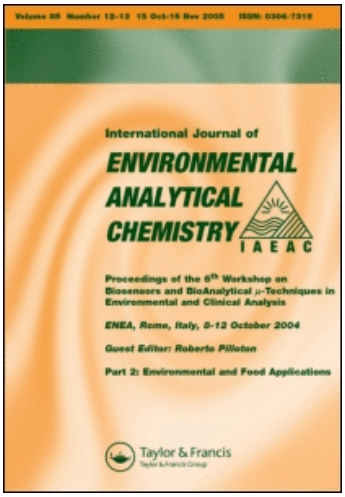

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APPLICATION OF LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETER TO STUDY LEAD DISTRIBUTION IN GREAT LAKES WATERS

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This paper reports for the first time the application of a Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) to study lead distribution in the Great Lakes waters. A class 100 clean laboratory for in-house work and a portable clean lab for field work were used for all sample handling, and an exhaustive cleaning procedure was used to clean all labware. Lead concentrations were determined by direct analysis of 20 μl water samples without any preconcentration steps, which are required by traditional analytical methods. Pb profiles were generated for numerous stations showing relatively high concentrations in the Niagara-Hamilton-Toronto region of Lake Ontario. The average concentrations of dissolved lead were found to be 25 ng/l for Lake Ontario, 9 ng/l for Lake Erie and 4 ng/l for Lake Superior. They are comparable to some recent data reported using graphite furnace atomic absorption spectrophotometric methods and clean room practices, but are much smaller than historical data generated by atomic absorption spectrophotometric—solvent extraction techniques. These latter data are most probably biased high as they were generated under less than ideal conditions using unproven sample handling techniques and insensitive analytical methods.

KEY WORDS: LEAFS, Laser-Excited Atomic Fluorescence Spectrometer, lead distribution, Great Lakes waters, lead profiles, class 100 clean room, sample handling.

INTRODUCTION

The Great Lakes watershed contains one fifth of the world's fresh water. The high levels of persistent toxic chemicals in the Great Lakes waters are of concern to the 40 million North Americans living in the area. Lead is one of these highly toxic contaminants and the availability of reliable data of lead concentration and distribution is of great interest and importance.

In spite of numerous previous studies dealing with Pb and other toxic metals[1-20], an accurate statement vis-à-vis elemental concentrations in the Great Lakes waters is still the subject of much discussion, much of which owes to the uncertainty of data generated via

minimal clean room practices, unproven sample handling techniques and insensitive methods. Atomic Absorption Spectrophotometer (AAS) has been the workhorse instrument for metal analysis of the Great Lakes waters, but AAS methods require tedious chelation/solvent extraction preconcentration steps before analysis can be made using flame or electrothermal atomization. Under the "Great Lakes Prevention Initiative", Canada's Green Plan calls for the development of "New Technologies" and an increase in "Analytical Capabilities". To meet this challenge, we have developed a very sensitive instrument, the Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) which enables direct, accurate determination of Pb in the Great Lakes waters[21].

This paper discusses the application of LEAFS and the clean room practices to study Pb distribution in the Great Lakes waters. Lead concentrations were determined by direct analysis of 20 μl of water samples without any preconcentration steps. The overall concentration as well as vertical profiles will be presented for many sampling stations in each of the three Great Lakes, Ontario, Erie and Superior. Our results, low ng/l (ppt), are comparable with those recently reported[17] for Lakes Erie and Ontario but are much smaller than most previous data.

EXPERIMENTAL

Laser-Excited Atomic Fluorescence Spectrometer

Figure 1 outlines the LEAFS system and its components are listed in Table 1. The system is described in detail elsewhere[21]. A few salient features of our apparatus and its operation are presented for clarity.

The 511 nm line of a Copper Vapor Laser was used to optically pump a Rhodamine 6G dye laser, which provides a tunable range of working wavelengths of 550 nm to 590 nm. Tuning of the dye laser was accomplished by using a lead Electrodeless Discharge Lamp[22]. The dye laser output (566 nm) was then frequency-doubled by a second harmonic generator to give the 283 nm UV light. This light, directed through a pierced mirror into a graphite furnace, was used to excite Pb atoms generated in the furnace. The fluorescent light (406 nm) emitted by the excited atoms was collected and measured via a monochromator-photomultiplier- boxcar system.

To manage the fluorescence signals, the dispersed fluorescence from the monochromator was photomultiplied, then amplified and averaged by a boxcar integrator, and finally acquired by an analog-to-digital converter mounted in a desktop computer. We wrote a software which enabled signal averaging, background subtraction, peak height analysis and printing of numerical as well as graphical data for fluorescence responses such as the ones shown in Figure 2.

For optimizing the detection of fluorescence signals, a custom interface was built to synchronize the detection system and the copper vapor laser. The circuitry electrically isolated the low level signals of the detection system from the laser power supply trigger. It also provided the necessary logic to operate the integrator in its "baseline 2" mode. In this

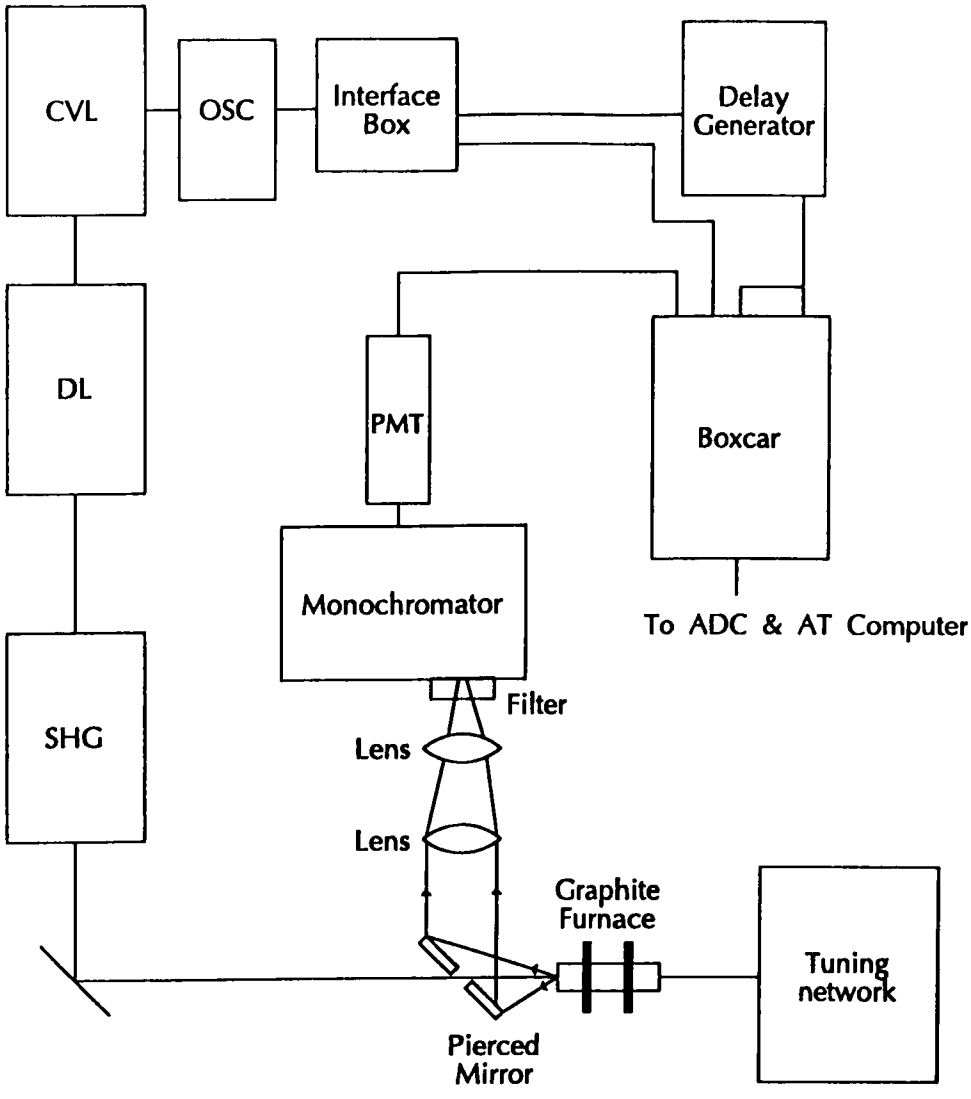

Figure 1 LEAFS system schematic: CVL = Copper Vapor Laser, DL = Dye Laser, SHG = Second Harmonic Generator, OSC = Oscillator, PMT = Photomultiplier.

mode, the baseline or background between two adjacent fluorescent signal pulses is subtracted from the signal pulse. This corrects for furnace blackbody emission since this emission is present both during and between laser pulses, whereas the fluorescence signal occurs only during or shortly after a laser pulse.

A major feature of our system in contrast to others is the use of the 6 kHz repetition rate of the Copper Vapor Laser. The high repetition rate allows us to average over many more

Table 1 Equipment and Operating conditions.

COPPER VAPOR LASER	MLT20 (Metalaser Technologies)
Pulse width	24 ns
Power input, Power output*	3.6 kW, 6 W
OSCILLATOR/FNCTION GENERATOR	HP 3311A
INTERFACE BOX	In-house built
DELAY GENERATOR	4144, EG&G PAR (delay = 215 ns)
DYE LASER	DL-13 (Laser Photonics)
Dye: Rhodamine 6G	0.2g/L (4.2 x 10^{-4} mole/L)
Setting for maximum fluorescence	283.31 nm
SECOND HARMONIC GENERATOR	Autotracker II (Inrad Inc.)
Crystal	KDP-B
VISIBLE LIGHT FILTER	UG5, 4mm (Schott Glass Technologies)
ELECTROTHERMAL ATOMIZER	Perkin-Elmer HGA 2100
Graphite Tube	8x28 mm
Dry, char, atomization	120, 500, 1800–2100C; 40, 40, 5 sec.
Sample injection, Internal gas flow	10–25 L, Stopped flow (Interrupt)
NARROW BANDPASS FILTER	Melles Griot (404.7±5nm)
MONOCHROMATOR I	Schoeffel GM 250, 0.25m
Aperture ratio	f/3.6
Slit width	0.8 mm
PHOTOMULTIPLIER I	Thorn EMI 9813
Voltage setting (Power Supply)	1.5–2.4 kV (Thorn EMI type PM28B)
BOXCAR AVERAGER (Software)	4121B, EG&G PAR (in-house software)
Gate width, Operation mode	1 μS, Baseline 2 mode
A to D CONVERTER	Computor Boards Inc. CIO-AD08
LEAD LAMP	EDL lamp, 8W (Perkin Elmer)
MONOCHROMATOR II	GCA/McPherson, EU-700–56, 0.35m
Aperature ratio	f/6.8 at 200nm
Slit width	0.3 mm
PHOTOMULTIPLIER II	1P28
Voltage setting (Power Supply)	0.9 kV (Hamamatsu C956–04)
BOXCAR AVERAGER	4121B, EG&G PAR
MULTIMETER	HP 3468A
ENERGY METER	Scientech 36–0201
Power range	0.1mW -25W

*With time the power output decreases; this value is less than half the value measured when copper metal was freshly loaded.

laser shots during atomization than would be possible had we used an Nd:YAG or an excimer laser as a pump source. This reduces noise and provides a more accurate value of the atomization peak signal.

Ideally, the laser energy should be adjusted to just saturate the atomic transition. This means that all illuminated Pb atoms (in the furnace) which quantum mechanical statistics

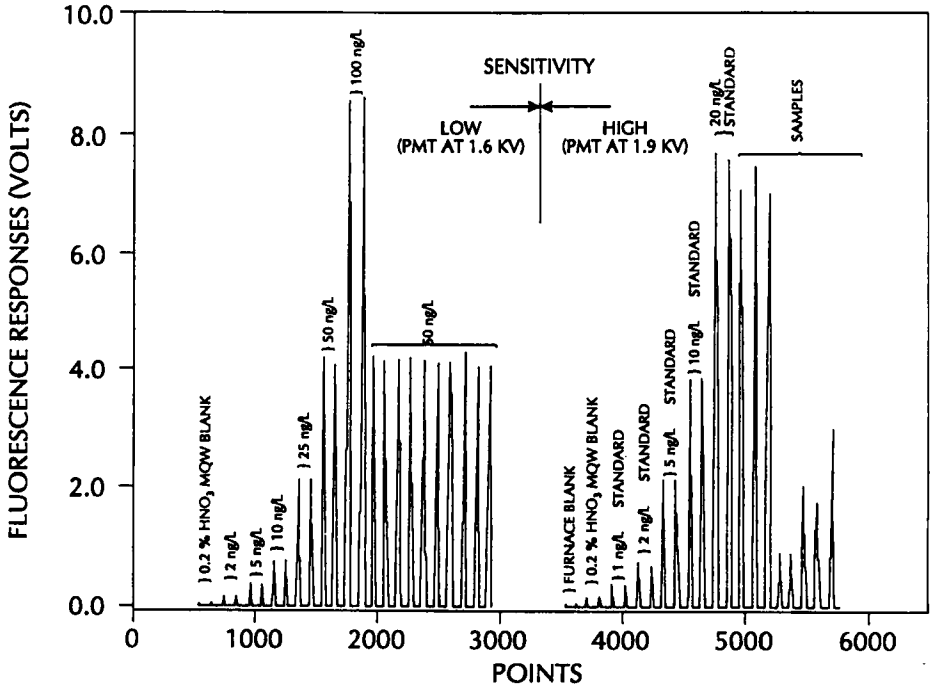

Figure 2 Typical fluorescence responses for standards and samples containing Pb (20 μL injection).

allow to be excited are indeed excited to an upper state. This will maximize the fluorescence. In practice however, we reduced the laser power so that peak irradiance of the 283 nm beam in the furnace was about 2 kW/cm^2 in order to increase the copper vapor laser lifetime. This was somewhat below saturation for high Pb concentrations. However, the reduced sensitivity was still more than adequate for our requirements.

Ultraclean rooms and ultrapure chemicals

A class 100 clean laboratory was constructed, which contains a high efficiency particle (HEPA) filter assembly through which about 100 air changes per hour take place. With the filter efficiency greater than 99.5% for 0.5 μm particles and the high frequency of air changes, the particle count is maintained at 100 particles per m^3. The clean room has a positive pressure relative to the surrounding environment. The fixtures are made of plastics and any unavoidable metal surfaces such as door knobs, HEPA filter housing, are coated with epoxy resin. The cabinets are made of wood and the counter tops are covered with teflon protective overlays. The sealed walls and ceiling are covered with five coats of epoxy resin. The floor consists of seamless, chemically resistant vinyl and the floor drain is capped with a plastic block. Any person in the room must wear full Tyvek coveralls with an attached hood, a Tafetta hair cap, Tyvek booties, and disposable, non-powdered polyethylene gloves.

For field work, a portable clean laboratory was constructed equipped with similar facilities as the class 100 laboratory, but the particle count was about 1000 per m^3.

The ultrapure water used was produced from a 3-stage demineralization process. The first stage is the delivery of the general purpose in-house reverse osmosis (RO) distilled water into a quartz still via plastic pipes and faucet. The second stage is the redistillation of the RO water in the quartz still (Corning AG-3 system). The doubly distilled water is collected in a precleaned 20-litre plastic bottle and finally fed into a Milli-Q system (Millipore Corp., Bedford, Mass.) situated in the class 100 room. The Pb blank concentration of the water is <0.4 ng/l. Doubly quartz distilled nitric and hydrochloric acids (Seastar, Victoria, B.C.) as well as other high purity chemicals were used. The ultrahigh purity nitric acid has a specified Pb content of 40 ng/l.

Labware and cleaning process

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. All labware and the filtration device are cleaned following a rigorous 9-step procedure adapted from that described by Tramontano *et al.*[23]. The cleaning 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 being done in the clean room using 0.2% nitric acid. All bottles and containers are stored filled with 0.2% nitric acid until use. Beakers, pipette tips, watchglasses, volumetric cylinders and other small items are placed in a small tub containing dilute 0.2% ultrapure nitric acid.

Great Lakes water collection and filtration

Surface water samples were collected from an inflatable rubber raft rowed to at least 100 m from the mother ship. Sampling was usually done by hand wearing acid-washed, shoulder-length polyethylene gloves. The bottle was dipped below the surface microlayer, opened to fill and then capped under water. The sample bottle was quickly put into its precleaned container bag. Surface samples were also collected from the rubber raft by means of a special rod sampler designed to open and close an intake manifold under water[28]. Depth samples were collected by means of 5-litre Go Flo bottles attached to Kelvar rope and tripped using a teflon messenger. The filled Go-Flo bottle was put back into its precleaned plastic bag and as with surface samples was quickly transported to the portable clean lab to be filtered through a polycarbonate (Nuclearpore) membrane filter with 0.45 μm pore size. (All fittings and tubing used as part of the filtration apparatus are made of teflon). Each filter had been acid-leached in 20% ultrapure nitric acid at least one week before a cruise and remained soaking in a Milli-Q water bath until use in the field. After the first 100 ml of filtered sample were discarded, each sample was acidified to 0.2% nitric acid (ultrapure). The sample bottles

were put back in their precleaned polyethylene bag (5 bottles per bag) and stored in a cold room until analysis. Field blanks were prepared in triplicate in the field usually at every other sampling station. They consist of aliquots of Milli-Q water which have been filtered, processed and exposed to the portable clean lab environment in a manner similar to actual lake samples. All samples were collected in the summer of 1991 from various stations in Lakes Ontario, Erie and Superior. For some sites, sampling was unsuccessful due to rough weather conditions so that in some profiles certain sites are missing. A protocol detailing the development of ultraclean laboratory and other measures to minimize contamination in the analysis of trace metals in the Great Lakes waters is being submitted for publication elsewhere[24].

Sample preparation and injection

All spikings and other sample manipulations were carried out in the class 100 clean room using the precleaned labware and the 0.2% HNO_3 Milli-Q water blank. Pb standards were prepared from a commercial AA 1000 mg/l stock by sequential dilution with Milli-Q water. The plastic micropipette tips used for sample injection were soaked in 0.4% acid for several days and each tip was rinsed a dozen times with acidified Milli-Q water and twice with the solution of interest before use. Usually 20 μl of sample or standard were directly injected into the graphite furnace for atomic fluorescence measurement by LEAFS as described above. In spite of very careful sample handling during sample injection into the furnace, some contamination from the surrounding air is expected since the LEAF spectrometer is located in an ordinary laboratory. But since the analysis time is very short and all the blanks, samples and standards are analysed the same way, this contamination effect was found to be minimal.

RESULTS AND DISCUSSION

LEAFS performance

Figure 2 shows typical fluorescence peaks for blanks, standards and samples generated using our newly written software as mentioned above. As can be seen, the instrument sensitivity can be easily adjusted by simply changing the PMT voltage instead of using neutral density filters; specifically 1.6 kV was for low sensitivity (where the responses for 50 ng/l generated ~4V responses) and 1.9 kV for high sensitivity (where 20 ng/l generated almost 8V responses). The ten replicate analyses of 50 ng/l standard show good reproducibility giving an RSD of 1.8%. Ten replicate analyses of 10 ng/l on a separate run resulted in a 4.9% RSD. Calibration curves with a linear dynamic range of four orders of magnitude can be obtained, as shown in Figure 3, which adequately covers the concentration range encountered in this work. Two certified reference materials, SRM 1643c of NIST and SLRS-2 of Canada's NRC, were analysed to test the method accuracy. Student t-tests showed no significant difference between certified values and those found, the maximum difference being only 3%. The detection limit was determined to be 0.4 ng/l, corresponding to 10 fg absolute for a 25 μl injection.

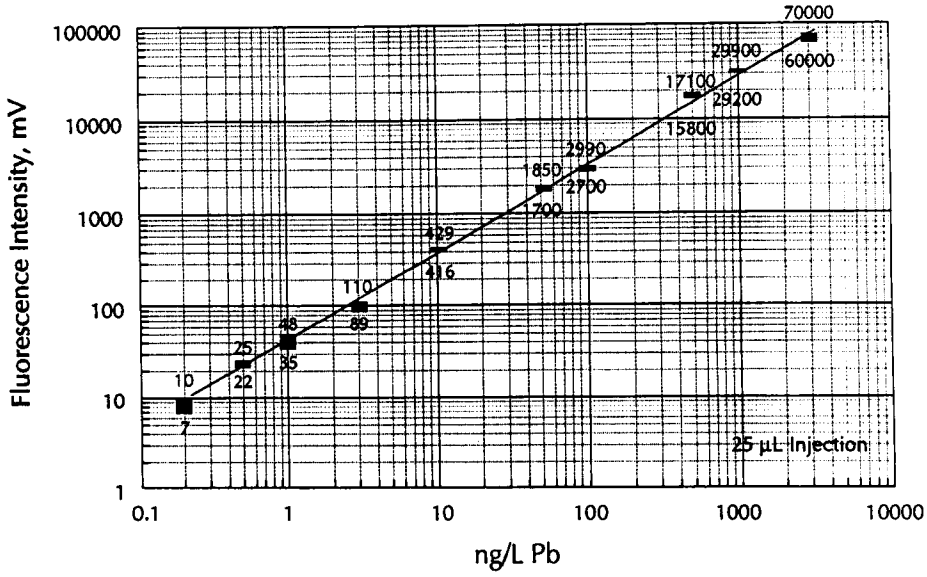

Figure 3 LEAF calibration curve for direct analysis of Pb in water.

Sample analysis and Pb profiles

To confirm the applicability of LEAFS to the analysis of Great Lakes waters, six different samples (two from each of the 3 lakes) were subjected to the Multiple Standard Addition (MSA) technique. For each sample, a regressed standard addition line was generated, which intersected the (concentration) abscissa producing one MSA value. The calculated student t results (Table 2) for these six samples indicate no significance difference between the MSA values and those generated by direct analysis.

Table 2. Comparison of results determined by MSA vs. direct analysis and by Student t-test vs. critical t values (95% confidence level).

*SAMPLE**	*MSA[a], ng/l*	*Direct analysis, ng/l*	*Student t values*	*Critical t values*
LE-23-50	42.4	42.5±2.4	0.03	3.18
LE-54-6	16.6	15.8±2.5	0.59	3.18
LO-79-19	9.2	8.6±0.5	1.92	4.3
LO-87-20	19.6	19.9±1.6	0.31	4.3
LS-2-12	24.4	25.4±0.1	0.53	12.7
LS-125-175	1.4	1.2±0.2	1.14	12.7

*LE = Lake Erie; LO = Lake Ontario; LS = Lake Superior. "LE-23-50" means Lake Erie - Station 23–50 m deep, and so on.

[a] Multiple Standard Addition at three different concentration levels overlapping the concentrations determined by direct analysis. For each sample, the MSA result is the intersection of the regressed line and the abcissa.

Every test sample including blanks and standards was analysed in duplicate or higher replicate. A total of fifty field blank samples were processed for the three lakes, and more than one hundred determinations made. The average blank concentration was, respectively, 1.3, 2.4 and 3.3 ng/l for Lakes Superior, Erie and Ontario and was subtracted from the gross concentration of each lake sample. Because these blanks were prepared "in-situ" at different locations and sometimes months apart, it is not surprising that variations occurred; as well, since they were prepared before and between sample filtration, some memory effect could have also occurred. Nearly two hundred water samples were collected from various sites in the three lakes and analysed the same way as blanks and standards.

Figures 4–6 give the general concentration trend for vertical Pb distribution of the three Lakes. Figure 4 shows typical vertical concentration profiles for Lake Superior, the biggest

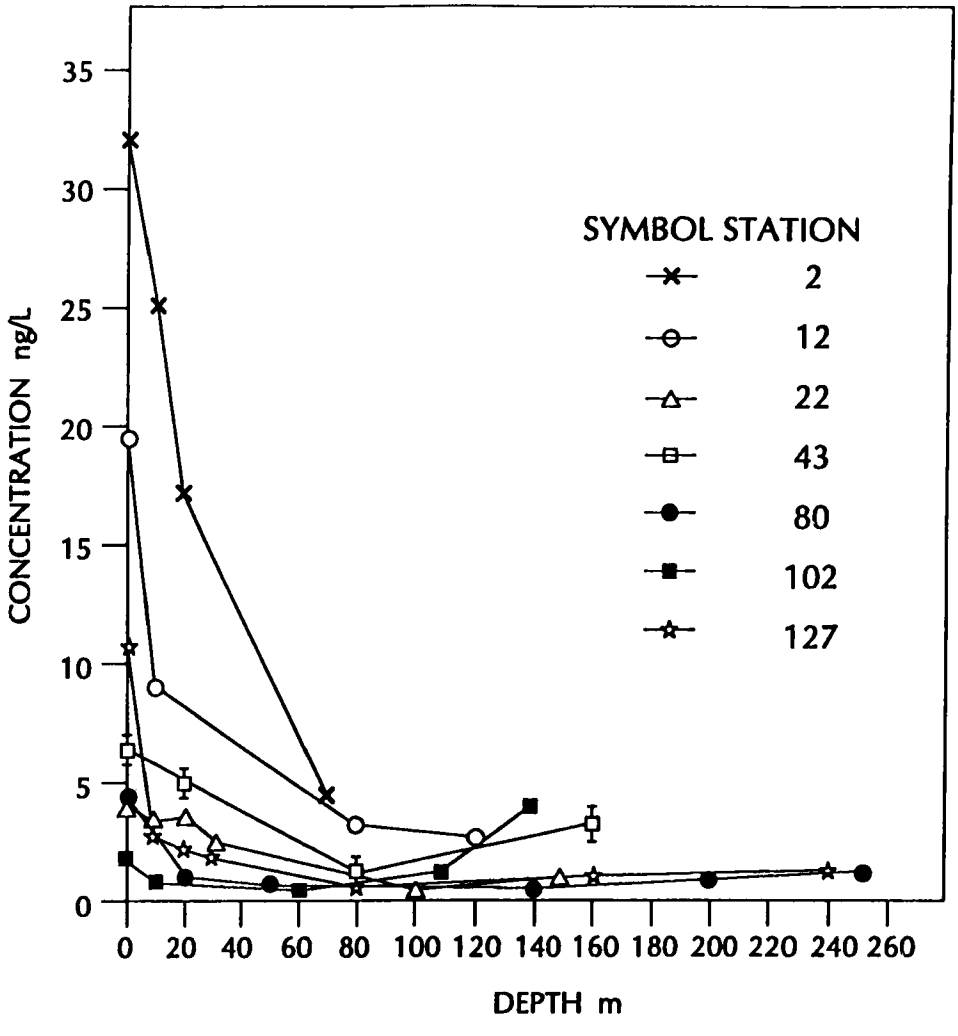

Figure 4 Typical vertical profiles of Pb in Lake Superior.

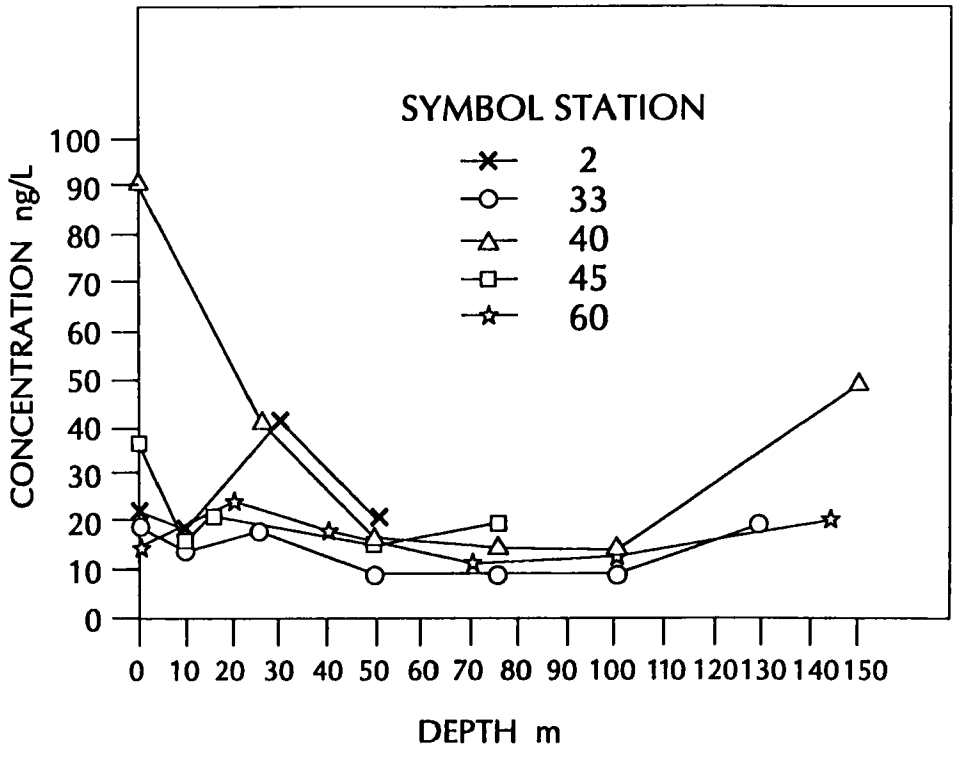

Figure 5 Typical vertical profiles of Pb in Lake Ontario.

and deepest of the Great Lakes. The general trend as a function of depth is almost asymptotic—high levels at surface sites which gradually decrease to a quasi plateau, particularly for the deepest sites at 250 metres deep (stations 80 and 127). This suggests significant atmospheric inputs into the lake but minimal water-sediment interactions at these sites, station 80 being 50 m away from the bottom sediment.

For Lake Ontario, the profiles tend to show a parabolic trend with the minimum concentration somewhere at mid-profile (Figure 5), which indicates active atmospheric as well as sediment inputs. This is particularly true for the three deep stations—stations 33, 40 and 45 with 130–150 m depth. For Lake Erie which is shallow and small compared to the other two Lakes, its water is relatively well mixed thus the atmospheric input is not so obvious and consequently surface concentrations appear to be lower than the other two Lakes. However, the very high concentration of the deepest sampling site for station 23 as well as that for station 357 (Figure 6) suggest there was extensive sediment resuspension in contrast to the deep Lake Superior.

Three profiles in Lake Superior were triplicated, that is three different samples were collected at each sampling site of the profiles. One of these profiles (station 43) is presented in Figure 4, where each open square represents the average concentration for each site; the

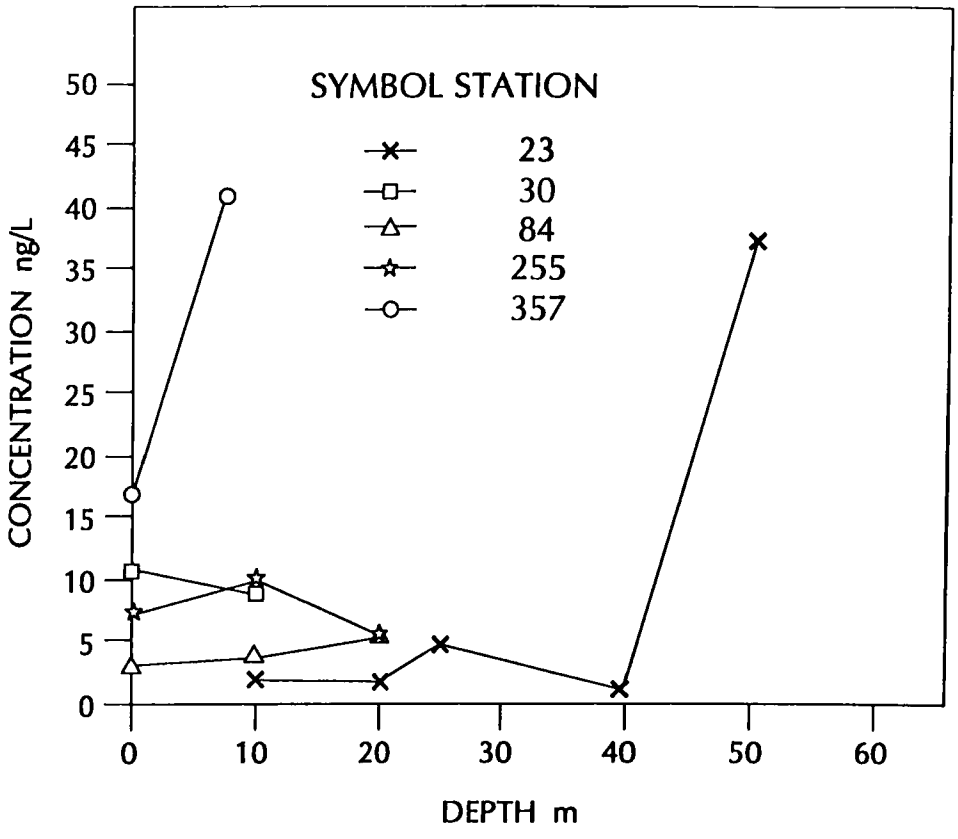

Figure 6 Typical vertical profiles of Pb in Lake Erie.

error bar above and below a square represents one standard deviation, and the corresponding relative standard deviation ranges from 15 to 32% for the four squares. The errors for the other two stations are in the same order of magnitude and are not presented as the figure will be too crowded. None of the profiles in Lakes Erie and Ontario was replicated. For the replicate analyses of all samples from the 3 Lakes, 95% of the relative standard deviations are below 25%.

Pb concentration in the Great Lakes

Across Lake Ontario, thirteen stations with a total of fifty four sampling sites (54 samples) were included in the study. For each station, the average concentration of Pb in the sampling sites was calculated and plotted in Figure 7, which shows particularly high Pb concentrations in the western part of the Lake, in the Niagara River-Hamilton-Toronto region (stations 21, 104 and 9B). The overall average concentration of Pb in Lake Ontario was calculated to be 25 ng/l (range 4–154 ng/l) which is in the same order of magnitude as the average of 35 ng/l

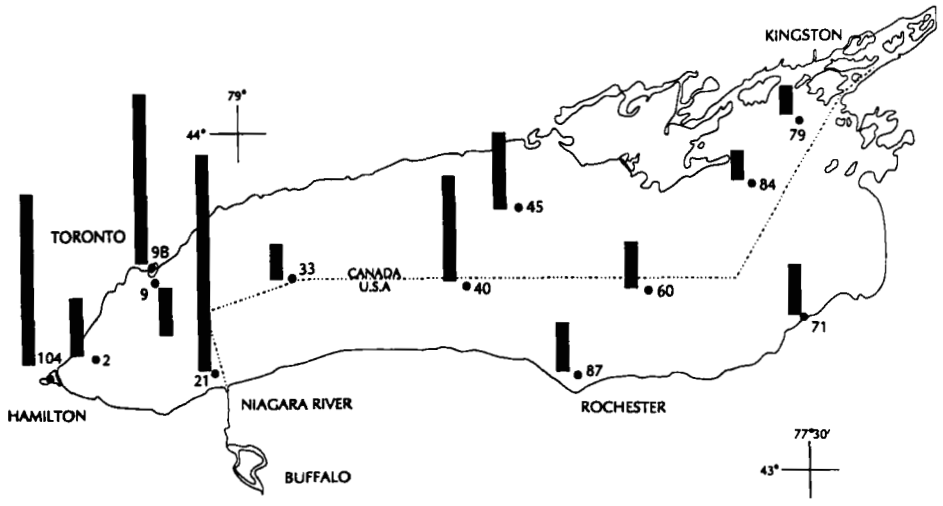

Figure 7 Average Pb concentration of each vertical profile for the studied stations in Lake Ontario.

(range 1–284 ng/l) reported by Coale and Flegal[17]. These authors handled their samples in class 100 clean labs and analysed them using graphite furnace AAS (L'Vov platform and standard addition technique) following a 200:1 preconcentration step via chelation and solvent extraction procedures[25–26]. Rossmann and Barres[15] using 100 µl samples for their GFAAS analysis found 91% of their data below the detection limit but reported a median result of 10 ng/l for their 1985 data. These three sets of results are lower than those reported by other workers: 140 ng/l in 1986 by Nriagu[13], 300 ng/l in 1990 by Allan and Ball[19], 500 ng/l in 1978 by Patterson and Kodukula[3], and 830 ng/l in 1970 by Chau *et al.*[1].

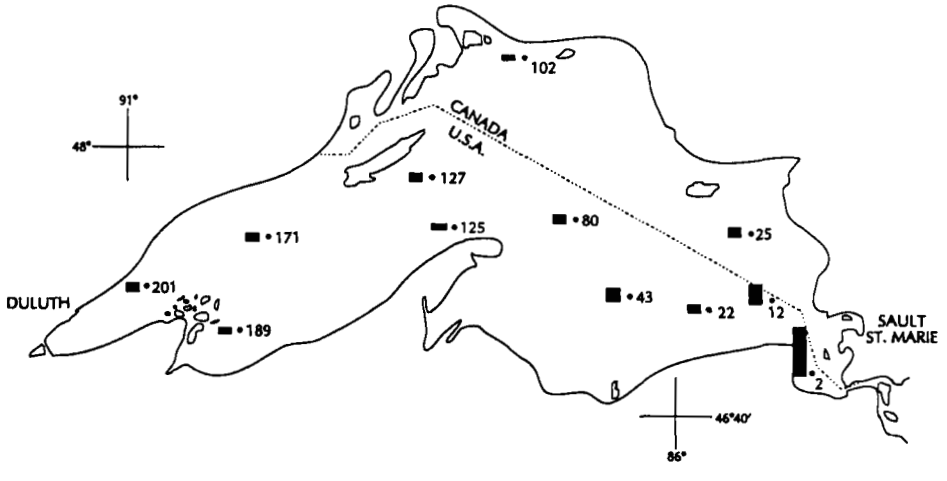

Figure 8 Average Pb concentration of each vertical profile for the studied stations in Lake Superior. (For station 125, the concentration is for the depth site of 175 m deep).

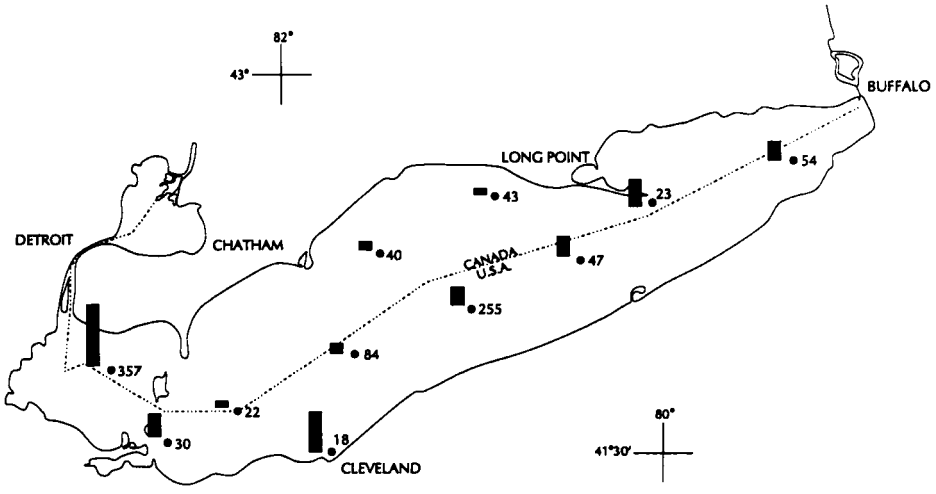

Figure 9 Average Pb concentration of each vertical profile for the studied stations in Lake Erie.

For Lake Superior, a total of ninety samples from twelve stations were investigated. The average concentration of each station shown in Figure 8 indicates relatively low concentrations throughout compared to Lake Ontario. The overall average of Pb concentration in Lake Superior was 4 ng/l compared to 14 ng/l (median 6 ng/l) reported in 1988 by Rossmann and Barres[15], 75 ng/l by Allan and Ball[19], 400 ng/l by Poldoski *et al.*[4], and 1000 ng/l by Patterson and Kodukula[3]. The data for Lake Erie (eleven stations with twenty eight sampling sites) are illustrated in Figure 9, showing concentration levels between those of Lakes Superior and Ontario. The overall average concentration of Pb in Lake Erie was 9.4 ng/l, which is in the same order of magnitude as 20±13 ng/l reported by Coale and Flegal[17]. Both findings are at least an order of magnitude smaller than others: 150 ng/l by Nriagu[13], 220 ng/l by Rossmann and Barres[15], 750 ng/l by Allan and Ball[19], and 2000 ng/l by Patterson and Kodukula[3].

Table 3 summarizes and compares our findings with some of the previously reported data including STAR File Data[27], which were generated between 1970–1985 using the preconcentration technique of chelation/extraction (APDC-MIBK) followed by AAS analysis. The average concentrations (>1000 ng/l) are by far the highest for all 3 lakes especially in comparison to ours (~25 ng/l or less) and are most probably biased high because the data were generated without clean room practices. In addition, the method used was insensitive, having a detection limit of 500 ng/l compared to 0.4 ng/l by our LEAFS method. It should be noted that the use of a laminar flow hood (not a class 100 clean room) by Rossmann and Barres[15] resulted in data which basically agree with ours for Lakes Ontario and Superior and with data by Coale and Flegal[17] for Lake Ontario (Table 3). This suggests that if a class 100 clean room is unavailable, a laminar flow hood may be a cost-effective alternative for ultratrace work.

Table 3. Comparison of dissolved Pb concentrations, ng/l, reported for the Great Lakes waters by various workers [given as mean ± s.d. (number of samples studied)].

Lake	*STAR file data*[a] *AAS*	*Patterson & Kodukula*[b]	*Poldoski et. al.*[c]	*Allan and Ball <1986†*	*Nriagu 1986*[e]	*Rossmann and Barres*[f]	*Coale and Flegal*[g]	*This work*[h] *LEAFS*
Ontario	1140±650 (24)	500	..	300	140	10–150 (23)	35±80 (12)	25±28 (54)
Erie	1400±800 (202)	2,000	..	750	150	220±140 (11)	20±13 (4)	9±11 (28)
Superior	1500±1200 (212)	1,000	450±200 (36)	75	..	14±31 (22)	—	4±5 (90)

[a]Method: AAS following solvent extraction (APDC-MIBK), near-surface samples[27]. Ontario (1971–1985); Erie (1970–1971); Superior (1970–1976). The "O" values are not included.
[b]Method: AAS - solvent extraction, Patterson & Kodukula[3]
[c]Method: GFAAS., unfiltered samples, Poldoski *et al.*[4]
†Allan and Ball[19], compiled data.
[e]Method: GFAAS, Chelex-100 followed by AAS, Precipitation/extraction-AAS. Nriagu[13].
[f]Method: GFAAS, 100μL injection; Rossmann 1984, Rossmann 1986, Rossmann and Barres 1988 in Allan and Ball (1990). For 1981, a single result was 150 ng/l; for 1985 data, the median result was 10 ng/l[12,14,15]
[g]Method: GFAAS following 200:1 chelation/extraction; Coale and Flegal[17], surface samples.
[h]Method: LEAFS; whole lake.

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