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## MANAGEMENT PERSPECTIVE

Thallium and its compounds are among the most toxic, bioaccumulative body poisons known to man. It's been reported that in mammals, thallium is more acutely toxic than lead, cadmium and mercury<sup>1</sup>. It is therefore very important to have reliable and accurate knowledge about the presence of thallium in the environment. In spite of this, thallium has not been studied at all to the same degree as other toxic metals such as lead, cadmium or mercury. The main reason appears to be historic difficulties with detection of Tl in the environment by conventional analytical methods. A case in point, based on our findings, is that the Great Lakes waters contain a higher thallium concentration than cadmium; yet there are no published Tl data available for this ecosystem compared to much published Cd data. The recent development of an ultrasensitive Laser-Excited Atomic Fluorescence Spectrometric (LEAFS) method has enabled direct detection of thallium in Great Lakes waters. The technique does not require the usual pre-concentration or separation steps. This paper reports for the first time the distribution of dissolved and total Tl in the waters of three Great Lakes including some point sources. The concentration of dissolved Tl in the lakes follows the order of Superior < Ontario < Erie.

<sup>1</sup> Zitko, V. 1975. Toxicity and pollution potential of thallium. *The Sci. Tot. Environment*, 4: 185-192.

**ABSTRACT.** *While being a highly toxic element, thallium has been studied to a much lesser degree than other toxic elements such as lead, cadmium or mercury. This is mainly because Tl is often undetected by classical analytical methods, which tend to have poorer sensitivity for Tl than for other elements. This is clearly evidenced by our findings that Tl is more concentrated than Cd in the Great Lakes waters, yet there has been no published Tl data compared to a good amount of published Cd data for this ecosystem. Recently, we have developed an ultrasensitive Laser-Excited Atomic Fluorescence Spectrometric (LEAFS) method which made possible the direct determination of thallium in lake waters. This paper reports for the first time the concentration and the distribution of dissolved and total Tl in the waters of three Great Lakes and some point sources. The median dissolved concentration of Tl are 1.2, 5.7, 9.4, and 25.7 ng/L in Lakes Superior, Ontario, Erie, and Hamilton Harbor, respectively. A range of sub-ng/L to 50 ng/L of Tl was found. The overall average ratio of dissolved over total Tl is 87% with a standard deviation of 8%. To our knowledge these Tl data are the first ones reported for this important ecosystem.*

**INDEX WORDS:** *Thallium, dissolved and total, Laser-Excited Atomic Fluorescence Spectrometry, LEAFS, Great Lakes, concentration profiles.*

## INTRODUCTION

There have been numerous trace metal studies relevant to the Great Lakes ecosystem as evidenced by a vast amount of pertinent publications, some of which are cited here (Chau *et al.* 1970; Cheam *et al.* 1976; Patterson and Kodukula 1978; Poldoski *et al.* 1978; Borgmann 1981; Nriagu *et al.* 1981; Rossmann 1982; Lum and Leslie 1983; Rosa *et al.* 1983; Hodson *et al.* 1984; Rossmann 1984; Nriagu 1986; Rossmann 1986; Rossmann and Barres 1988; Strachan and Eisenreich 1988; Coale and Flegal 1989; Gatz *et al.* 1989; Allan and Ball 1990; Mudroch and Mudroch 1992). In these papers there are no Tl data reported, and to our knowledge there has not been any Tl data reported for the Great Lakes waters. This is rather surprising considering the fact that Tl is listed among the thirteen priority pollutant metals along with lead, cadmium and mercury by the United States Environmental Protection Agency (Keith and Telliard 1979) and it is more toxic than Pb (Vercruysse 1984). In fact, it is well known that thallium and its compounds are very toxic, its toxicity being reported soon after its discovery in 1861 (Korenman 1963; Mathews and Anzarut 1968; Zitko 1975; Zitko *et al.* 1975; Venugopal and Luckey 1978; Jaworski 1981). Tl-based rodenticides and insecticides were extensively used but had to be terminated due to its high toxicity (Smith and Carson 1977). An annual average of 13 thallium poisoning cases were reported between 1958 and 1964 in Canada (Mathews and Anzarut 1968). Twenty four percent of bald eagles found sick or dead in 18 states during 1971-1972 were poisoned by Tl (Cromartie 1975). "Thallium is neither essential nor stimulatory in either man or animals. It is the most highly toxic cumulative cation" (Venugopal and Luckey 1978).

Economically, thallium is not as important as other trace metals such as Pb, Hg, Cr, Cu, Ni or Zn for example. It is seldom recovered from metal-based mining, ore-processings or smelting operations and is therefore discarded as part of the tailings into the environment. Although these point sources are obviously of environmental concerns, it is the air emissions from coal-burning power plants which form the largest collective source of thallium discharge into the environment (Smith and Carson 1977). In spite of these discharges and of its high toxicity, Tl has not been studied to the same degree as other toxic elements. The reason appears to be historic difficulties with the detection of Tl in the environment by conventional analytical methods, which normally have poorer sensitivity for Tl than for other trace elements.

While Tl has seen relatively limited commercial use in the past, it is finding more and more applications in today's hi-tech components such as fiber optics and nuclear spectrometer crystals. This suggests increased future industrial usage. Also, recently improved techniques are permitting measurement of Tl at much lower levels than ever before and are now making high quality Tl data available to researchers. Zitko (1975) compared Tl toxicity to that of other elements such as Cd, Pb, Hg, Zn and Cu, and reported that Tl is the most acutely toxic in mammals, its toxicity being exceeded only by that of methyl mercury. Furthermore, our own data clearly demonstrate Tl concentrations in the Great Lakes waters are present at higher levels than those of Cd. Given these facts -- increased industrial applications, improved availability of Tl data, high toxicity of Tl, and concentration of Tl > Cd in the Great Lakes system -- one must come to the conclusion that Tl may well be on the verge of receiving at least as much attention as Pb, Cd and Hg have received in the past.

A recently developed ultrasensitive method using a Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) was used to study Tl distribution, vertical and horizontal, in three Great Lakes -- Ontario, Erie and Superior. Requiring only 5-10  $\mu$ L of lake water sample per analysis without the need of any sample cleanup or sample preconcentration and by adhering to clean room practices, Tl concentration lower than 0.03 ng/L (0.6 fg absolute) can be detected. This paper reports for the first time the concentration of dissolved and total Tl in the Great Lakes. The concentration of dissolved Tl in the lakes follows the order of Superior < Ontario < Erie and is higher than dissolved Cd. The levels and the overall averages of dissolved and total Tl, as well as the ratios of dissolved over total Tl will be discussed. We are presently expanding this survey study to include porewaters, sediments and mining effluents at various key sites of Canada.

## **EXPERIMENTAL**

### **Laser-Excited Atomic Fluorescence Spectrometer**

The details of the spectrometer have been described elsewhere (Cheam et. al. 1992, 1993a). Some essential features are given here. The 511 nm line of a copper vapor laser (Metalaser Technologies MLT20) was used to optically pump a dye laser (Laser Photonics) using Rhodamine 575 (Exciton). The dye laser output (554 nm) was then frequency-doubled by a

second harmonic generator (Autotracker II, Inrad Inc.) to give the 276.79 nm UV light. This light, directed through a pierced mirror into a graphite furnace (Perkin-Elmer HGA 2100), was used to excite Tl atoms generated in the furnace. The Stokes direct-line fluorescence light (352.94 nm) emitted by the excited atoms was collected and measured via a narrow bandpass filter (1 nm) - monochromator- photomultiplier- boxcar system. A 6 kHz laser repetition rate was used. Dye laser tuning was achieved using a thallium EDL lamp as was detailed earlier (Cheam et. al. 1993b). The spectrometer is schematically shown in Figure 1.

The copper vapor laser used was originally designed to use pure neon as the flowing buffer gas. Recently, by replacing pure neon with a mixture of 0.8 % hydrogen and 99.2 % neon, we were able to boost the laser output power by nearly 90 %. Figure 2 shows the increase in power versus time as the laser gas manifold was switched from pure neon to the hydrogen-neon mixture while the laser was operating. The increase in laser efficiency has been attributed to an increase in the impedance of the discharge permitting a better coupling of the electrical power to the laser gain medium (Withford et. al. 1993). Nevertheless, the detailed mechanisms of the effect remain poorly understood. We find that this increased efficiency permits longer operating periods between copper refilling. Extra power is useful for elements requiring higher laser powers to ensure saturation. Alternatively, the repetition rate may be increased while maintaining the same pulse energy. Since the signal to noise is proportional to the square root of the repetition rate, lower detection limits can be achieved. The efficiency may be further doubled by using HBr in the buffer gas (Jones et. al. 1993). However, this requires the use of halogen scrubbers in the exhaust and additional expense.

### **Labware Cleaning Procedure**

A rigorous nine-step procedure was used and is briefly described here. The process takes over a week and consists of a 24 h soap bath, followed by the following baths: acetone, concentrated HCl, concentrated nitric acid, 72 h of 6 M nitric acid, and 72 h of 2 M nitric acid at 50°C. The rinsing was done using 0.5% nitric acid followed by the final rinsing carried out in the clean room using 0.2% nitric acid. All bottles and containers are stored filled with 0.2% nitric acid until use. Sample bottles are made of low density linear polyethylene plastic. Beakers, separatory funnels, washbottles, watchglasses, stir bars and rods, tweezers, and all fittings as well

as tubings used in the filtration apparatus are all made of teflon. Volumetric flasks, measuring cylinders, pipettes and pipette tips are made of polypropylene. Beakers, pipette tips, watchglasses, volumetric cylinders and other small items are placed in a small tub containing dilute 0.2 % ultrapure nitric acid and rinsed with ultrapure water when needed (Nriagu et. al. 1993).

### **Sample Collection**

For the three Great Lakes (Superior, Erie and Ontario), surface water samples were collected using a raft rod sampler, whereas the depth samples were collected using Go-flo bottles. The samples were immediately brought to the mobile clean laboratory equipped with such facilities as clean suit, clean polyethylene gloves, clean plasticware/glassware, and Milli-Q-Water system. A fraction of a lake sample was immediately poured into a clean bottle and acidified to 0.2% nitric acid (Seastar) for determination of total Tl, and the remaining sample was immediately filtered through 0.4  $\mu\text{m}$  filter into a clean bottle and then acidified to 0.2%  $\text{HNO}_3$  for determination of dissolved Tl. This manner of collecting sample is rigorous enough as evidenced by the very low blank values of 0.03 ng/L of Tl. Lake Superior water was collected in the summer of 1991, Lake Ontario water in the summer of 1993, and Lake Erie water during the summer of 1994.

Hamilton Harbor and St. Clair River waters were collected in the summer of 1994 using Van Dorn bottles but without the portable clean laboratory; this resulted in higher blank values of 0.2 ng/L of Tl. Similarly collected were the samples from Niagara River, which were obtained in late December 1994. Unfiltered samples were collected from the same aliquots of lake samples used for filtration.

### **Field Blanks and Sample Handling**

For the three Great Lakes, field blanks were prepared in triplicate, usually at every other sampling station. They were aliquots of Milli-Q Water which were processed similarly as actual lake samples were in the clean portable laboratory. For Hamilton Harbour, St. Clair and Niagara Rivers, duplicate field blanks were obtained for each sampling cruise as follows. Right before and after sample collection, one liter of doubly deionized distilled water was used to rinse the Van



Dorn bottle, and the rinsing solution was saved and used as blank. The average blank concentration was found to be 0.2 ng/L of Tl. (The concentration of doubly deionized distilled water was  $\ll$  0.2 ng/L of Tl). Filtration was done in a class 100 clean hood, and the blank concentration was as low as the concentration of the ultrapure water itself.

Sample handling was carried out in a class 100 clean room and in a class 100 laminar flowhood (Microzone Corporation). In spite of very careful sample handling before and during sample injection into the furnace, some contamination from the surrounding air may be expected since the furnace is located 1.2 m away from the clean hood. However, this contamination effect was found to be minimal perhaps because the furnace is right in the path of the clean air flow from the hood. Ultrapure chemicals were used. Milli-Q Water acidified to 0.2 % with ultrapure (Seastar) nitric acid was used as standards matrix and carrier.

#### **In situ Known Addition Analysis**

Details of this technique have been described earlier (Cheam et. al. 1994a). A programmable micropipette (Rainin Instrument Co.) was used to carry out *in situ* known addition pick-ups and injections into the graphite furnace. The pick-up sequence 10/5/2/5 (10  $\mu$ L of MQW carrier followed by 5  $\mu$ L of sample, 2  $\mu$ L of air spacer, and 5  $\mu$ L of MQW or standard) as well as 15/5/2/5 was used. Standard concentrations used varied from 0.1 to 50 ng/L and all computations utilized peak height readings.

### **RESULTS AND DISCUSSION**

#### **LEAFS Analytical Method**

A LEAFS analytical method has been recently developed for the direct determination of thallium in lake waters (Cheam et. al. 1994b). The method characteristics are briefly outlined. The *in situ* known addition technique was used for all analyses of lake waters. Via matrix matching, this technique was shown to nullify interference effects caused by sample matrices and to compensate instrument drifts more effectively than the standard curve calibration technique. Only 5-10  $\mu$ L of water sample was needed for each analysis; duplicate analysis was carried out for

every sample, as can be seen in Figure 3, which shows actual data of several groups of measurements.

Over 50 spike recoveries were studied on 6 different lake samples and were satisfactorily recovered. Also a Reference Material (NIST SRM 1643c) was used to further ascertain the accuracy of Tl determination. This SRM is the only one available on the market and has a Tl value of  $7.9 \mu\text{g/L}$  or  $3.95 \text{ ng/L}$  following a 2000-fold dilution. We found  $4.18 \pm 0.36 \text{ ng/L}$  of Tl. The NIST value was also confirmed by ICPMS analyses (J. Carrier, NWRI, 1995). Furthermore, several acid digestions of unfiltered samples were carried out followed by LEAFS analysis and the results confirmed those obtained by direct analysis of unfiltered samples. The precision of the 19 groups of replicate analyses (Fig. 3) ranged from 0.2 % to 14 % with a median relative standard deviation of 4.7 %. A linear dynamic range of six orders of magnitude was obtained, and a detection limit of  $0.03 \text{ ng/L}$  ( $0.6 \text{ fg}$ ) was achieved. Over forty different measurements of  $20 \mu\text{L}$  of blank (MQW acidified to 0.2%  $\text{HNO}_3$ ) were made over a period of 4 months, resulting in a mean value of  $0.02 \text{ ng/L}$  of Tl.

### Dissolved Thallium

Across Lake Ontario, nine stations with a total of 47 depth sampling sites were included in this study. Nine field blanks were obtained and analysed giving an average of  $0.03 \pm 0.02 \text{ ng/L}$  of Tl. For each numbered station, represented by a solid circle in Figure 4, the average concentration of Tl at the sampling sites was computed and plotted as a vertical solid bar by the station number. As can be seen, thallium is about evenly distributed across the lake except for station 21 at the mouth of the Niagara River, where a somewhat higher concentration was found; this is discussed below in more detail. For Hamilton Harbor (HH) the average Tl concentration of 4 stations (8 sampling sites) is obviously quite a bit greater than the averages in Lake Ontario (Figure 4).

Likewise for Lake Erie, the average concentration of Tl at the sampling sites for each of the six stations is plotted in Fig. 4. Except for station 357, the other 5 stations show higher Tl averages than Lake Ontario's. For comparison, eight different samples from along the St. Clair River were collected and analysed, giving an average of  $5 \pm 1 \text{ ng/L}$  of Tl. This concentration is slightly lower than that found in station 357. For Lake Superior, four stations with 26 different

depth sampling sites were studied. As Figure 4 shows, the average Tl concentration for each station is definitely smaller than for the other two lakes.

There is no definite pattern in the vertical profiles of Tl in Lake Superior unlike the case of dissolved Pb, where the concentration is high at the surface but gradually decreases with depth (Cheam et. al. 1993a). Thallium concentration is basically constant throughout. Figure 5 which plots Tl concentration against sampling depth down to 250 m clearly demonstrates this invariability. This observation agrees with the conservative (constant values) behavior of Tl found in seawater even down to 2500 m deep (Bruland 1983). The overall average concentration of Tl in Lake Superior is  $1.2 \pm 0.2$  ng/L ( $\pm$  standard deviation,  $n = 26$ , range 0.9 - 1.4 with a median of 1.2 ng/L of Tl) compared to the median Pb value of 2.3 ng/L reported earlier by Cheam et. al. in 1993. Thus the concentration of dissolved Pb is about 2 times that of Tl.

Since the dissolved concentration of Tl in the St. Clair River is  $\sim 4.5$  ng/L or less (the dissolved fraction is 83-89 % of 5 ng/L of total Tl, see discussion below), the concentration of dissolved Tl in Lake Huron may well be between 1 and 4 ng/L.

Figure 5 also shows the concentration-depth plots for Lake Erie and Lake Ontario. Again there is no real pattern for the vertical profiles except for a fairly constant value from the surface to the depth of 150 m for 8 of 9 stations in Lake Ontario; the exception is station 21 (LO-21). This station was sampled at 3 depths represented by the solid squares connected by a line. It shows the highest concentration of 8 ng/L near the surface, a fairly high concentration of 6.5 ng/L at depth of 5 m, and a concentration of 5.4 ng/L at depth of 11 m. The fact that the station is at the mouth of the Niagara River, which is known to contain high concentration of some pollutants, may explain this pattern of high surface concentration. In summertime, the river water being warmer than Lake Ontario water likely remains on top for sometimes before being mixed with lake water, thus the apparent concentration gradient. The concentration of Tl in the Niagara River was later determined to be  $7.7 \pm 0.4$  ng/L using six samples collected in wintertime from six different sampling sites along the river. This concentration is in the bulk part of 8 ng/L found in summertime in the surface sample of station LO-21.

Similar to station LO-21, it is noteworthy that in Hamilton Harbor the surface concentration of Tl is also significantly higher than the bottom concentration for six of seven stations. The average surface concentration was 38 ng/L compared to 30 ng/L for bottom

samples. This resulted in a concentration gradient of 27%. Thus although Tl is known to be a conservative element (constant concentration) for oceanic waters (Bruland 1983) and apparently for the three Great Lakes as well (Fig. 5), it appears that this isn't so for point sources and shallow waters.

The overall average concentration of dissolved thallium in Lake Ontario was found to be  $5.8 \pm 0.6$  ng/L (with a median value of 5.7 ng/L). For comparison, dissolved lead concentrations for these same samples, also determined by LEAFS, averaged  $11.6 \pm 5.4$  ng/L (with a median value of 9.4 ng/L of Pb). Also for these samples, the average concentration of cadmium determined by Graphite Furnace Atomic Absorption Spectrometry is  $5.1 \pm 3.1$  ng/L. In October 1993 more samples were collected and analysed for Tl and Cd. The mean results were  $5.9 \pm 0.7$  ng/L of Tl and  $3.1 \pm 1.3$  ng/L of Cd. Thus the order of dissolved concentrations for the three elements is  $Pb > Tl > Cd$  in Lake Ontario.

Similar to the other two lakes, there isn't any real definite profile for Lake Erie either, even though the data from surface to about 10 m deep are more scattered than those at deeper depths (Fig. 5). It is somewhat surprising that Station 357 (LE-357, two open squares connected by a line) contains relatively low levels of Tl when the station was found to contain high Pb concentration relative to most sampling sites in Lake Erie (Cheam et. al. 1993a). On the other hand it could be argued that since the St. Clair River is found to have only  $\sim 4 - 4.5$  ng/L of Tl (Fig. 4) it is reasonable to expect that station 357 (near the mouth of the river) would also have low levels of Tl.

The overall average of dissolved Tl in Lake Erie is  $9.1 \pm 1.5$  ng/L ( $\pm$  standard deviation,  $n = 18$ , range 5.9 - 11.7 with a median of 9.4 ng/L). This concentration is comparable to the average Pb concentration of  $9.4 \pm 10.9$  ng/L (Cheam et.al. 1993a). On the other hand, the average concentrations of cadmium over time were found to be smaller:  $3.0 \pm 2.0$  ng/L,  $5.4 \pm 2.4$  ng/L,  $2.7 \pm 1.4$  ng/L, and  $3.0 \pm 1.8$  ng/L for, respectively, the samples collected in the summer of 1993, June 1994, August 1994, and October 1994. This resulted in an overall spatial mean value of 3.5 ng/L of Cd. Clearly the concentration of Cd is significantly lower than the concentrations of Tl and Pb. Also, even though the atomic weight of Cd is only about half that of Tl and Pb, its molar concentration ( $3.1 \times 10^{-11}$  M) is still smaller than that of Tl and Pb ( $4.5 \times 10^{-11}$  M).

Table 1 summarizes and compares the observed range, median and mean values of dissolved thallium in the three lakes and Hamilton Harbor. If the median concentration in Lake Superior is taken as unity, Lake Ontario would be about 5 times, Lake Erie ~ 8 times, and Hamilton Harbor ~ 21 times more concentrated.

### **Total and Dissolved Thallium**

To ensure that the determination of total Tl is reliable, four different unfiltered samples were analysed by the multiple standard addition technique; the results obtained agreed with those from direct analysis of untreated samples. Furthermore, three unfiltered samples (unspiked and spiked) were digested and analysed for Tl. Again the results for digested samples agree well with those obtained from direct analysis of undigested samples.

Table 2 summarizes the data for dissolved, total and their ratio for Lake Ontario, Hamilton Harbour and Lake Erie; respectively, the average dissolved fractions are 89%, 83% and 87%. This is somewhat similar to the dissolved fraction of copper (82%) reported earlier by Rossmann & Barres (1988) for their 1985 Lake Ontario data. The Tl and Cu dissolved fraction is considerably higher than that of Pb, which averaged only 25% for Lake Ontario surveyed in 1993,  $n = 19$ , (work in progress). Also Rossmann and Barres (1988) reported a similar Pb dissolved fraction of 30% for their 1985 Lake Ontario data.

For samples collected in areas shallower or more turbulent than open lake waters, one expects the ratio to be higher because there would be more particulates in unfiltered samples. To confirm this, we made a brief survey of the Niagara River. Five stations along the river from Lake Erie to Lake Ontario were chosen, and surface and bottom samples were collected in December 1994. For the ten sampling sites, the average ratio of dissolved over total Tl was  $36 \pm 6 \%$  and there is no significant difference between the ratios for surface and bottom samples.

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**TABLE 1. Concentration of dissolved Thallium (ng/L) in Lakes Superior, Erie and Ontario, and Hamilton Harbour**

Lake	Range	Median	Mean	St. Dev.	No. Samples
Superior	0.9 - 1.4	1.2	1.2	0.2	26
Erie	5.9 - 11.7	9.4	9.1	1.5	18
Ontario	4.5 - 8.0	5.7	5.8	0.6	47
H. Harbour*	23.0 - 36.0	25.7	26.8	4.2	8

\* Four key stations (eight samples, 4 surface ones and 4 bottom ones) out of ten stations were chosen to be filtered. In nine out of ten stations studied, the concentration of total Tl is equal to or greater than 25 ng/L, the tenth station being in the remote Southeast corner containing only 3 ng/L. Even if 3 ng/L is included, the overall average of total Tl is 31 ng/L (instead of 33 ng/L when 3 ng/L is excluded).

TABLE 2. Dissolved and total (ng/L), and dissolved/total ratio of Tl in Lake Ontario, Hamilton Harbor and Lake Erie

LAKE ONTARIO				HAMILTON HARBOR				LAKE ERIE			
Station	Dissolved	Total	%Diss/Tot	Station	Dissolved	Total	%Diss/Tot	Station	Dissolved	Total	%Diss/Tot
LO-2-5	5.1	6.22	82	HH-1-1	26.25	35.15	75	LE-18-4	11.74	12.82	92
LO-2-50	5.6	6.23	90	HH-1-7	25.22	29.62	85	LE-18-9	9.69	13.51	72
LO-21-5	6.45	8.76	74	HH-6-1	26.9	35.39	76	LE-22-4	8.39	9.32	90
LO-21-11	5.36	7.38	73	HH-6-23	23.35	26.08	90	LE-22-10	8.39	9.18	91
LO-33-10	5.46	5.82	94	HH-7-1	29.03	34.25	85	LE-22-17	9.62	10.31	93
LO-33-50	5.02	5.06	99	HH-7-19	23.02	24.87	93	LE-23-1	10.49	10.79	97
LO-33-90	5.53	5.76	96	HH-8-1	36.04	48.09	75	LE-23-8	10.37	11.84	88
LO-33-130	5.9	6.49	91	HH-8-16	24.22	28.08	86	LE-23-16	9.78	11.20	87
LO-45-10	4.93	5.46	90					LE-23-30	10.56	11.83	89
LO-45-40	6.1	6.67	91					LE-23-55	8.98	11.53	78
LO-45-70	5.68	6.46	88					LE-43-1	10.23	11.55	89
LO-74-5	7.01	8.11	86					LE-43-7.5	9.10	12.46	73
LO-74-15	5.94	7.17	83					LE-43-12.5	9.35	11.37	82
LO-74-45	5.64	6.37	89					LE-84-1	7.48	10.11	74
LO-84-10	6.19	6.63	93					LE-84-10	8.19	8.62	95
LO-84-33	6.85	7.34	93					LE-84-21	9.55	10.5	91
LO-87-10	6.52	6.66	98					LE-357-1	6.72	7.27	92
LO-87-30	5.67	6.42	88					LE-357-8	5.86	5.97	98
mean = 89				mean = 83				mean = 87			
stdev = 7				stdev = 7				stdev = 8			
n = 18				n = 8				n = 18			

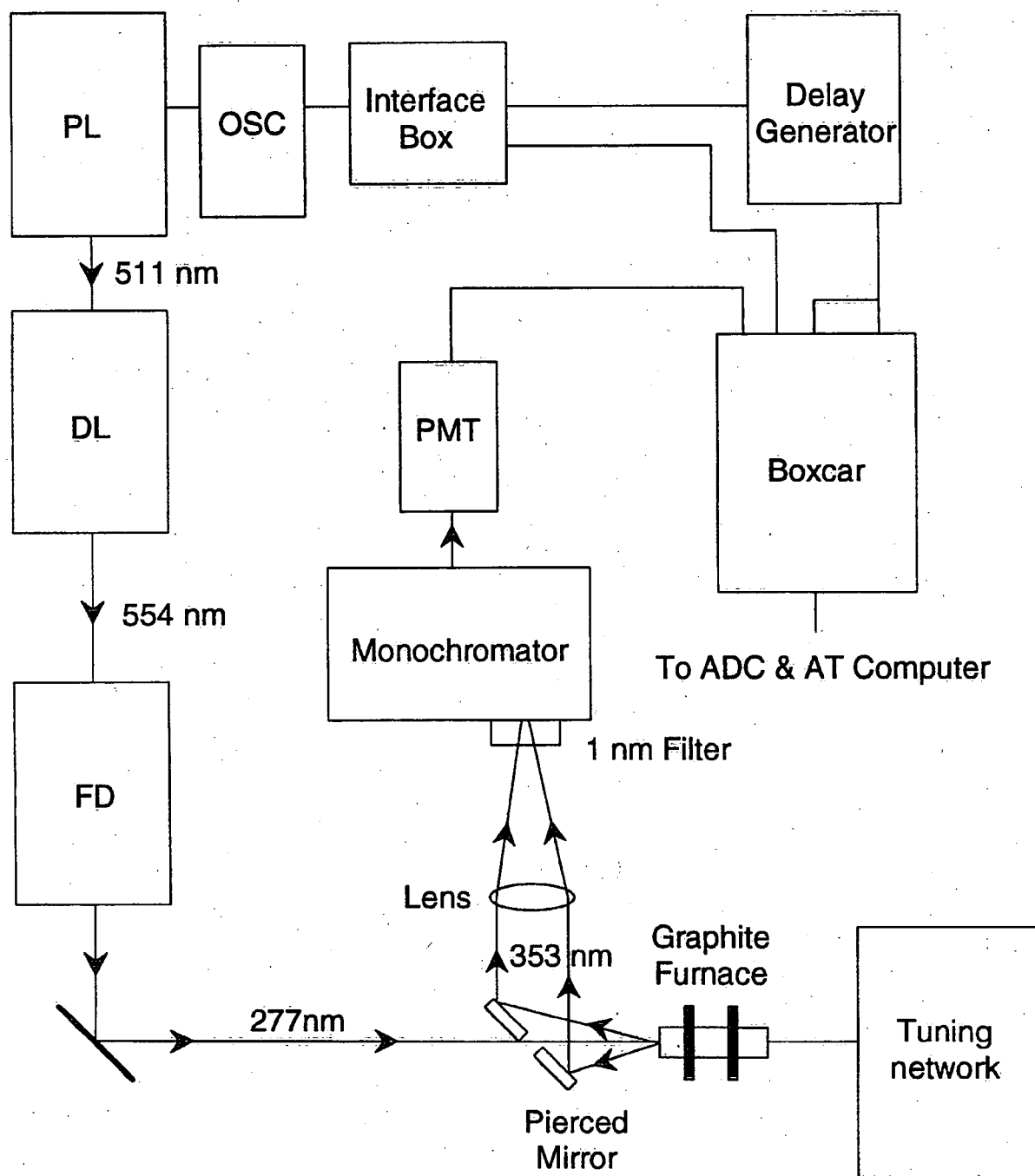


Figure 1. LEAFS schematic: PL = Pumping Laser, DL = Dye Laser, FD = Frequency Doubler, OSC = Oscillator, PMT = Photomultiplier

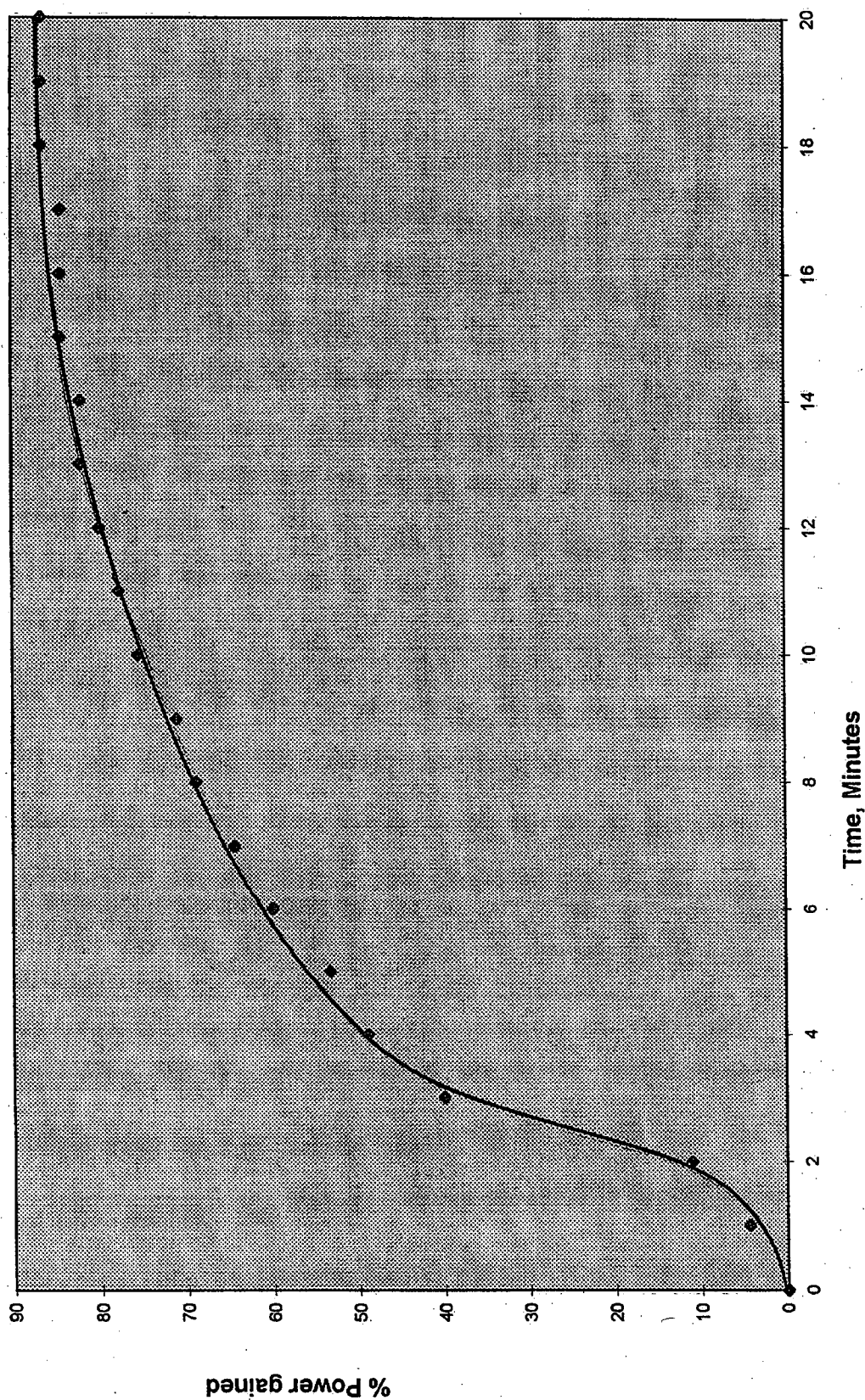
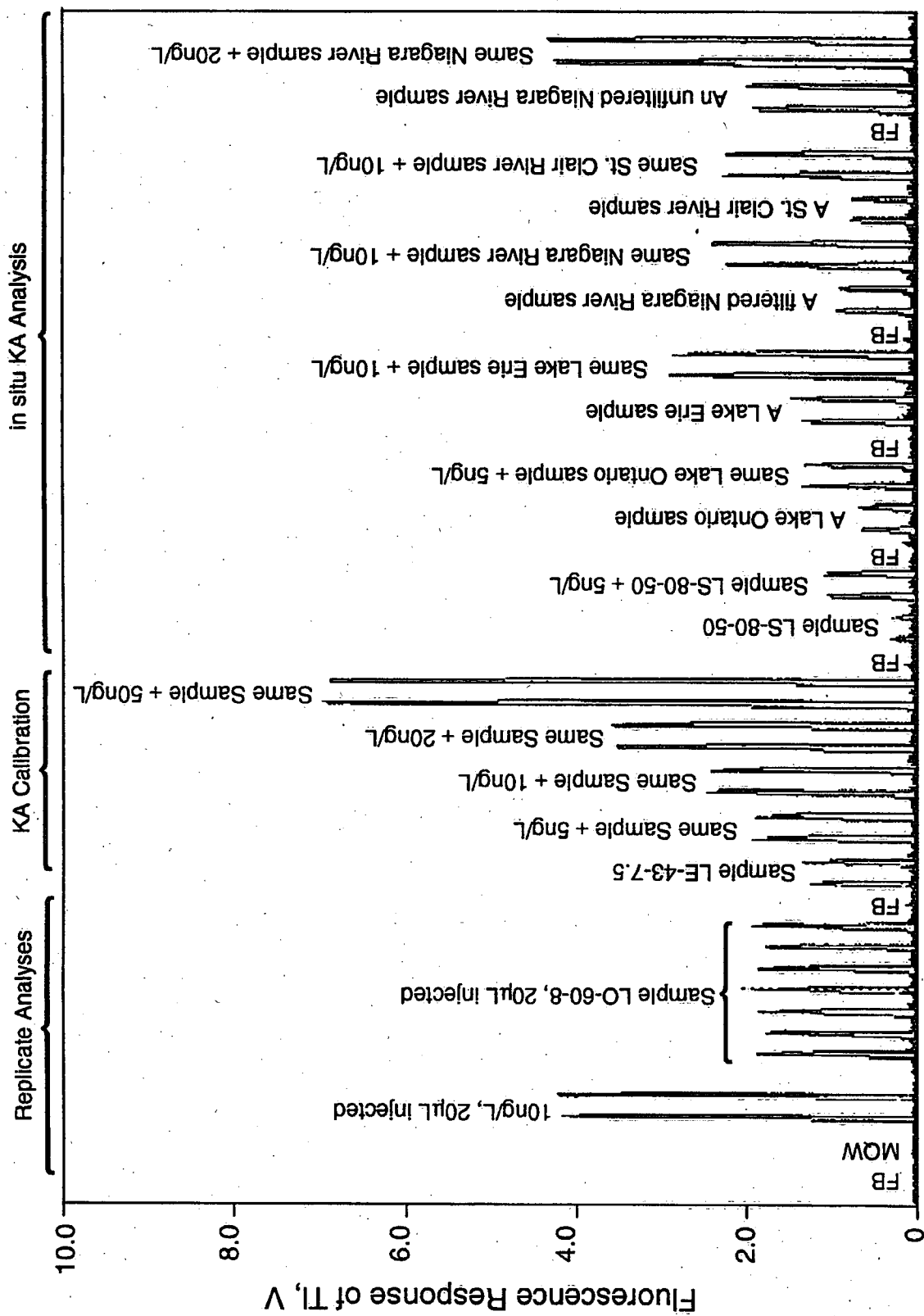


Figure 2. Power gained vs. time when Ne is replaced with 0.8% H<sub>2</sub> - containing Ne



Samples

Figure 3. Replicate Responses for analysis of various samples.

(FB = Furnace blank; MQW = 0.2% HNO<sub>3</sub> Milli-Q water blank;

KA = Known Addition)

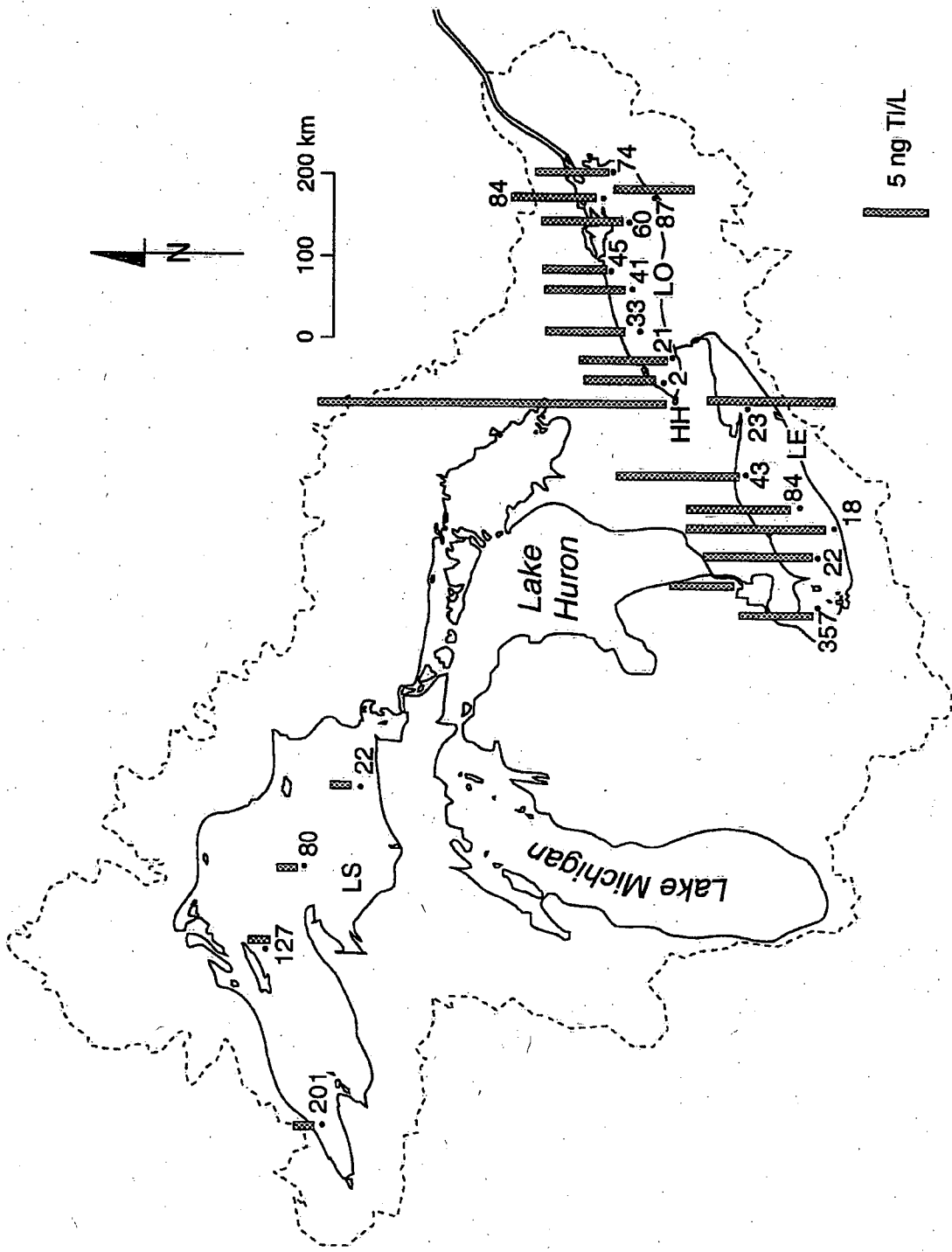


Figure 4. Mean of dissolved Tl concentration for each vertical profile of numbered stations in Lake Superior (LS) Lake Erie (LE), Lake Ontario (LO) and Hamilton Harbour (HH).

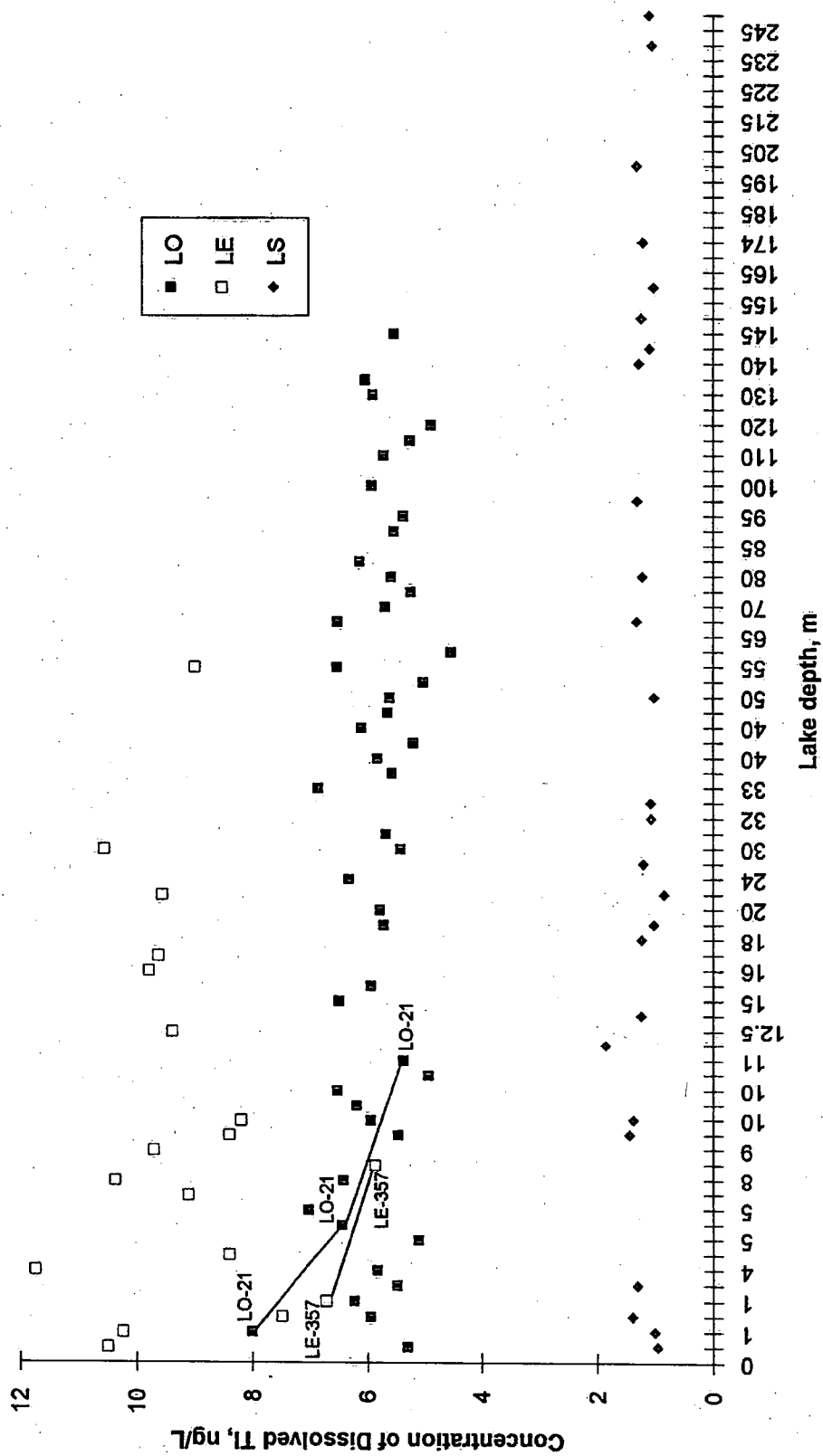


Figure 5. Comparison of Tl concentrations at various stations and depths for Lake Ontario (LO), Erie (LE), and Superior (LS)



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