) and for Cu (18%) were reported earlier [17].

3.3 A "cold dissolution" procedure for sediment and LEAFS analysis

The successful determination of total Tl and Pb in unfiltered samples led us to seek for a simple procedure to "dissolve" sediments for LEAFS determination of Tl, one which avoids the usual hot acid digestion. We tested HNO_3 , HCl, aqua regia and obtained low recoveries ($< 70\%$) of Tl from a sediment standard reference material NIST 2704. This implies that the silica lattice of the sediment composition has to be broken down also. HF was then incorporated with the other acids at various proportions and dissolution times. It seems that a simple "cold dissolution" procedure may have been found by using HNO_3 and HF: weigh 0.1 g of sediment into a clean plastic bottle, add 2.5 ml of concentrated HNO_3 , let stand for 2 hrs; add 2.5 ml of HF and let stand overnight. Pipette 1 ml of the acid solution and dilute to 100 ml, followed by LEAFS analysis. We found 1.14 ± 0.09 $\mu\text{g/g}$ ($n = 19$) which compares well with the certified value of 1.06 ± 0.07 $\mu\text{g/g}$ of Tl. To further confirm the effectiveness of the proposed dissolution procedure, microwave acid digestions were carried out using 2 different acid mixtures, aqua regia and HNO_3 -HF; the results found were 1.06 ± 0.16 $\mu\text{g/g}$ ($n = 6$) and 1.16 ± 0.07 $\mu\text{g/g}$ ($n = 4$), respectively.

The detection limit was estimated to be about 1 ng/g of sediment. The procedure is being

tested using more certified reference materials of various origins and detailed performance characteristics will be reported. This procedure was used to determine Tl in 36 sediment samples taken from the core. The average Tl concentration was $0.8 \mu\text{g/g}$ of dry sediment. This result is used in the assessment of geochemical transport below.

3.4 Dynamics of Tl in a Lake Erie water/pore water/sediment system

Fig. 3 shows the concentration profile of Tl in water and pore water collected from the peeper. Thallium concentrations increase from the surface water (1 m) to the water-sediment interface (24 m) and reach the maximum at 2 cm deep in the sediments. The depth distribution of Tl in pore water reflects the physico-chemical conditions (O_2 , pH, etc.) at the sampling time, being very sensitive to minor chemical changes. The Tl profile is characterized by a maximum below the water-sediment interface, with concentration four times greater than in the overlying water. Such a profile is typical of redox species in pore water of sediments with aerobic surface layers. At the sampling time, the overlying water was still oxidic, so that the first few centimeters (perhaps even down to 5 cm in the sediment - see Fig.3) was still oxidic. It is not surprising that the concentration in the pore water at ≥ 6 cm is lower than the overlying water's since it's been known that in anoxic environments, Tl precipitates as metal or as Tl_2S [18, 19].

The distinct Tl sediment pore water profile, probably the first one reported, suggests that diagenetic redox cycling of Tl occurs at the sediment-water interface. The Tl peak-concentration at 2 cm deep may have derived from the mineralization of sulfidic/organic matter (early diagenesis) and acts as a transient source of Tl for the overlying lake water. This seems evidenced by the Tl concentration in the overlying water being greater than the water column's (Fig.3). There must exist a truly dynamic geochemical transport of Tl between i) the peak-concentration oxidic milieu and the sediments, and ii) between this oxidic milieu and the overlying water.

Fig.3 indicates an upward flux of Tl toward the overlying water. The vertical diffusional Tl flux from the sediments (F in $\text{ng}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$) and the accumulation of Tl in the sediments (S in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$) were calculated with Fick's first law in one dimension [20]. The estimated depositional flux for Tl ($S = 0.147 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{y}^{-1}$) is very similar to that

calculated for Cd, probably due to scavenging of dissolved species by suspended particles. The calculated diffusional flux ($F = 2.2 \text{ ng.cm}^{-2}.\text{y}^{-1}$), at the sampling time of this study, showed small sediment loss of Tl to overlying waters in the Central Basin of Lake Erie. The ratio of Tl concentration in core-top pore water to that in bottom water ranges from 1.5 to 3.3 which is very similar to that for Cd, 2 to 3 [21]. This and the similarity between the depositional fluxes of Tl and Cd strongly suggest similar geochemical transport. The upward diffusive remobilization from sediments to lake water may play an important role particularly during processes of hypolimnetic anoxia. A more detailed analysis of the seasonal variations in the geochemistry of Tl and Cd in Lake Erie is being carried out by our group.

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Table 1. Comparison of Pb and Tl concentrations in Lake Ontario water columns: dissolved, particulate and total (ng/l), and dissolved/total ratio

STATION	LEAD				THALLIUM			
Sample	Dissolved	Particulate	Total	%Diss/Tot	Dissolved	Particulate	Total	%Diss/Tot
LO-2-5	18.97	22.02	40.99	46	5.1	1.12	6.22	82
LO-2-50	13.66	59.36	73.02	19	5.6	0.63	6.23	90
LO-21-5	---	---	---	---	6.45	2.31	8.76	74
LO-21-11	---	---	---	---	5.36	2.02	7.38	73
LO-33-10	7.35	55.91	63.26	12	5.46	0.36	5.82	94
LO-33-50	11.58	45.67	57.25	20	5.02	0.04	5.06	99
LO-33-90	8.75	24.62	33.37	26	5.53	0.23	5.76	96
LO-33-130	12.01	16.32	28.33	42	5.9	0.59	6.49	91
LO-45-10	9.41	26.57	35.98	26	4.93	0.53	5.46	90
LO-45-40	6.34	25.78	32.12	20	6.1	0.57	6.67	91
LO-45-70	13.24	115.21	128.45	10	5.68	0.78	6.46	88
LO-60-4	18.33	26.08	44.41	41	---	---	---	---
LO-60-15	5.58	23.91	29.49	19	---	---	---	---
LO-60-55	16.23	24.34	40.57	40	---	---	---	---
LO-60-135	7.73	47.4	55.13	14	---	---	---	---
LO-74-5	8	20.42	28.42	28	7.01	1.1	8.11	86
LO-74-15	11.51	39.84	51.35	22	5.94	1.23	7.17	83
LO-74-45	20.88	72.32	93.2	22	5.64	0.73	6.37	89
LO-84-10	10.32	25.51	35.83	29	6.19	0.44	6.63	93
LO-84-33	8.54	44.47	53.01	16	6.85	0.49	7.34	93
LO-87-10	8.54	35.08	43.62	20	6.52	0.14	6.66	98
LO-87-30	7.35	35.51	42.86	17	5.67	0.75	6.42	88
mean =	11	39	51	25	6	1	7	89
stdev =	4	23	25	10	1	1	1	7
n =	20	20	20	20	18	18	18	18

FIGURE CAPTIONS

Fig. 1. Laser power gain vs. time when pure Ne is replaced with Ne containing 0.8% H₂.

Fig. 2. Replicate analyses of various samples (std = standard; FB = furnace blank; MQW = 0.2% HNO₃ Milli-Q-Water; UF = unfiltered).

Fig. 3. Tl concentration profile for water and sediment pore-water collected from station 84 in Lake Erie.

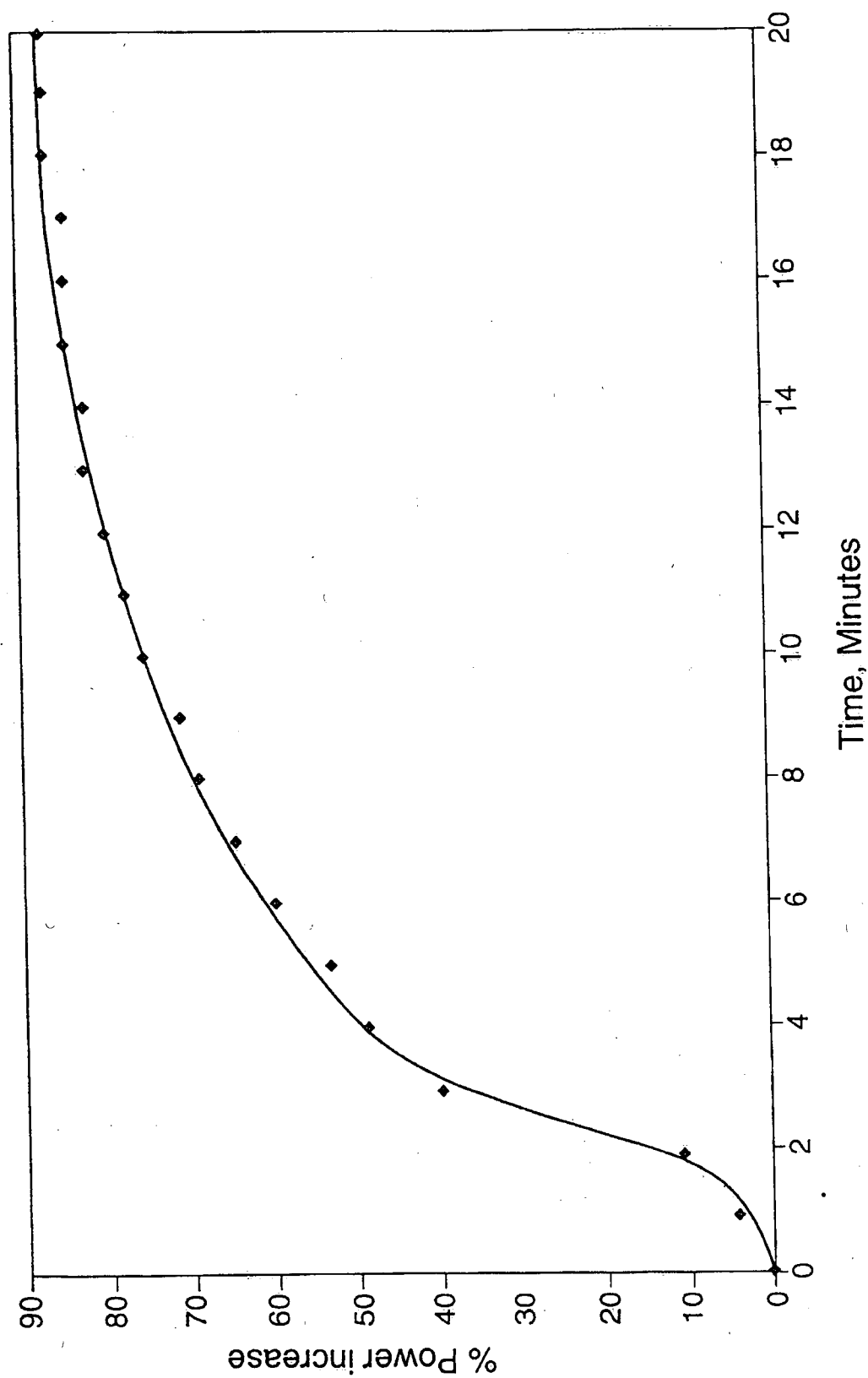


Figure 1. Laser power gain vs. time when pure Ne is replaced with Ne containing 0.8% H_2

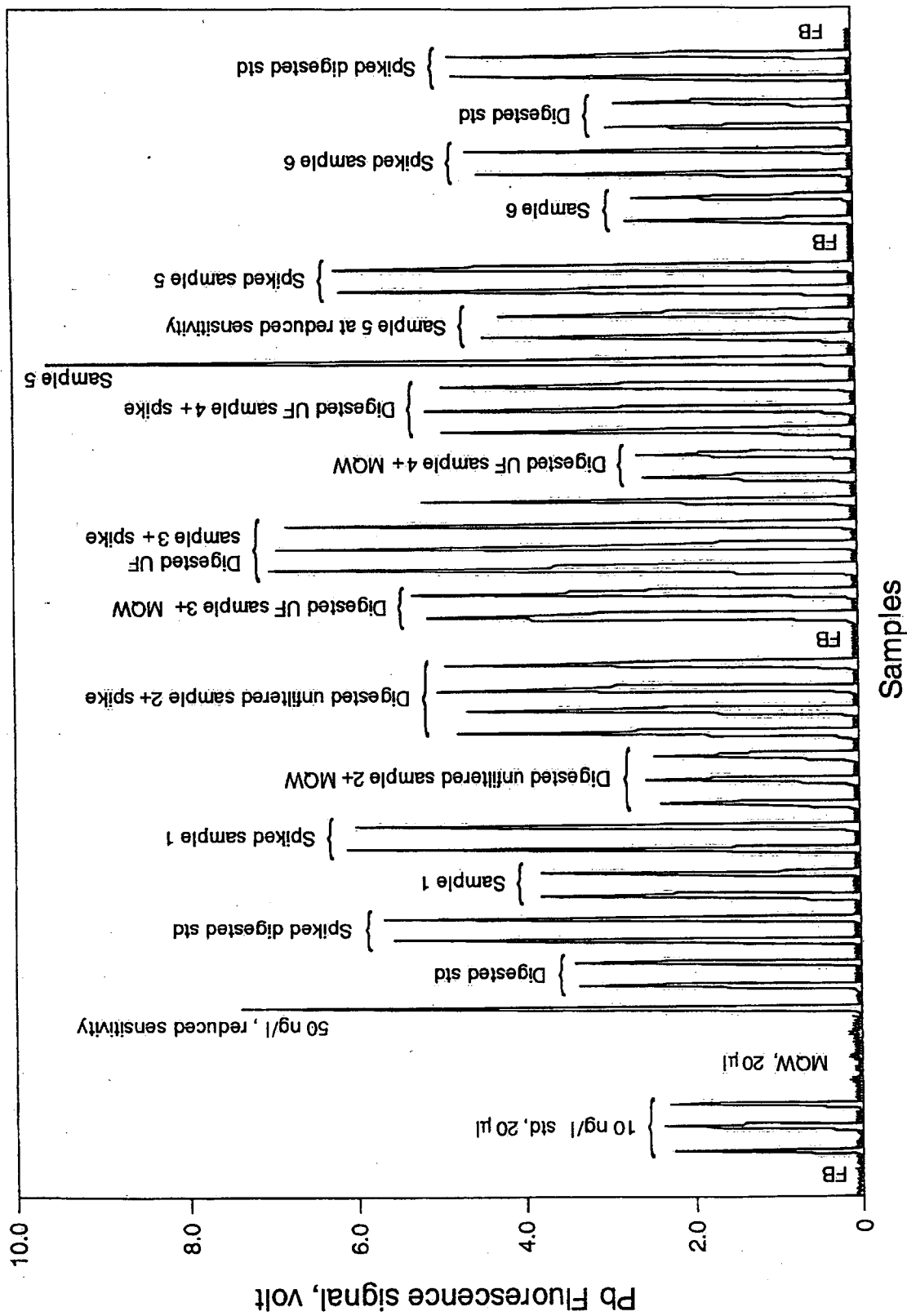


Figure 2. Replicate analyses of various samples (std = standard; FB= furnace blank; MQW= 0.2% HNO₃ Milli-Q water; UF= unfiltered.)

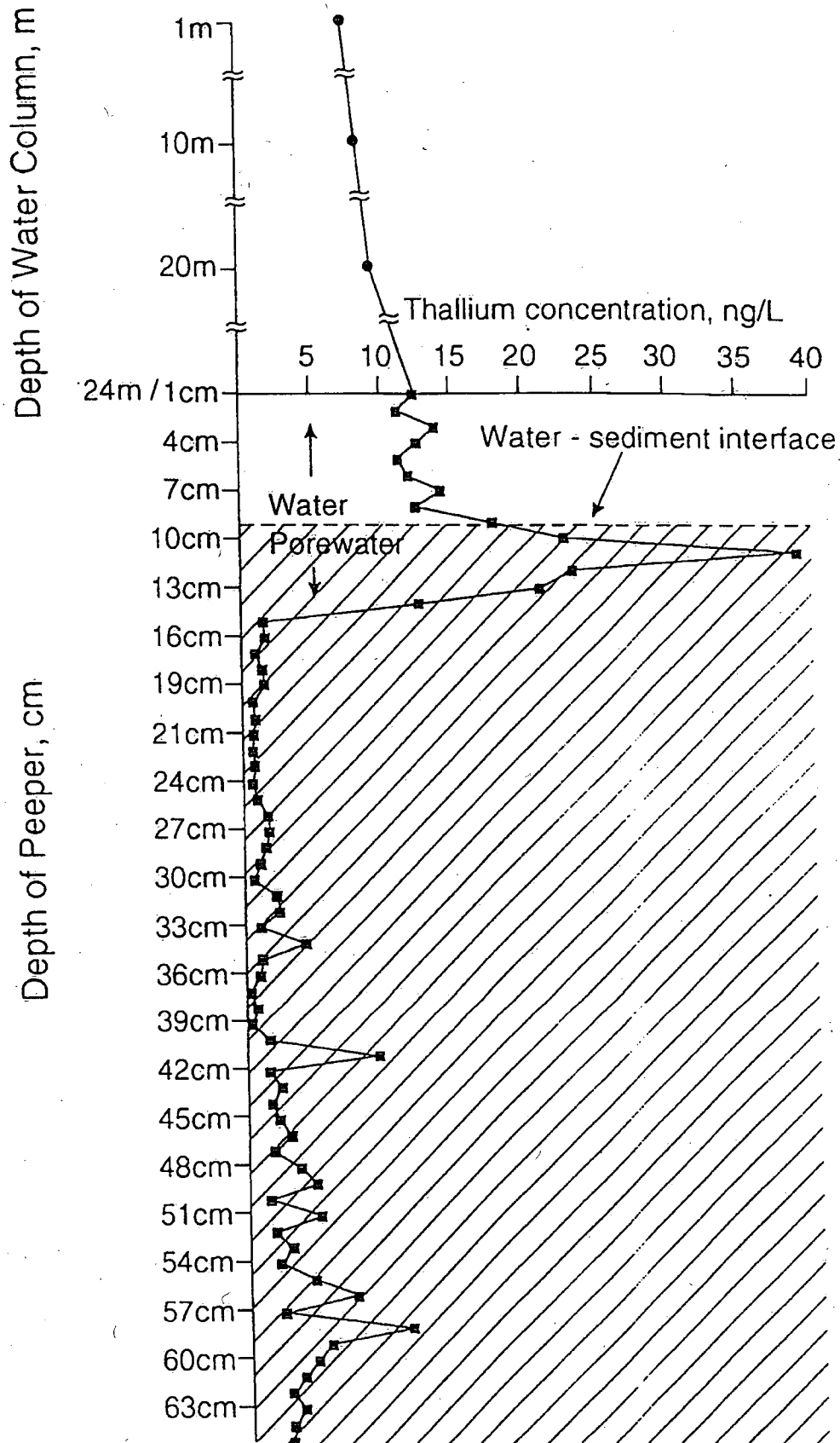


Figure 3. TI concentration profile for water and sediment pore-water collected from station 84 in Lake Erie

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