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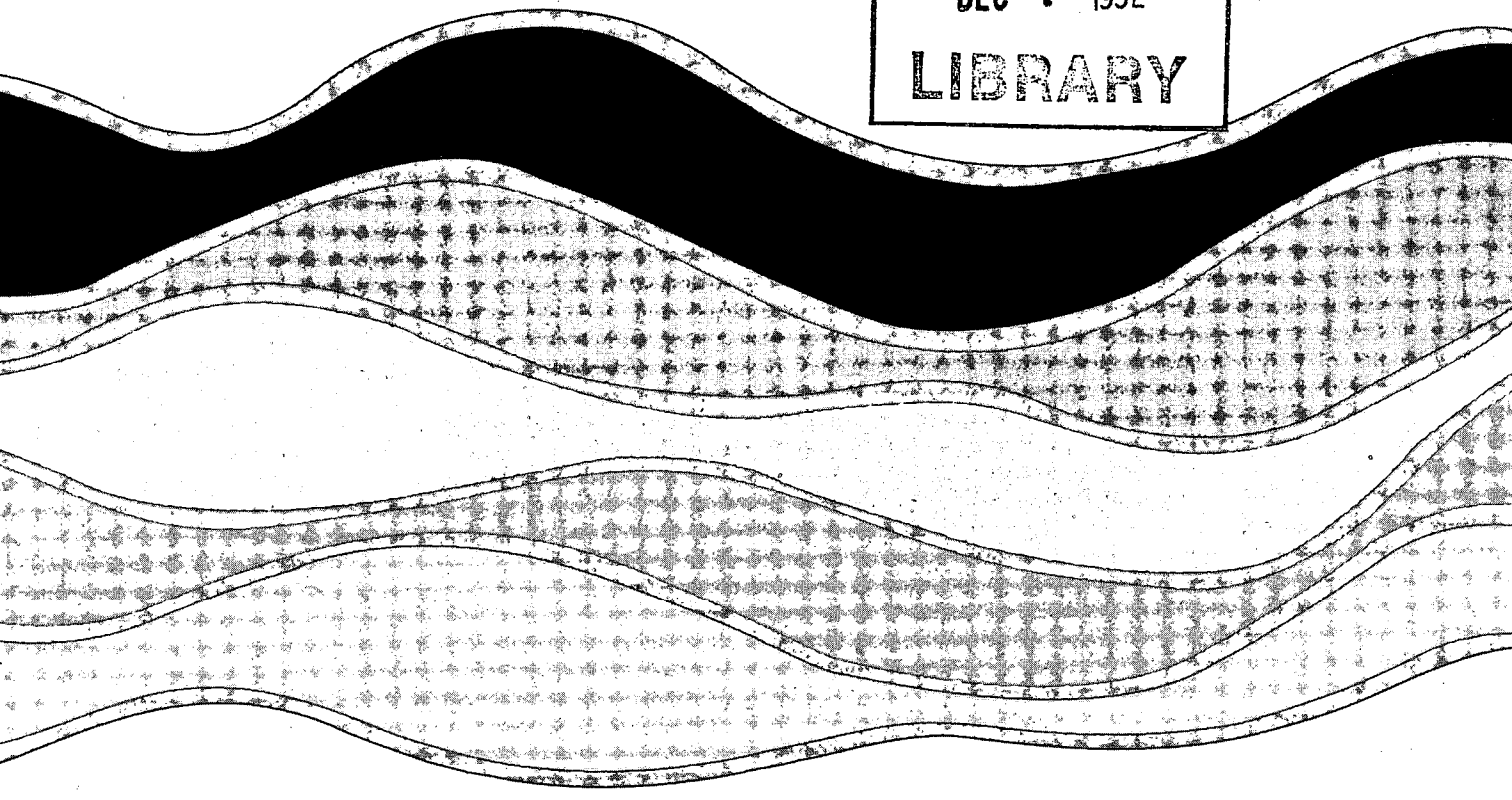

APPLICATION OF LASER-EXCITED ATOMIC FLUORESCENCE SPECTROMETER TO STUDY LEAD DISTRIBUTION IN GREAT LAKES WATERS

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NWRI Contribution No. 92-22

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

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MANAGEMENT PERSPECTIVE

The determination of ultratrace metals in environmental samples by conventional methods requires various preconcentration and separation steps. These complicated procedures include addition of chemicals and reagents as well as tedious manual sample handling operations. Due to the possible contamination of the samples during this process, the quality of generated data is questionable. 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 been developing an ultrasensitive instrument, the Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) which enables direct, accurate determination of Pb in the Great Lakes waters. Our data show that the average level of dissolved lead in Lakes Ontario, Erie and Superior is low, 25 ppt or less, which is quite low in comparison to most previous reported data.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le dosage par les méthodes classiques des métaux ultratraces contenus dans les échantillons prélevés dans le milieu nécessite différentes étapes de préconcentration et de séparation. Ces méthodes compliquées passent par l'addition de réactifs et de composés chimiques et comprennent un certain nombre de manipulations fastidieuses des échantillons. Vu les risques de contamination des échantillons qu'implique cette démarche, la qualité des résultats obtenus est douteuse. Dans le cadre de l'initiative pour la prévention de la pollution des Grands Lacs, le Plan vert du Canada souhaite la mise au point de nouvelles techniques et une augmentation de la capacité d'analyse. C'est pourquoi nous avons mis au point un instrument ultrasensible, le spectrophotomètre d'absorption atomique à fluorescence excitée par laser (LEAFS), qui permet le dosage précis et direct du Pb dans l'eau des Grands Lacs. Nos résultats indiquent que la teneur moyenne de plomb dissous dans les lacs Ontario, Érié et Supérieur est faible, 25 ng/L ou moins. Par comparaison à la plupart des résultats antérieurs, cette concentration est très faible.

ABSTRACT

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 region of Lake Ontario. The overall average concentration of dissolved lead for Lakes Ontario, Erie and Superior waters was, respectively, 25, 9 and 4 ppt, which are comparable to some recent data reported using GFAAS and clean room practices, but are much smaller than historical data generated by AAS- solvent extraction technique. 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 Spectrometry, lead distribution, Great Lakes waters, lead profiles, class 100 clean room.

RÉSUMÉ

Cet article fait état de la première application du spectrophotomètre d'absorption atomique à fluorescence excitée par laser (LEAFS) à la distribution du plomb dans l'eau des Grands Lacs. La manipulation de tous les échantillons a été faite dans un laboratoire propre de classe 100, pour les travaux en laboratoire, et dans un laboratoire propre portatif, pour les travaux sur le terrain. On a appliqué une méthode de nettoyage poussé de toute la verrerie de laboratoire. La concentration en plomb a été déterminée par analyse directe d'échantillons d'eau, d'un volume de 20 μL, sans que soit pratiquée aucune étape de préconcentration comme on le fait avec les méthodes classiques de dosage. Des profils du Pb ont été tracés à de nombreuses stations; ils montrent une concentration assez forte du Pb dans la région de Niagara-Hamilton, sur le lac Ontario. La concentration moyenne d'ensemble du plomb dissous dans les lacs Ontario, Érié et Supérieur était de 25, 9 et 4 ng/L, respectivement; cela est comparable à de récents résultats obtenus par spectrophotométrie d'absorption atomique (flamme à gaz) et par l'application des méthodes de travail en laboratoire propre. Mais les concentrations que nous avons mesurées sont considérablement inférieures à celles obtenues depuis longtemps par la technique d'extraction par solvant et celle de la spectrophotométrie d'absorption atomique. Ces derniers résultats sont fort probablement le fruit d'une surévaluation systématique puisqu'ils ont été obtenus dans des conditions qui étaient loin d'être idéales, par des méthodes non vérifiées de manipulation des échantillons et par des méthodes peu sensibles de dosage.

MOTS CLÉS : LEAFS, spectrométrie d'absorption atomique à fluorescence excitée par laser, distribution du plomb, eau des Grands Lacs, profils du plomb, laboratoire propre de classe 100.

INTRODUCTION

The Great Lakes form the largest body of fresh water in the world, containing one fifth of the world's fresh, surface water. As an ecosystem, the Great Lakes basin is a single, complex living organism whose self-balancing, self-cleansing processes and water cycle have been severely stressed by some 40 million North Americans living in the area. The basin is the industrial heartland of North America, and nearly half of Canada' s manufactured goods are produced here. If treated without understanding and care, the Great Lakes water quality will be quickly degraded by abundant nutrients and persistent toxic organics and trace metals, lead (Pb) being one of the well known ones.

In spite of the many works dealing with Pb and other toxic metals[1-20], an accurate statement vis-a-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 Spectrometer (AAS) has been the workhorse instrument for metal analysis in the Great Lakes waters, but AA 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 been developing an ultrasensitive instrument, the Laser-Excited Atomic Fluorescence Spectrometer (LEAFS) which enables direct, accurate determination of Pb in the Great Lakes waters[21]. Successful LEAFS application to the analysis of Antarctic and Greenland ancient ice and recent snow for Pb and Cd has been recently made by Bolshov and coworkers[22].

This paper reports for the first time the application of LEAFS to study Pb distribution in the Great Lakes waters. Lead concentrations were determined by direct analysis of 20 μL 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 ppt (ng l^{-1}), 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

The green light (511 nm) 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. The 566 nm light from the dye laser was then selected and frequency-doubled by a second harmonic generator to give the 283 nm UV light needed to excite Pb atoms generated in the graphite furnace. The fluorescent light (406 nm) emitted by the excited atoms was collected and measured via a monochromator-photomutiplier- boxcar system. The developed spectrometer is schematically shown and described elsewhere[21].

A monostable circuit was built to control the atomization sampling period without affecting the furnace firing time (Fig.1). On atomization, the Perkin Elmer model 2100 graphite furnace power supply generated a trigger which was buffered and passed to a 74HC4538 circuit, thus forming a pulse. The pulse width, corresponding to the atomization sampling period, can be set between 0 and 10 seconds using a front panel potentiometer. This capability to adjust the sampling period has very much simplified our data collection, as it automatically (no longer manually) dictates the start and stop of a sampling period. Consequently the sampled responses (fluorescence peaks) are evenly spaced and the secondary unwanted peaks are easily omitted (Fig. 2) without affecting quantitation since peak heights are used.

An analog and digital I/O board (model CIO-AD08, Computer Boards Inc.) was connected to the PC AT bus and used for data acquisition and control. The board allowed either a ±5V, a ±10V or a 0 to 10V range but not a 0 to -10V range. Since a negative high voltage powered the photomultiplier, the boxcar output ranged from 0 to -10V. In order to maximize the resolution it was preferable not to use the ±10V range which would have sacrificed one bit or 2.5 mV resolution. Thus an integrated circuit opamp OP07CP was used to build an inverter with a nominal gain of -1. This was coupled to the I/O board set at the 0 to 10V range.

Initially we used the boxcar software provided by EG&G Princeton Applied Research. It served us well for several months but with increasing use limitations in the software became evident. Data rates were limited by the IEEE-488 bus software. We could not trigger the data acquisition from an external source. Averaging of the data within a single scan was not possible. Integration and peak detection were also not possible. A data acquisition, analysis and presentation program was therefore written. The program was coded in "C" using Borland Turbo C++ with graphics extensions provided by Scientific Endeavors "GraphiC v. 6.0". The program controls the Computer Boards Inc. CIO-AD08 data acquisition board (ADC). This board acquires samples at 1Khz rate under software control. Twenty of these samples are acquired and averaged for each point giving an effective 50 Hz data rate. Multiple averaging is done to reduce analog to digital conversion noise. Up to 5,000 of these points are collected while the program is waiting for an atomization trigger signal. Once the trigger is sensed, the program acquires data until the atomization trigger signal returns to a logical low. The program then computes the following: 1) The 50 points i.e 2.5 seconds worth of data prior to the atomization trigger are averaged to form a baseline signal. This corrects for ADC and boxcar offsets. This is called "base". 2) The peak signal during the atomization is called "peak". The "base" signal is subtracted to form "peak-base". 3) A cumulative sum of all the points measured during the atomization period is computed. This is a crude integration, which is termed "csum". 4) The baseline value "base" is multiplied by the same number of points in the computation of "csum". This is called

"cbase" and is subtracted from the cumulative sum "csum" to form "csum-cbase". The values "peak-base", "csum-base" ,"base", "cbase" plus any comments are displayed on the screen, printed to a hard copy printer and are stored in a file.

All the data points used to compute the above values are stored in a separate file. These data points may be viewed graphically by selecting a function key. A computer mouse may then be used to zoom in on particular portions of the plot. The plot may be dumped to a printer or to a file as a Postscript file for manipulation by data presentation software such as Corel Draw for example. To analyse the next sample, the program prompts the user to continue or to end the session. The number of points stored is presently limited to 6,000 points. This is about 40 to 45 analyses which is a typical afternoon run. The graphical data may be viewed after the session using the programs "Play" and "Replay". "Play" is used to view the run of data which was last taken. No file name prompts are requested. "Replay" is used to view any of the previous files. It requests a file name. Usually our data are stored with the file name bearing the SI date format e.g. 920622_1 refers to the first file on June 22, 1992.

Table 1 summarizes the equipment and conditions used.

Ultraclean rooms and ultrapure chemicals

A class 100 clean laboratory was developed, which contains a high efficiency particle (HEPA) filter assembly through which about 100 air changes per hour takes 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 resistant epoxy resin. The floor consists of seamless, chemically resistant vinyl and the floor drain is capped with a plastic block. Any individual 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 works, 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 general purpose in-house reverse osmosis (RO) distilled water. The second stage is the redistillation of the RO water in a quartz still (Corning AG-3 system). The redistilled water is finally fed into a Milli-Q system (Millipore Corp., Bedford, Mass.) situated in the class 100 room. The Pb blank of the water is <0.4 ppt. Doubly quartz distilled nitric and hydrochloric acids (Seastar, Victoria, B.C.) as well as other highest purity chemicals were used. The ultrahigh purity nitric acid has a specified Pb content of 40 ppt.

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 filtration system are all made of teflon. Volumetric flasks, measuring cylinders, pipets and pipet 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, pipet 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. The design and performance of this sampler is being written up[28]. Depth samples were collected by means of 5-L 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 polycarbonate (Nuclearpore) membrane filter with 0.45μm 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 was 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 some profiles are missing certain sites. 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 ppm stock by sequential dilution with Milli-Q water blank. 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 was 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 described 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 ppt generated ~4V responses) and 1.9 kV for high sensitivity (where 20 ppt generated almost 8V responses). The ten replicate analyses of 50 ppt standard show

good reproducibility giving an RSD of 1.8%. Ten replicate analyses of 10 ppt on a separate run resulted in a 4.9% RSD. Calibration curves with a linear dynamic range of four orders of magnitude can be easily obtained, as shown in Figure 3, which easily 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 ppt, corresponding to 10 fg absolute for 25 μL injection.

Sample analysis and Pb profiles

To confirm the applicability of LEAFS to the analysis of Great Lakes waters, six different such samples (two from each of the 3 lakes) were subjected to the Multiple Standard Addition (MSA) technique. Each regressed standard addition line intersected the (concentration) abscissa producing an 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.

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 analyses made. The average blank concentration was, respectively, 1.3, 2.4 and 3.3 ppt for Lakes Superior, Erie and Ontario and was subtracted from the gross concentration of each lake sample. Nearly two hundred water samples were collected from various sites in the three lakes and analysed the same way as blanks and standards.

Figure 4 shows several vertical concentration profiles for Lake Superior, the biggest and deepest of the Great Lakes. The concentration 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 (Fig. 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, the smallest and shallowest of the Great Lakes, the very high concentration of the deepest sampling site for station 23 (Fig. 6) suggests there was extensive sediment resuspension in contrast to the deep Lake Superior.

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 Region (stations 21, 96 and 104). The overall average concentration of Pb in Lake Ontario was calculated to be 25 ppt (range 4-154 ppt) which is in the same order of magnitude as the average of 35 ppt (range 1-284 ppt) 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 ppt for their 1985 data. These three sets of results are lower than those reported by other workers: 140 ppt in 1986 by Nriagu[13], 300 ppt in 1990 by Allan and Ball[19], 500 ppt in 1978 by Patterson and Kodukula[3], and 830 ppt in 1970 by Chau et. al.[1].

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 ppt compared to 14 ppt (median 6 ppt) reported in 1988 by Rossmann and Barres[15], 75 ppt by Allan and Ball[19], 400 ppt by Poldoski et. al.[4], and 1000 ppt 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 ppt, which is in the same order of magnitude as 20±13 ppt reported by Coale and Flegal[17]. Both findings are at least an order of magnitude smaller than others: 150 ppt by Nriagu[13], 220 ppt by Rossmann and Barres[15], 750 ppt by Allan and Ball[19], and 2000 ppt 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 ppt) are by far the highest for all 3 lakes especially in comparison to ours (~25 ppt 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 ppt compared to 0.4 ppt 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 works.

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TABLE 1. Equipment and Operating conditions

COPPER VAPOR LASER Pulse width Power input, Power output*	MLT20 (Metalaser Technologies) 24 ns 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 Dye: Rhodamine 6G Setting for maximum fluorescence	DL-13 (Laser Photonics) 0.2g/L (4.2 x 10^{-4} mole/L) 280.60 - 280.61 (for Pb)
SECOND HARMONIC GENERATOR Crystal	Autotracker II (Inrad Inc.) KDP-B
VISIBLE LIGHT FILTER	UG5, 4mm (Schott Glass Technolog.)
ELECTROTHERMAL ATOMIZER Graphite Tube Dry, char, atomization Sample injection, Internal gas flow	Perkin-Elmer HGA 2100 8x28 mm 120, 500, 1800-2100C; 40, 40, 5 sec. 10-25 L, Stopped flow (Interrupt)
NARROW BANDPASS FILTER	Melles Griot (404.7±5nm)
MONOCHROMATOR I Aperture ratio Slit width	Schoeffel GM 250, 0.25m f/3.6 0.8 mm
PHOTOMULTIPLIER I Voltage setting (Power Supply)	Thorn EMI 9813 1.6-2.4 kV (Thorn EMI type PM28B)
BOXCAR AVERAGER (Software) Gate width, Operation mode	4121B, EG&G PAR (RJD in-house) 1 µS, Baseline 2 mode
A to D CONVERTER	4161A, EG&G PAR
LEAD LAMP	EDL lamp, 8W (Perkin Elmer)
MONOCHROMATOR II Aperture ratio Slit width	GCA/ McPherson, EU-700-56, 0.35m f/6.8 at 200nm 0.3 mm
PHOTOMULTIPLIER II Voltage setting (Power Supply)	1P28 0.9 kV (Thorn EMI type PM28B)
BOXCAR AVERAGER	4121B, EG&G PAR
MULTIMETER	HP 3468A
ENERGY METER Power range	Scientex 36-0201 200 mV 0.1mW - 25W

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

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], ppt	Direct analysis, ppt	Student t values	Critical t values
LE-23-50	42.45	42.48±2.39	0.03	3.18
LE-54-6	16.59	15.84±2.53	0.59	3.18
LO-79-19	9.17	8.57±0.54	1.92	4.3
LO-87-20	19.57	19.86±1.63	0.31	4.3
LS-2-12	24.42	25.39±0.09	0.53	12.7
LS-125-175	1.42	1.25±0.21	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.

TABLE 3. Comparison of diolved Pb concentrations, ppt, 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 e et. al.[c]	Allan and Ball <1986[d]	Nriagu 1986[e]	Rossmann and Barres[f]	Coale and Flegal[g]	This work[h] LEAFS
Ontario	1140±650 (24)	500	....	300	140	10-150	35±80	25±28
Erie	1400±800 (202)	2,000	....	750	150	220±140	20±13 (4)	9±11
Superior	1500±1200 (212)	1,000	450±200	75	....	14±31 (22)	---	4±5 (90)

[a] Method: AAS following solvent extraction (APDC-MIBK), near-surface samples[27]. Ontario (1971-1985); Erie (1970-971); Superior (1970-1976). The "0" values are not included.
[b] Method: AAS - solvent extraction, Patterson & Kodukula[3]
[c] Method: GFAAS, unfiltered samples, Poldoski et. al.[4]
[d] Allan and Ball
[e] Method: GFAAS, Chelex-100 followed by AAS, Precipitation/extraction-AAS. Nriagu[13].
[f] Method: GFAAS, 100 µL injection; Rossmann 1984, Rossmann 1986, Rossmann and Barres 1988 in Allan and Ball (1990). For 1981, a single result was 150 ppt; for 1985 data, the median result was 10 ppt[12, 14,15].
[g] Method: GFAAS following 200:1chelation/extraction; Coale and Flegal[17], surface samples.
[h] Method: LEAFS; whole lake.

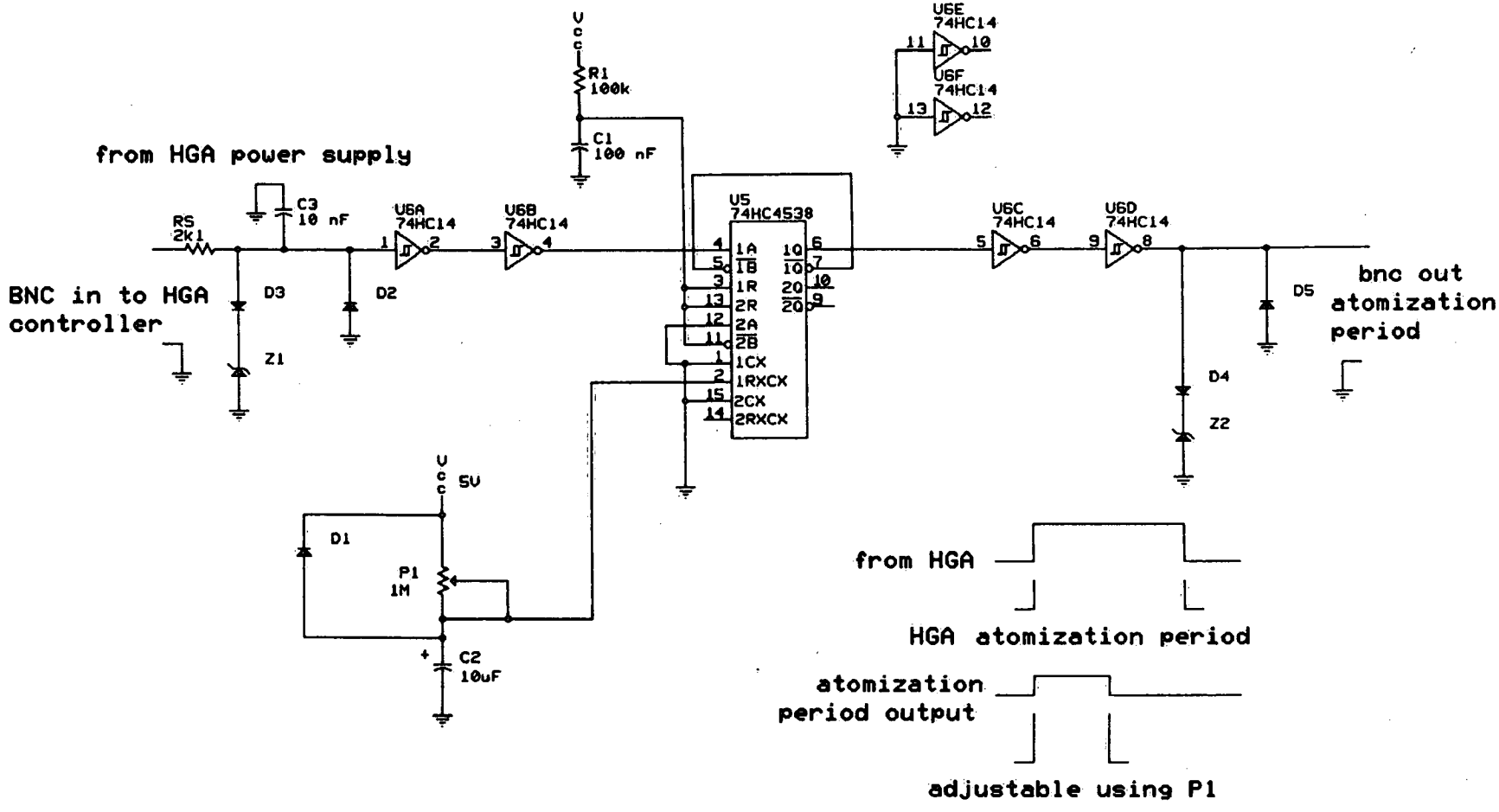


Figure 1. Atomization sampling period circuit.
(Diodes D1 to D5 are 1N4148; Zener diodes Z1, Z2 are 1N5231B)

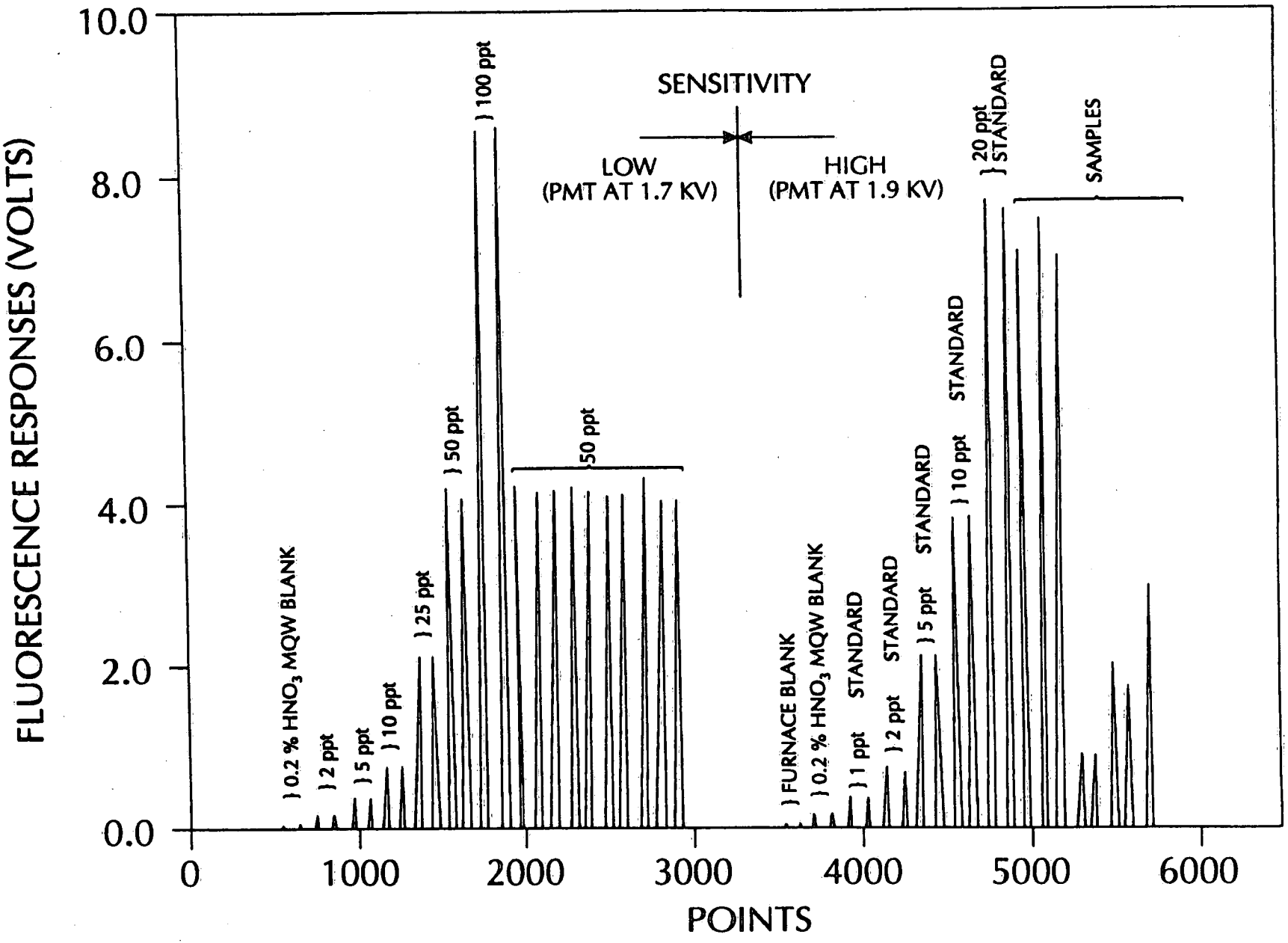


Figure 2: Typical fluorescence responses for standards and samples containing Pb (20µL injection)

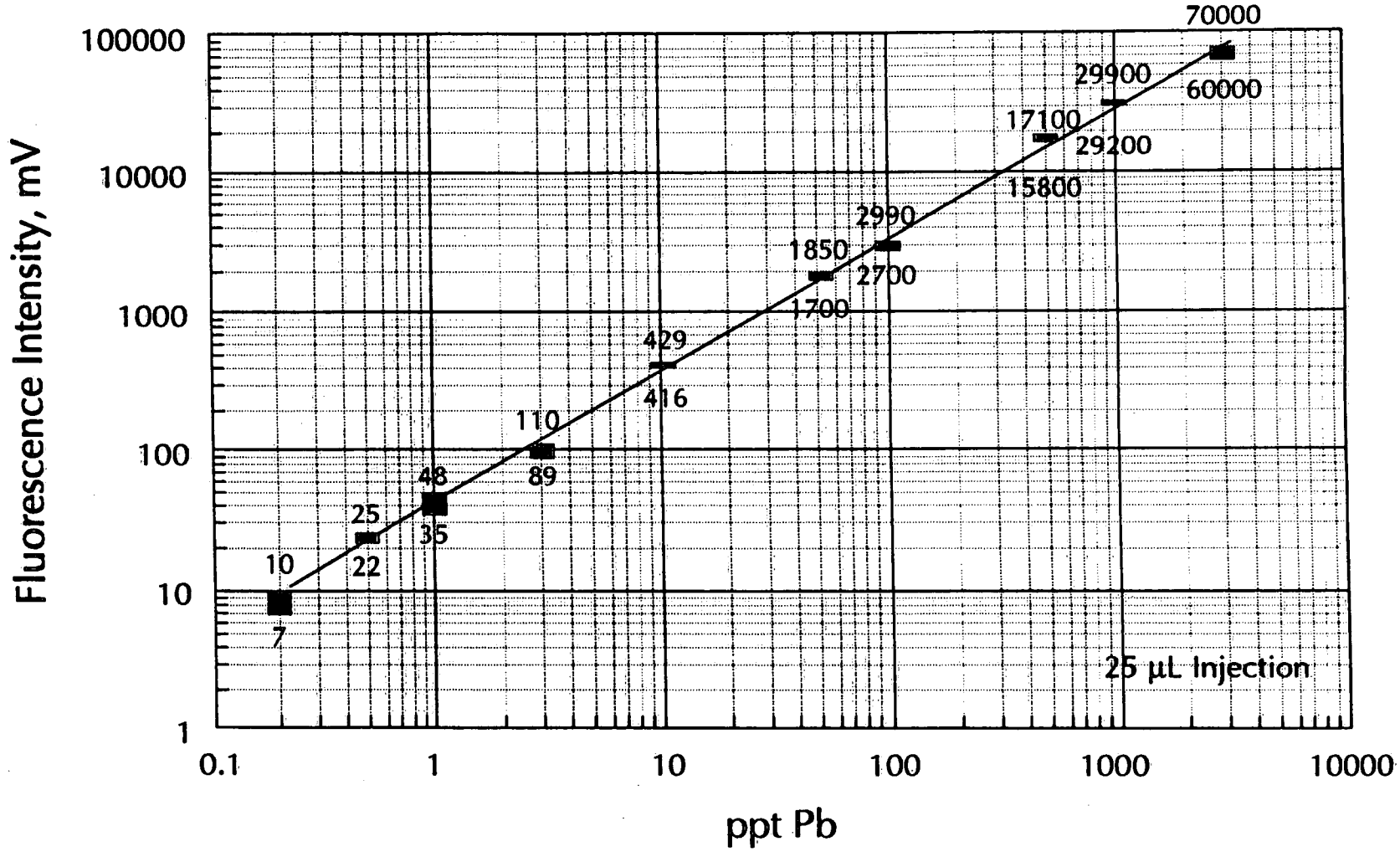


Figure 3: LEAF calibration curve for direct analysis of Pb in water

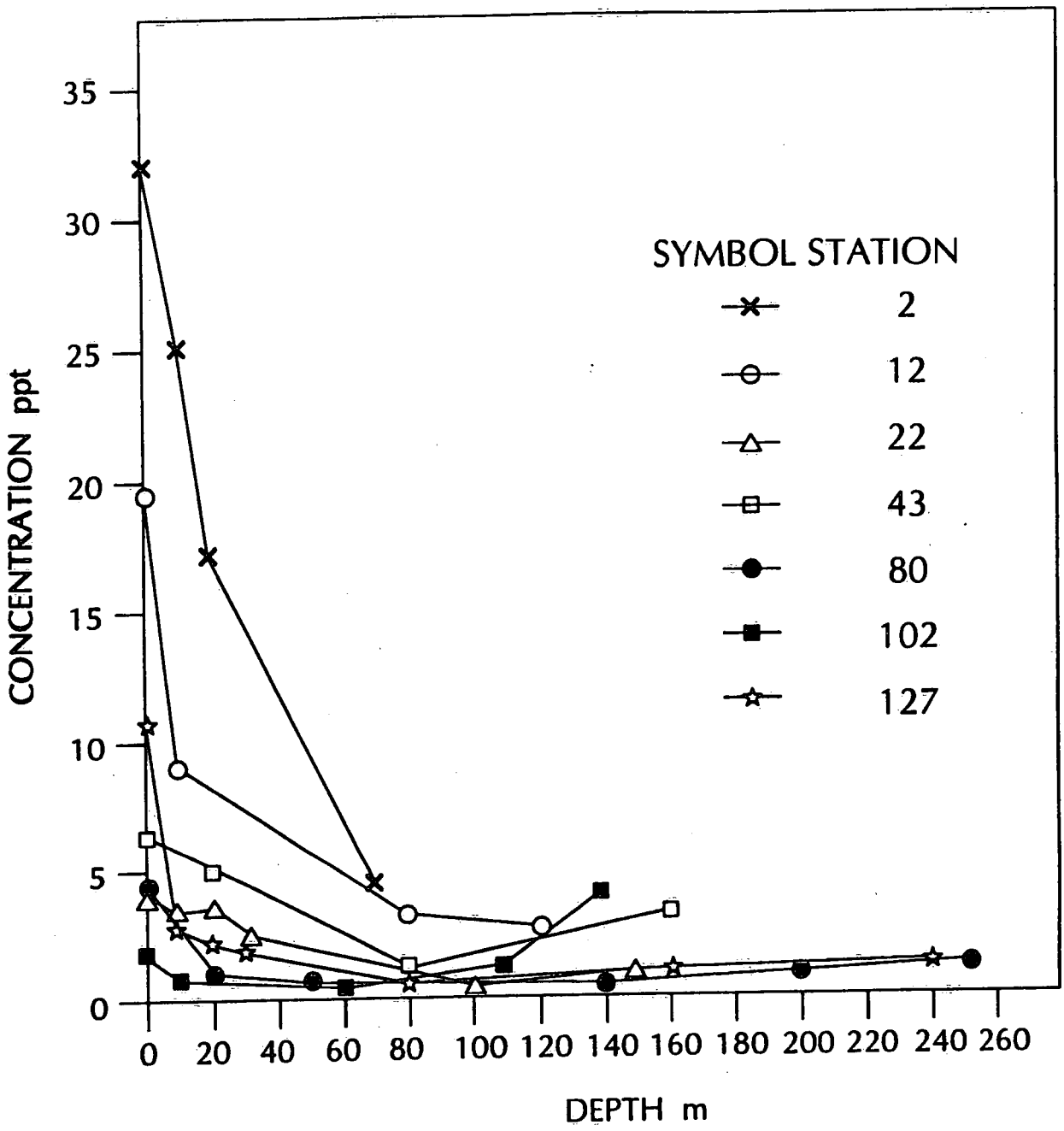


Figure 4: Vertical profile of Pb in Lake Superior

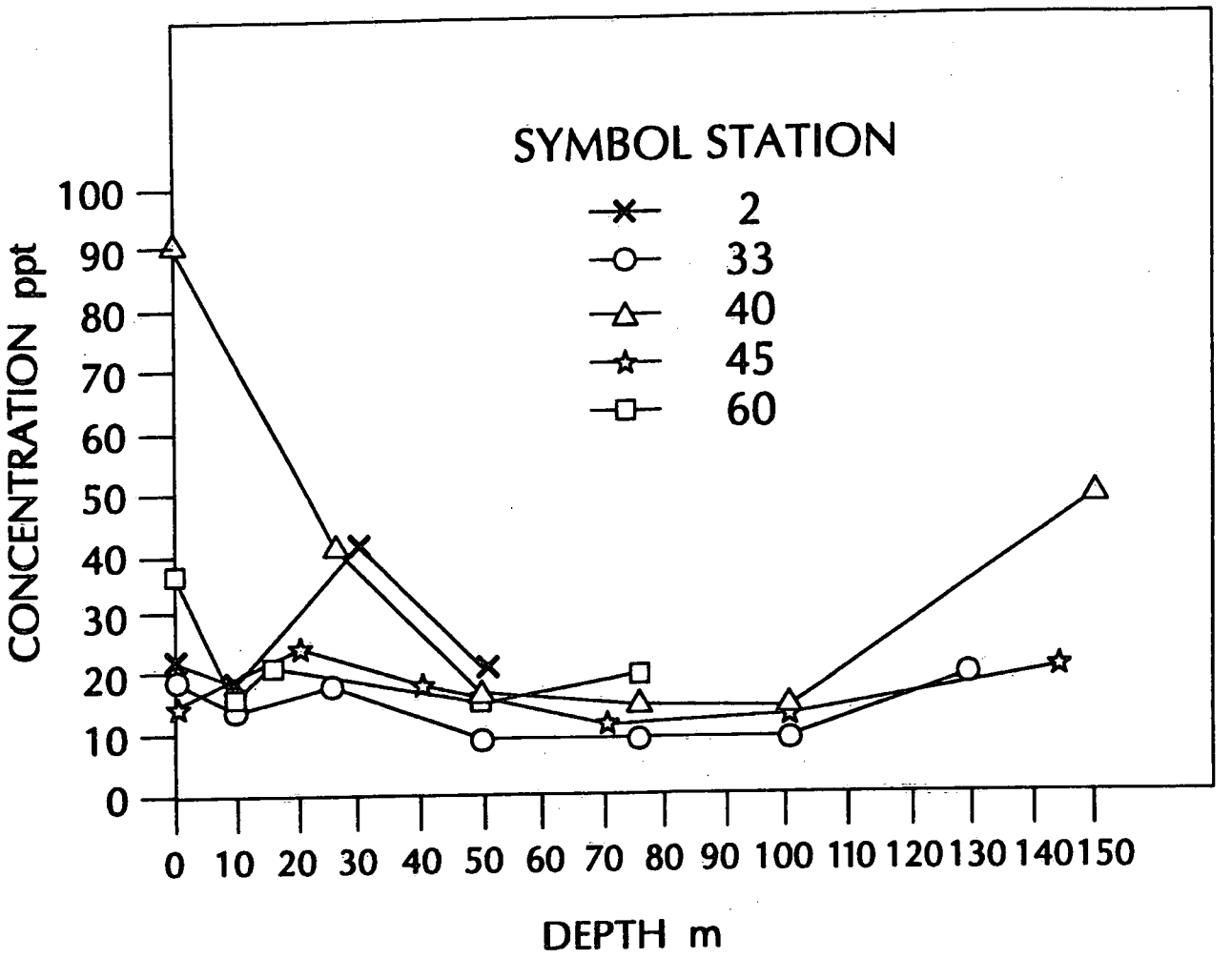


Figure 5: Vertical profile of Pb in Lake Ontario

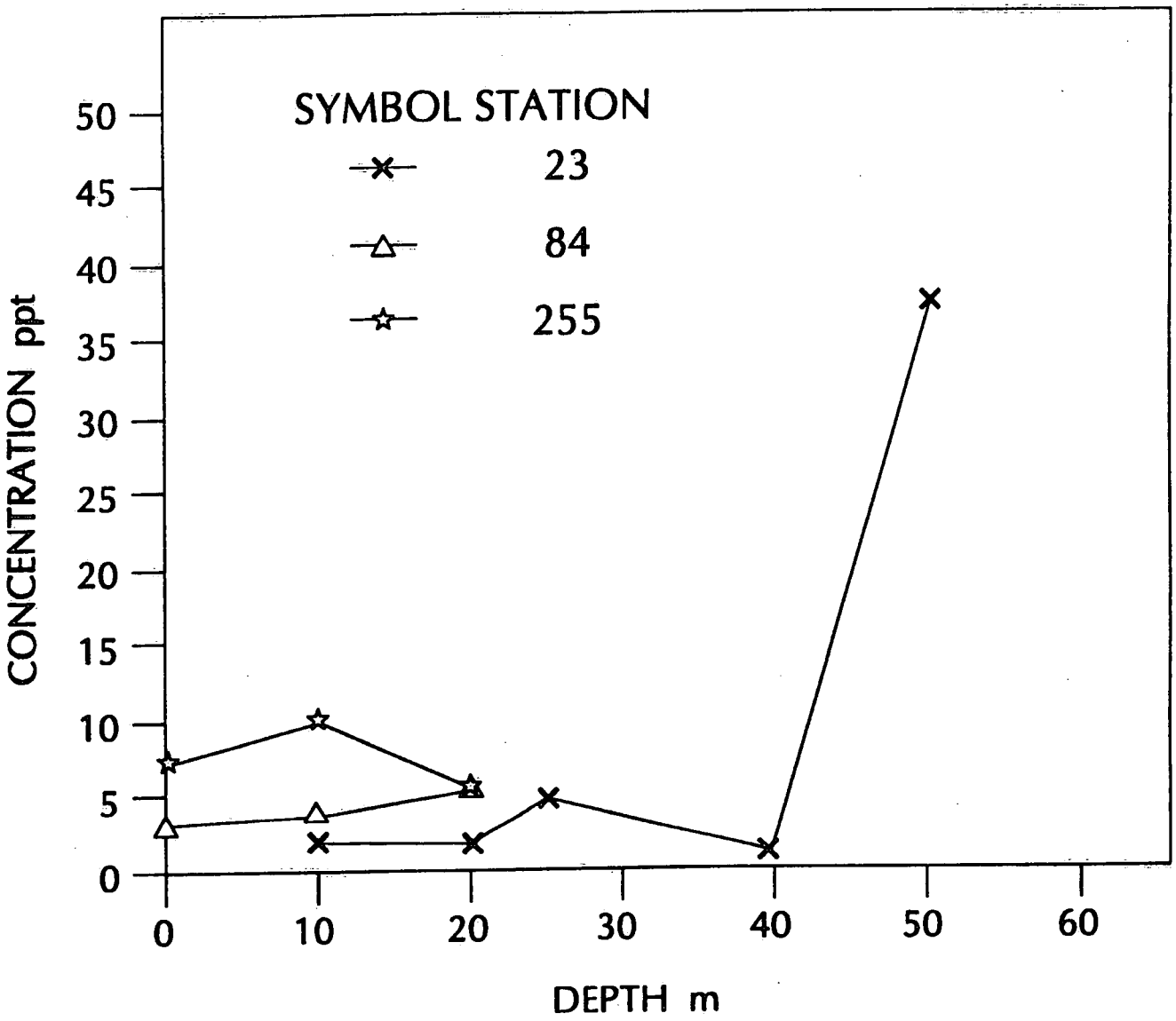


Figure 6: Vertical profile of Pb in Lake Erie

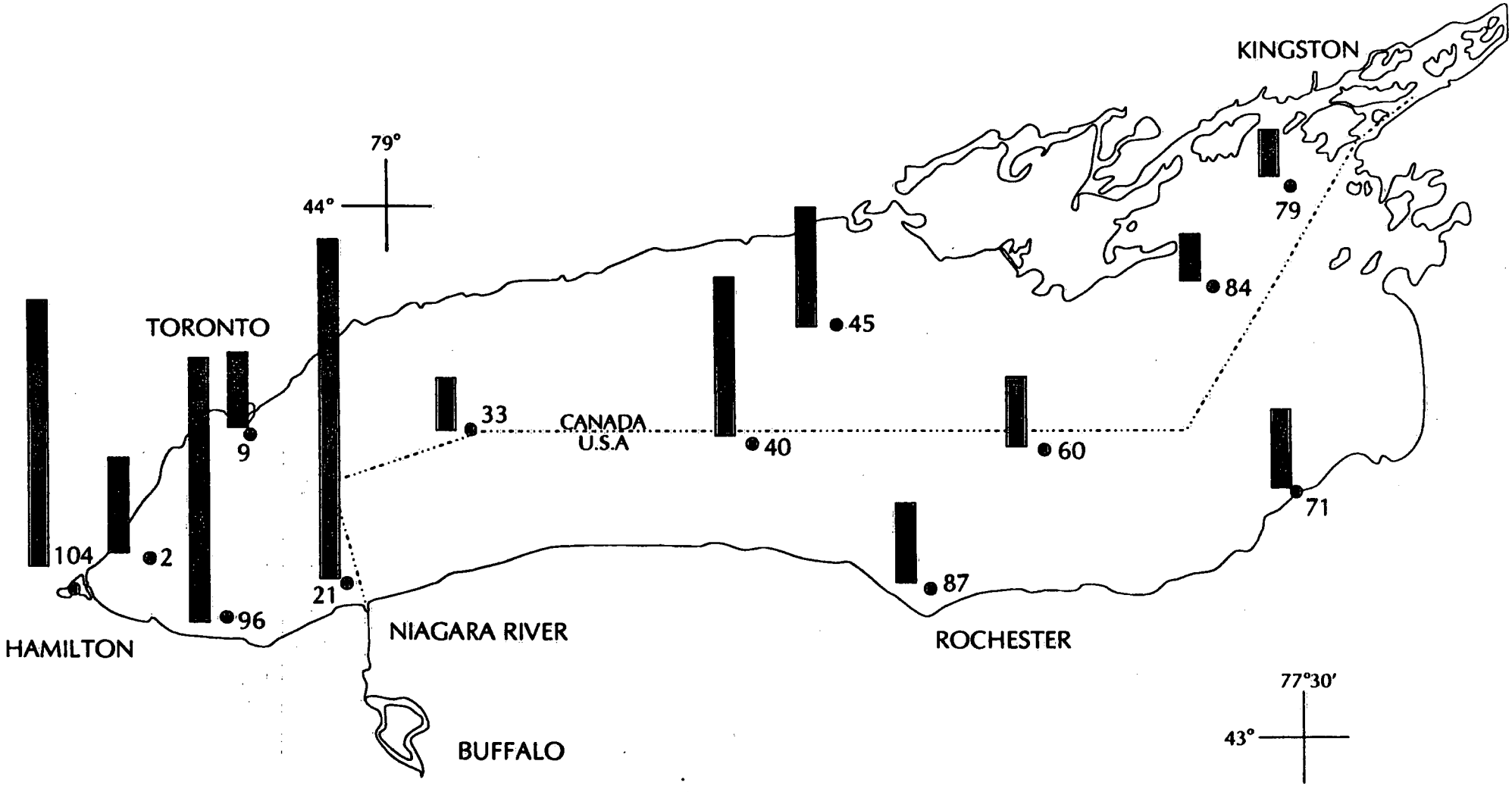


Figure 7: Average Pb concentration (▮ = 10 ppt) of each vertical profile for the studied stations in Lake Ontario

Fig. 7 Pb concentration in the Great Lakes (Cheam et. al.)

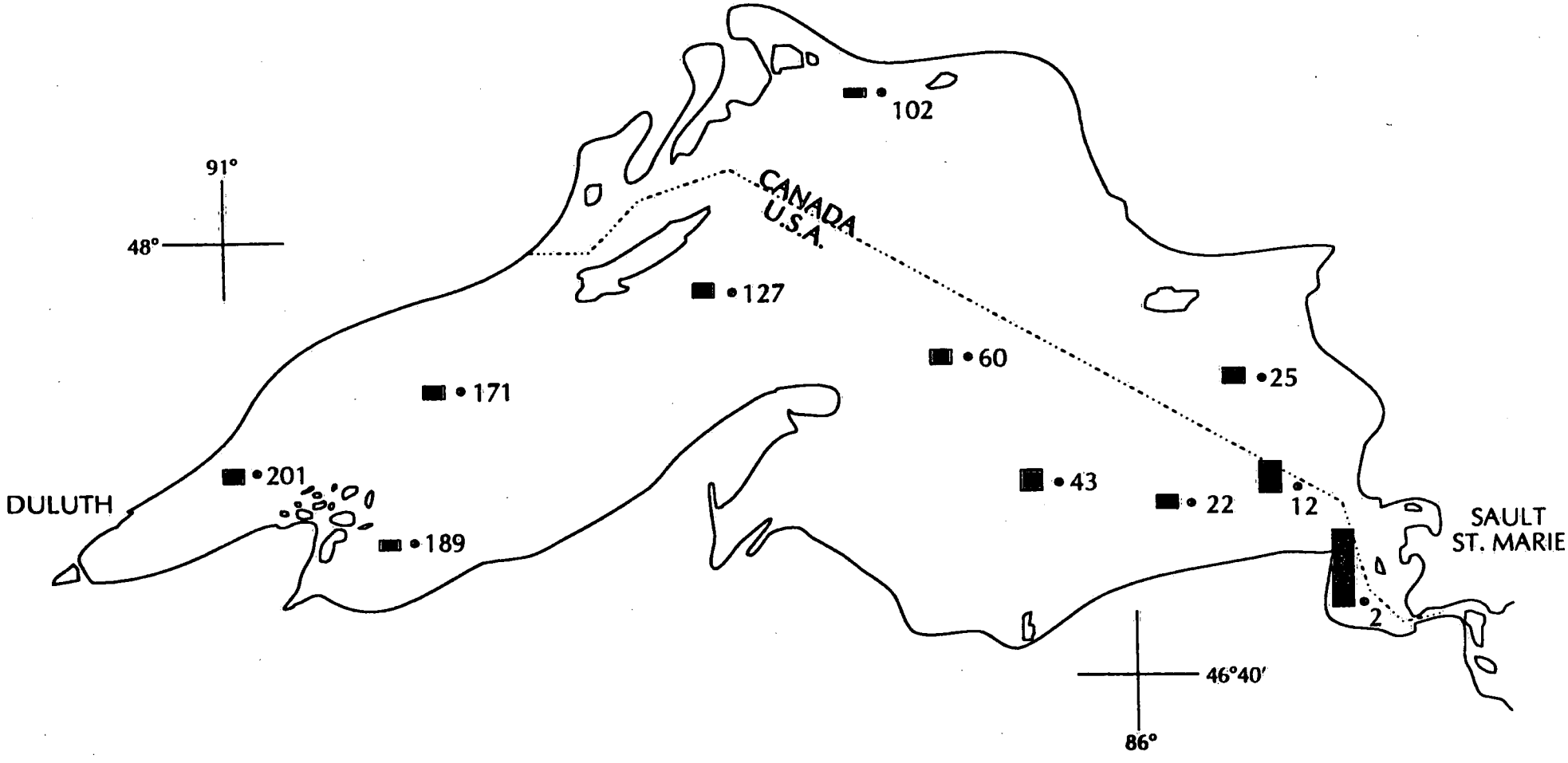


Figure 8: Average Pb concentration (■ = 10 ppt) of each vertical profile for the studied stations in Lake Superior

Fig. 8 Pb concentration in the Great Lakes (Cheam et. al.)

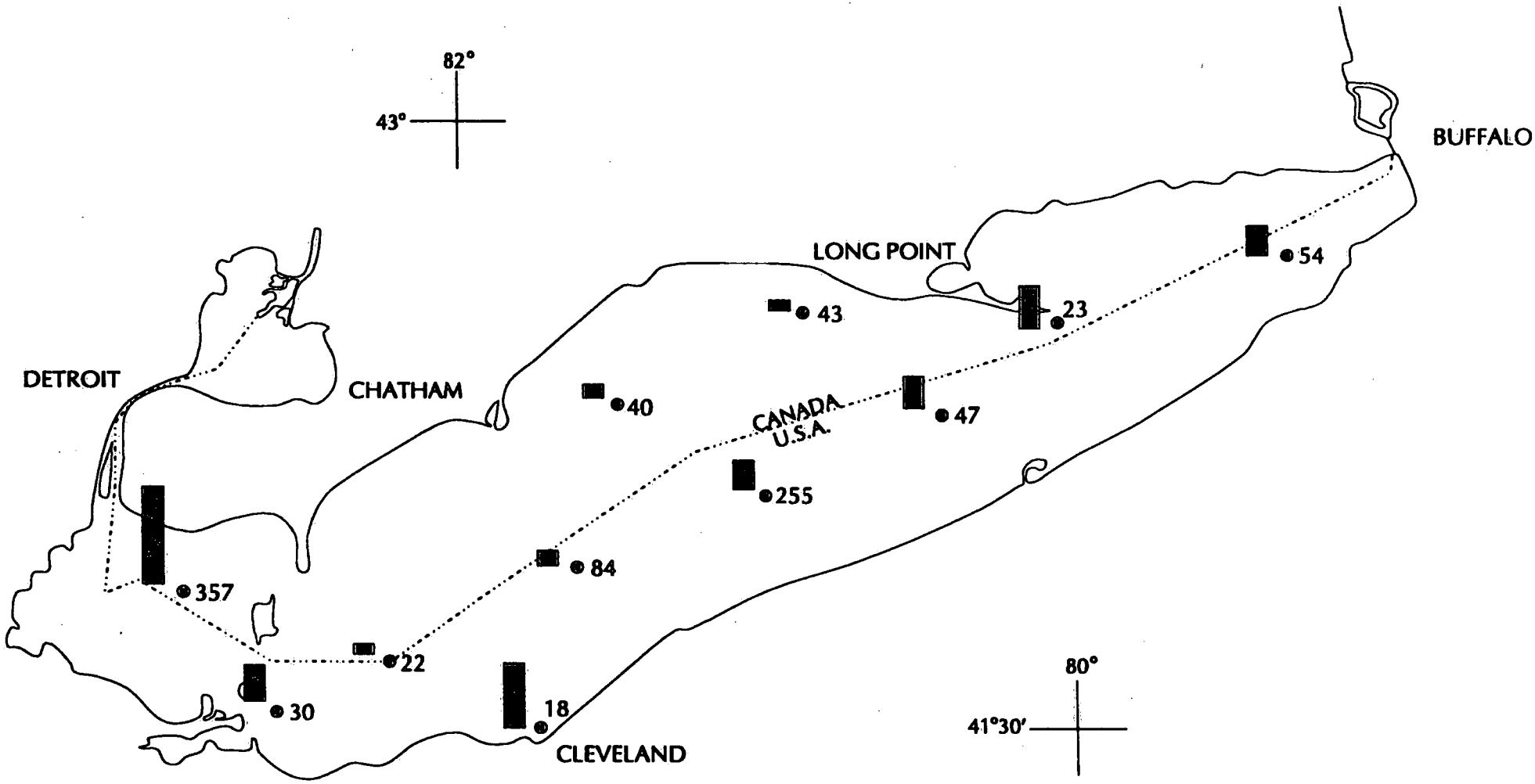
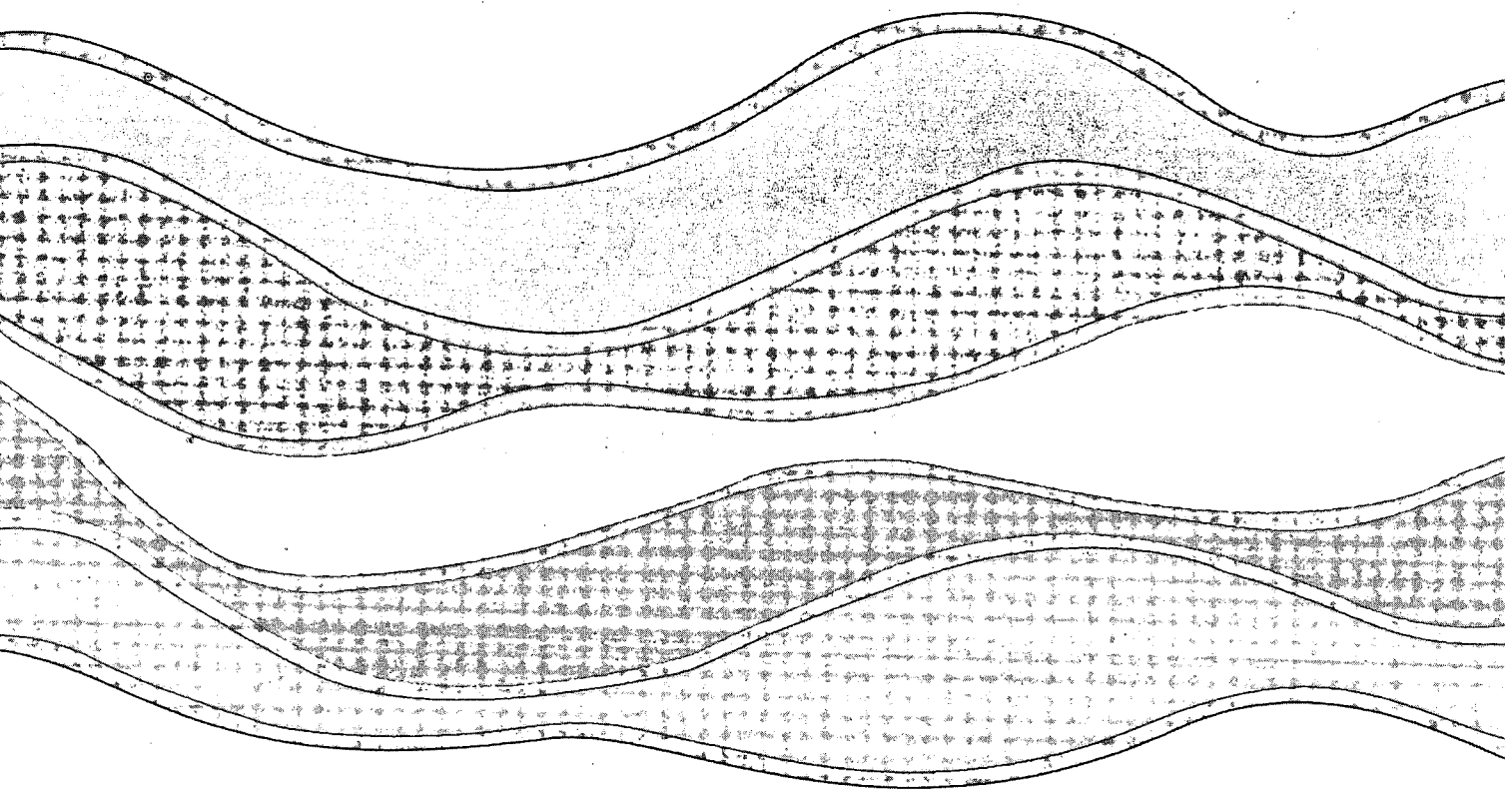


Figure 9: Average Pb concentration (■ = 10 ppt) of each vertical profile for the studied stations in Lake Erie

Fig. 9 Pb concentration in the Great Lakes (Cheam et. al.)



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