Inland Lakes Sediment Trends: Sediment Analysis Results for Five Michigan Lakes

Yearly report: 2001-2002
Cadillac Lake
Crystal Lake (Benzie County)
Mullett Lake
Paw Paw Lake
Whitmore Lake

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Introduction

Contaminated sediments can directly impact bottom-dwelling organisms and represent a continuing source of toxic substances in aquatic environments that may impact wildlife and humans through food or water consumption (Catallo et al., 1995). Therefore, an understanding of the trends of toxic chemical (e.g., polychlorinated biphenyls, lead) accumulation in the environment is necessary to assess the current state of Michigan's surface water quality and to identify potential future problems. A common fate of chemicals in a lake is to associate with fine-grained particulate matter and settle to the bottom (Evans and Rigler, 1983). As this deposition occurs over time, sediments in lakes become a chemical tape recorder of the temporal trends of toxic chemicals in the environment as well as of general environmental change over time (von Guten et al., 1997). Sediment trend monitoring is consistent with the framework for statewide surface water quality monitoring outlined in the January 1997 report prepared by the Michigan Department of Environmental Quality entitled, "A Strategic Environmental Quality Monitoring Program for Michigan's Surface Waters" (Strategy). A key goal of the Strategy is to measure trends in the quality of Michigan's surface waters, and one activity designed to examine these trends is the collection and analysis of high-quality sediment cores. This report details the activities and findings of the third year of the sediment trend component of the Strategy, and builds upon the results from the five lakes sampled in 1999 (Year 1)(Simpson et al., 2000), and two lakes sampled in 2000 (Year 2) (Yohn et al., 2001).

Summary

Sediment cores were collected from six lakes in 2001 to evaluate the spatial and temporal variations in lake sediment quality in Michigan, and as a continuation of the trend monitoring component of the Strategy (Simpson et al., 2000). Lakes include: Cadillac (Wexford County), Crystal (Benzie), Hubbard (Alcona), Mullett (Cheboygan), Paw Paw (Berrien), and Whitmore (Livingston and Washtenaw) Lakes. Sediment cores were collected from one site in each lake, dated with ^{210}Pb and ^{137}Cs, and analyzed for a suite of metals and organic compounds. Dating is not yet completed for Hubbard Lake, and therefore data for this lake will be reported in 2002-2003 year end report. Analysis for a suite of metals rather than just target anthropogenic metals (e.g., Pb, Cu) allows for interpretations about the sources for different chemicals. Additionally, porewater was collected from each of the lakes and analyzed for a similar suite of metals. Key findings include:

- Sediment cores from Crystal B, Mullett, and Cadillac Lakes reach background levels (before significant human influence).
- Sediment cores from Paw Paw and Whitmore Lakes did not reach background levels.
- Of the five lakes sampled, concentrations of polyaromatic hydrocarbons are highest in Cadillac Lake, and concentrations of DDTs are highest in Paw Paw Lake.
- Overall, surface sediments in Cadillac, Whitmore, and then Paw Paw Lakes have the highest surface concentrations of cadmium, copper, lead and zinc.
- Cadillac Lake has significantly higher concentrations of copper then all other lakes, due to the addition of copper sulfate. Copper concentrations in the most recently deposited sediments remain significantly elevated.
- Spatial and temporal patterns of lead deposition indicate that atmospheric deposition of lead has been an historically important source, but that local sources are becoming more important in the last decade.

Methods

Sediment cores were collected from Cadillac (Wexford County), Crystal (Benzie), Hubbard (Alcona), Mullett (Cheboygan), Paw Paw (Berrien), and Whitmore (Livingston and Washtenaw) Lakes in 2001 (Fig. 1). Sediment cores were collected from the deepest portion of each lake using a MC-400 Lake/Shelf Multi-corer deployed from the Monitoring Vessel Nibi. The M/V Nibi was designed to, and has successfully provided access to both major and remote inland lakes throughout Michigan. Collected sediment cores were described and examined for color, texture, and signs of zoobenthos. Cores were then extruded and sectioned at 0.5 cm intervals for the top 8 cm, and at 1 cm intervals for the remainder of the core.

^{210}Pb was measured on one sub-core from each lake to determine porosity, accumulated dry mass, sedimentation rates, sediment ages and focusing factors (Freshwater Institute in Winnipeg, Manitoba, Canada). Results from all lakes were verified using ^{137}Cs. Dating was not completed on Hubbard Lake at the time of this report, therefore results will be reported in the 2002-2003 yearly report.

Sediments were frozen, freeze-dried and digested by nitric acid in a CEM-MDS-81D microwave (Hewitt and Reynolds, 1990). Standard reference material (NIST RM 8704 Buffalo River Sediment) and procedural blanks were processed to test for accuracy and contamination. The concentrated-acid digests were filtered through an acid-washed, e-pure (Barnstead) rinsed 0.40 µm polycarbonate filter. Samples were then analyzed using a Micromass Platform inductively coupled, plasma, mass spectrometer with hexapole technology (ICP-MS-HEX). Sediments were analyzed for a suite of metals and metalloids including Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Ba, Pb, and U.

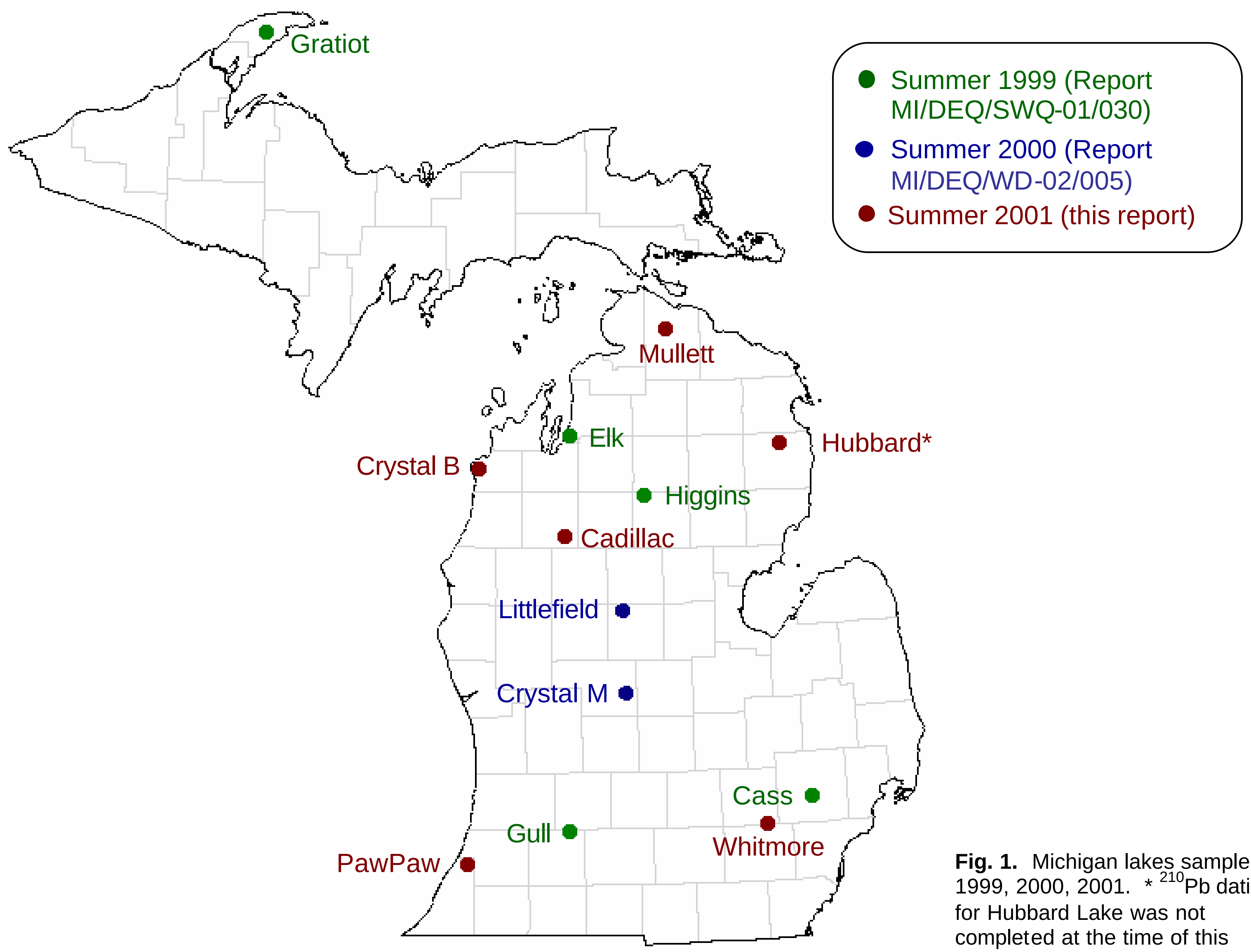


Fig. 1. Michigan lakes sampled in 1999, 2000, 2001. * ^{210}Pb dating for Hubbard Lake was not completed at the time of this report; therefore the data will be included in the 2003-2004 report.

Another sub-core was sectioned and used for analysis of organic contaminants. There was insufficient material for analysis in the topmost sediments, so the first two sections were combined, and the third and fourth sections were combined. Polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), organochlorine (OC) pesticides (screening only), alkylphenols, and bisphenol A (BPA) were analyzed (Khim et al., 1999a; Khim et al., 1999c). A portion of the sediment was dried at 100°C to determine moisture content. Sediment samples were Soxhlet extracted for 20 h using dichloromethane (DCM; Burdick & Jackson, Muskegon, MI, USA). Extracts were then treated with acid-activated copper granules to remove sulfur. Aliquots of extracts were concentrated to approximately 5 ml by rotary evaporation (39^{o}C), and then to 1 mL under a gentle stream of nitrogen.

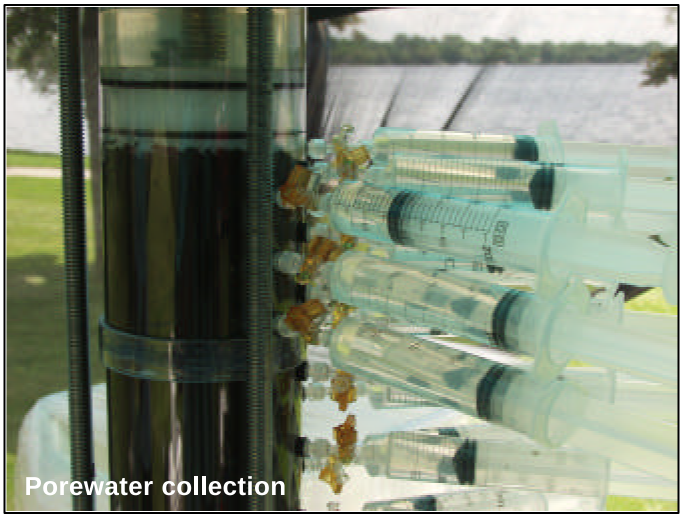
Extracts were passed through 10 g of activated Florisil (60-100 mesh size; Sigma, St. Louis, MO, USA) packed in a glass column (10 mm i.d.) for clean up and fractionation. The first fraction (F1) eluted with 100 mL of hexane (Burdick & Jackson) contained PCBs and *p,p'*-DDE. Remaining OC pesticides and PAHs were eluted in the second fraction (F2) using 100 mL 20% DCM in hexane. Nonlyphenol (NP), octylphenol (OP) and BPA were eluted in the third fraction (F3) with 100 mL 50% DCM in methanol (Burdick & Jackson). Recoveries of target analytes through all the analytical steps were between 90 and 105%. Further details regarding the fractionation procedure are presented elsewhere (Khim et al., 1999b; Khim et al., 1999c). PAHs were quantified using a Hewlett Packard 5890 series II gas chromatograph equipped with a 5972 series mass spectrometer detector. A fused silica capillary column (30m × 0.25 mm i.d.) coated with DB-17 [(50% phenyl)-methyl polysiloxane; J&W Scientific, Folsom, CA, USA] at 0.25 µm film thickness was used. The column oven temperature was programmed from 80°C (1 min hold) to 100 °C at a rate of 25°C/min, and then ramped at a rate of 5°C/min to 300°C with a final holding time of 6 min. The injector and detector temperatures were maintained at 250°C and 300°C, respectively. The PAH standard (AccuStandard, New Haven, CT, USA) consisted of 16 priority pollutant PAHs identified by the U.S. Environmental Protection Agency (U.S. EPA; Method 8310). The mass spectrometer was operated under selected ion monitoring (SIM) mode using the molecular ions selective for individual PAHs (Khim et al., 1999a). Calibration standards were prepared at 0.25, 0.5, 1, 2, and 5 µg/mL. Concentrations based on individually resolved peaks were summed to obtain the total PAH concentrations. The detection limits of PAHs for sediment samples were 10 ng/g dry wt.

PCBs and OC pesticides were quantified using a gas chromatograph (Perkin Elmer series 600) equipped with ^{63}Ni electron capture detector (GC-ECD). A fused silica capillary column coated with DB-5MS [(5%-phenyl)-methylpolysiloxane, 30m × 0.25mm i.d.; J&W Scientific, Folsom, CA, USA] having a film thickness of 0.25 µm was used. The column oven temperature was programmed from 120°C (1 min hold) to 180°C at a rate of 10°C/min (1 min hold) and then to 260°C at a rate of 2°C /min with a final holding time of 12 min. Injector and detector temperatures were kept at 250°C and 300°C, respectively. Helium and nitrogen were used as carrier and make up gas, respectively. A solution containing 98 individual PCB congeners with known composition and content was used as a standard and concentrations of 98 individually resolved peaks were summed to obtain total PCB concentrations (Khim et al., 1999a). OC pesticides were screened based on the peak retention time and areas of standards. Detection limits of sedimentary OC pesticides and PCBs were 5 and 1 ng/g dry wt, respectively.

Reverse phase high performance liquid chromatography (HPLC) with fluorescence detection was used to quantify NP, OP, and BPA (Khim et al., 1999b). High purity *p*-nonylphenol and *p*-*tert*-octylphenol standards (Schenectady International, Freeport, TX, USA) and BPA (4,4'-isopropylidenediphenol; Sigma Chemical Co., St. Louis, MO) were prepared in high purity acetonitrile (ACN; Burdick & Jackson) at 0.32, 0.63, 1.25, 2.5, 5, and 10 μg/mL for the calibration run. Standards were injected freshly along with every set of samples and the r^2 for calibration was maintained at ≥0.99. Samples and standards were injected (10 μl) by a Perkin Elmer Series 200 autosampler (Perkin Elmer, Norwalk, CT, USA) onto an analytical column, Prodigy™ ODS (3), 250 × 4.6 mm column (Phenomenex, Torrance, CA, USA), which was connected to a guard column (Prodigy™ ODS (3), 30 × 4.6 mm), and eluted with a flow of ACN and water at a gradient from 50% ACN in water to 98% ACN in water delivered by Perkin Elmer Series 200 pump for 20 min. Detection was accomplished using a Hewlett Packard 1046A fluorescence detector (Hewlett-Packard, Wilmington, DE, USA) with an excitation wavelength of 229 nm and an emission wavelength of 310 nm. NP, OP, and BPA detection limits for the analytical method were 5 ng/g dry wt (Khim et al., 1999b).

The fourth sub-core was used for the collection of porewater. The sediment core was squeezed 5-6 cm, forcing water through Porex into syringes placed every 1 cm (10 samples) then 2 cm (18 samples) from the top. The collected water was filtered through an acid washed, DDW rinsed 0.40 µm polycarbonate filter and preserved with nitric acid and gold (for mercury analysis). These solutions were analyzed on the ICP-MS-HEX in a similar fashion as the digested sediments.

Descriptions of the calculations for data analysis follow this section.


Porewater collection

^{210}Pb and sedimentation rates

^{210}Pb is frequently used to date lake sediment due to its relatively constant input from the atmosphere, and its appropriate half-life ($t_{½}$ = 22.3 yr) that allows sediment deposited in the last 100-150 years to be dated. ^{210}Pb present in the sediment is divided into the supported and unsupported portions. Supported ^{210}Pb originates from ^{226}Ra found in the sediment that decays to ^{222}Rn, and further to ^{210}Pb within the sediment (Robbins and Edgington, 1975), while unsupported ^{210}Pb originates from ^{222}Rn decay in the atmosphere and water column (Sanchez-Cabeza et al., 2000). The unsupported, or excess ^{210}Pb, decays as it is buried in the sediment and can be described by an exponentially declining curve. Four different models were used in this study to date sediment cores using unsupported ^{210}Pb activities. The first is the constant flux constant sedimentation model (CF:CS), the second is a modification of this method, the segmented CF:CS (SCF:CS). The CF:CS model assumes a constant flux of ^{210}Pb to the sediment and a constant rate of sedimentation. Accumulated dry mass is plotted versus excess ^{210}Pb on a logarithmic scale. The slope is related to the sedimentation rate through the equation:

$$C(z) = C(s)e^{(-kz/W)}$$

where z is the mass depth (g/cm^2), C(z) is the unsupported ^{210}Pb activity (Bq/cm^2) at mass depth z, C(s) is the unsupported ^{210}Pb activity at the surface (Bq/cm^2), k is the decay constant (0.0311 y^{-1}), and W is the sedimentation rate (g/cm^2/y) (Golden et al., 1993). This model assumes the rate of sedimentation remains the same throughout the entire core, but if there is a clear change in sedimentation rate the segmented CF:CS (SCF:CS) model may be used (Heyvaert et al., 2000). The SCF:CS has the same assumptions as the CF:CS model, but allows for several sedimentation rates that remain constant over a certain length of the core.

The third model, the rapid steady state mixing model (RSSM), is also a modification of the CF:CS method, but accounts for a sediment mixing zone. This model assumes that material added to the sediment surface is mixed completely throughout the mixed zone (S, g/cm^2). Sediment below the mixed zone is assumed to be undisturbed (Robbins, 1982). Similar to the CF:CS model, accumulated dry mass is plotted versus excess ^{210}Pb on a logarithmic scale. The mixed zone appears as a straight vertical line, and the slope below the mixed zone is related to the sedimentation rate through the equation:

$$C(z) = C(m)e^{(-k(z-S)/W)}$$

The final model is the constant rate of supply model (CRS). This model assumes a constant rate of supply of ^{210}Pb to the sediment, but does not assume a constant sedimentation rate. The sediment age (years from present) is determined by:

$$A(x) = A(0)e^{-kt}$$

where A(x) is the inventory of unsupported ^{210}Pb from the depth x to the bottom of the sediment, A(0) is the total inventory of unsupported ^{210}Pb, and t is the age (years from the present). The sedimentation rate is then determined by:

$$W = d / T$$

where d is the dry weight at depth x (g/cm^2), and T is the number of years required to form the section at depth x (Sanchez-Cabeza et al., 2000). Inventories of excess ^{210}Pb cannot be calculated and the CRS model cannot be used if ^{210}Pb activities do not reach supported values in the collected core.

For all models, sediment deeper than the presence of excess ^{210}Pb cannot be dated. Cores from Cadillac, Mullett and Crystal B Lakes all had 16-18 samples below the presence of excess ^{210}Pb. Therefore dates older than this were determined for these lakes by extrapolation, using the assumption that sedimentation rates remain constant below this depth. For the RSSM, CF:CS, and SCF:CS model, the sedimentation rate in the lower portion of the core was used to extrapolate dates. For the CRS model, the average sedimentation rate in the last five samples was used. The sedimentation rate chosen to use for extrapolation has a significant effect on the resulting dates, and all dates older than 1850 should be considered guesses that are reported primarily for graphing purposes.

Sedimentation rates in each lake were determined using all models possible for that lake, and then the models were evaluated to ascertain which was the most appropriate to use in determining sediment ages. There is no consensus as to which model is more appropriate in all cases (Oldfield and Appleby, 1984), and several factors were considered when choosing a model. Visual examination of the ^{210}Pb profile gave some insight into the most appropriate model to be used. The RSSM or CRS models are more appropriate for lakes with large mixing zones, and the SCF:CS or CRS models are more appropriate for lakes with clear changes in sedimentation. Additionally, this study uses two other indicators to determine the most appropriate model to use: profiles of cesium-137 (^{137}Cs) activity and stable lead concentration profiles. ^{137}Cs is an artificial radionuclide that was produced by atmospheric testing of nuclear weapons in the late 1950s and early 1960s. The peak level of fallout occurred in 1963, and therefore the peak activity in the sediment should occur in the early 1960s (Walling and Qingping, 1992). The second indicator is the stable lead peak. Stable lead has an historical pattern of deposition that is very consistent among lakes, with lead concentrations increasing from the mid-1800s to the early to mid-1970s, and decreasing to the present. The peak in lead concentrations in the mid-1970s due to the removal of lead from gasoline is consistent enough to use for dating verification. Therefore the dating method with both the most appropriate date for the ^{137}Cs peak (1963-64) and stable lead peak (early to mid-1970s) was chosen. For many of the lakes, the model chosen influences the dates by less than five years in the 1900s. Analysis of each lake will be described below.

Neither Paw Paw nor Whitmore Lakes reached supported ^{210}Pb activities, and therefore could not be dated with the CRS method. Excess ^{210}Pb was estimated with ^{226}Ra. The CF:CS model was used to date Paw Paw Lake, and the SCF:CS model for Whitmore Lake (Table 1). Mullett Lake was also dated with the SCF:CS model. There was some scatter in the ^{210}Pb activities in the upper portion of the Mullett Lake core (Fig. 2a), however, the SCF:CS model seems to describe the decay appropriately (^{137}Cs peak: 1965, Pb peak: 1973). In all three of these lakes the different models provided relatively similar dates.

Cadillac Lake had a very deep mixing zone, approximately 14 cm, and could not be dated using the CF:CS model (Fig. 2b). The RSSM and CRS models provided very different dates. The RSSM model places the ^{137}Cs peak at 1877 and the Pb peak at 1919. These dates are much older than anticipated, and therefore this model was not used. The CRS model places the lead peak in

1973, indicating that this may be a good dating method. The ^{137}Cs peak occurs in 1940, older then the expected 1963-64. However, the ^{137}Cs profile looks disturbed compared to the profiles from other lakes, indicating the 137Cs peak may not be a good age indicator in this lake. The dates from the CRS model cause the data to be the most consistent with results from other lakes, and therefore this model was chosen.

The dating of Crystal B Lake was also complicated, most likely resulting from the large changes in sediment type throughout the core, with layers of sand present. The lead and ^{137}Cs peaks occur at the same depth, signifying that one of these indicators is not appropriate for this lake. The CF:CS, CRS and RSSM dating models place the peaks in the 1960s, near the appropriate time for the ^{137}Cs peak, but too early for the stable lead peak. The SCF:CS model places the peaks in 1977, more appropriate for the lead peak, but too late for the ^{137}Cs peak. The ^{210}Pb decay profile indicated that the CRS or SCF:CS would be the most appropriate, since there were clear changes in slope, and therefore the CF:CS and the RSSM models were not chosen. Because the stable lead profile is a somewhat different shape then seen in other lakes and may have been disturbed, we chose the CRS model, which places both the ^{137}Cs and stable lead peak in 1966. Dates for Crystal B Lake were extrapolated for sediments older then 1853 in a similar fashion to

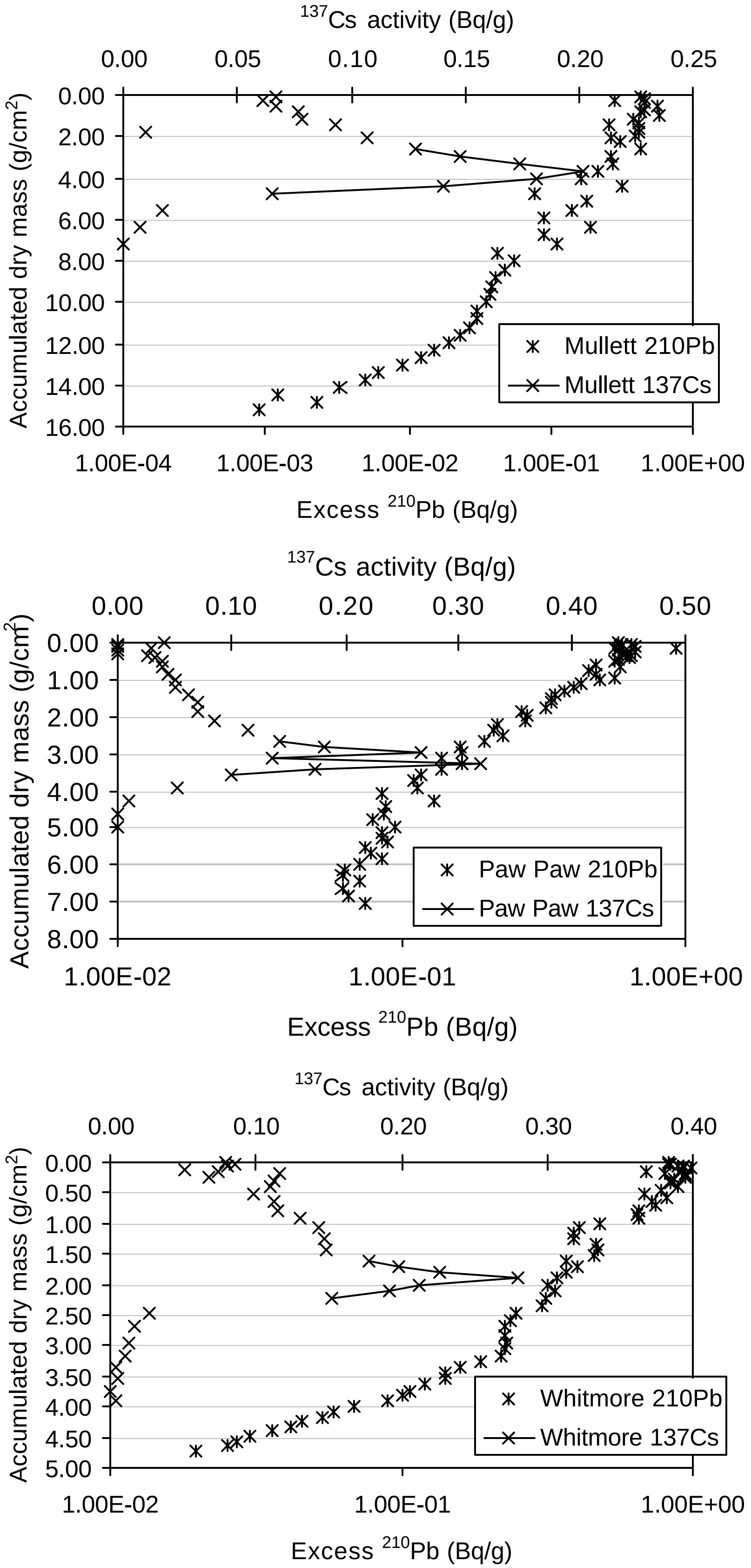


Fig. 2a. ^{137}Cs and ^{210}Pb activities (Bq/g) versus accumulated dry mass in Mullet, Whitmore and Paw Paw Lakes. ^{137}Cs is plotted on the top scale.

Mullett and Cadillac Lakes. However, due to the changes of sediment type in the core, it seems likely that this extrapolation is not valid. The deposition of a sand layer, for example, may be due to a storm event causing a much higher sedimentation rate. Therefore extrapolated dates older then 1853 in this core may have significant error and must be used with caution.

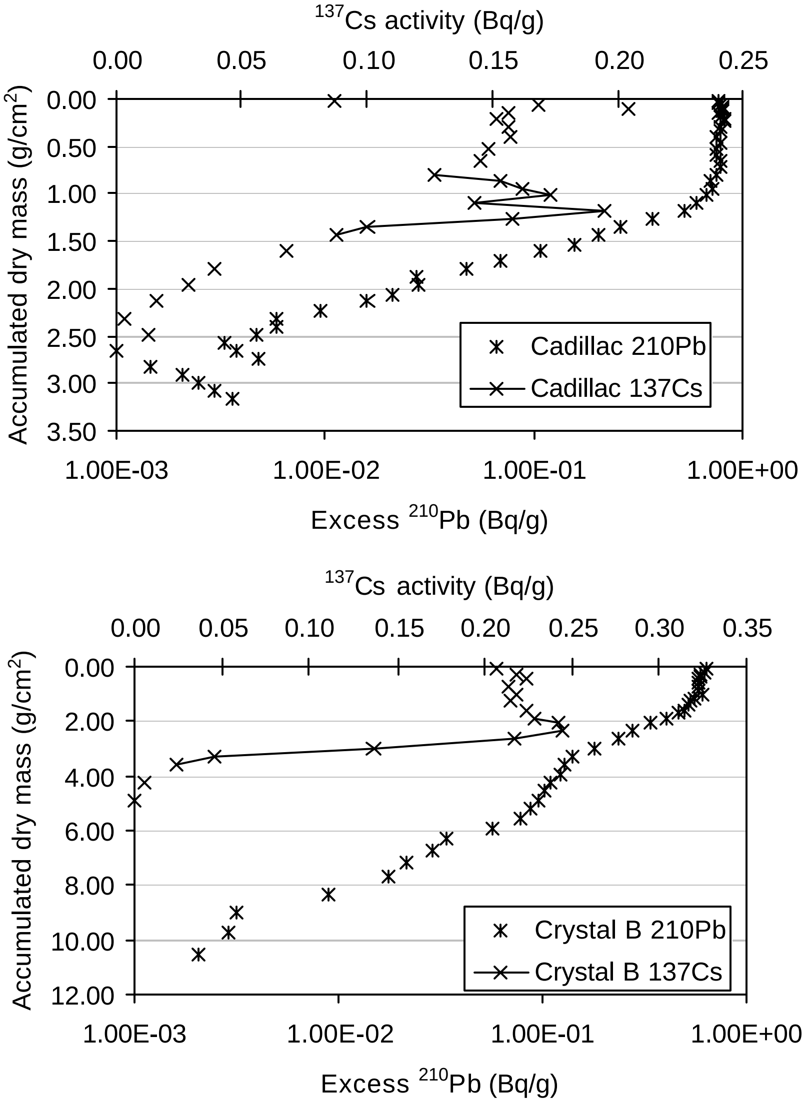


Fig. 2b. ^{137}Cs and ^{210}Pb activities (Bq/g) versus accumulated dry mass in Cadillac and Crystal B Lakes. ^{137}Cs is plotted on the top scale.

Table 1. Selected data determined from ^{210}Pb analysis, including the model used for dating, the age of the stable lead and ^{137}Cs peaks, the mixed depth as defined by the RSSM model, the focusing factor (FF), and the oldest section in the core.

	Model	Stable Pb peak	^{137}Cs peak	Mixed depth (RSSM)	FF	Oldest section
Cadillac	CRS	1973	1940	14 cm	1.71	1829*
Crystal B	CRS	1966	1966	4.3 cm	2.86	1516*
Mullett	SCF:CS	1973	1965	3.6 cm	3.56	1708*
Paw Paw	CF:CS	1974	1963	3.2 cm	2.7**	1923
Whitmore	SCF:CS	1976	1967	6.3 cm	2.8**	1887

* Estimated dates based on extrapolation.

** Estimated focusing factors based on extrapolation.

Focusing Factors

One difficulty in trying to compare data (e.g., accumulation rates, inventories) among lakes is due to differences in within lake processes. One of the most significant processes is sediment focusing, or the tendency of fine-grained sediment to move towards the deepest portion of the lake (Davis and Ford, 1982; Hilton et al., 1986). In order to be able to represent one lake with one core, it is necessary to be able to account for this focusing. Because the rate of ^{210}Pb input is known (Kada and Heit, 1992), and therefore the expected inventory can be calculated, the actual inventory divided by the expected inventory can be calculated (focusing factor [FF]) (Golden et al., 1993), and used to correct for focusing.

$$\mathrm{FF} = \frac{\text{actual } {}^{210}\text{Pb inventory}}{\text{theoretical } {}^{210}\text{Pb inventory}}$$

Kada and Heit (1992) used this method when examining atmospheric inputs to eight remote Adirondack lakes. The inventories of six anthropogenic metals varied among lakes, despite the fact that the only source was atmospheric, and should have remained relatively constant over the region. However, after correction with ^{210}Pb, the inventories were very similar among lakes. This implies that it is appropriate to use the focusing factor to account for sediment movement when comparing data among lakes.

Focusing factors were calculated for each of the study lakes in Michigan, and ranged from 1.7 to 3.6 (Table 1). The focusing factors for Whitmore and Paw Paw Lakes were estimated using extrapolation to calculate the inventory of excess ^{210}Pb, since supported ^{210}Pb levels were not reached. Extrapolation was performed by assuming that the dry weight per sample and rate of ^{210}Pb decay remain constant. Because ^{210}Pb values in the deepest section are close to supported activities in both cores, focusing factors calculated without extrapolation differ little from focusing factors calculated with extrapolation, indicating that the focusing factors calculated with extrapolation are reasonable estimations of the true values.

Organics

Concentrations of organic contaminants are generally highest in Cadillac Lake, and low in Mullett and Paw Paw Lakes (Table 2). All lakes have low concentrations of polychlorinated biphenyls (<1 ng/g), but most lakes contain polyaromatic hydrocarbons (PAHs) and pesticides.

The five lakes sampled are similar in concentration to those analyzed in previous years (Fig 3). Concentrations of total PAHs in Cadillac Lake are higher then all lakes except Cass Lake. Concentrations in Crystal B and Whitmore Lakes are similar to other lakes sampled in the lower peninsula, while Mullett and Paw Paw Lakes are most similar to Gratiot Lake.

Table 2. Concentrations (ng/g dry wt) of various organic compound for five Michigan lakes.

	Cadillac 1	Cadillac 2	Crystal B 1	Crystal B 2	Mullett 1	Mullett 2	Pawpaw 1	Pawpaw 2	Whitmore 1	Whitmore 2
cm depth[1]	0-2	2-4	0-2	2-4	0-2	2-4	0-2	2-4	0-2	2-4
Age[2]	2001	1998	1999	1993	1999	1994	2001	2000	2001	1999
Total polychlorinated biphenyls (PCBs)	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Total polyaromatic hydrocarbons (PAHs)	6580.7	7512.0	201.2	214.5	<10	5.3	<10	<10	489.3	520.4
Naphthalene	54.8	166.7	<10	<10	<10	<10	<10	<10	<10	<10
Acenaphthylene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Acenaphthene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Fluorene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Phenanthrene	509.6	689.3	<10	<10	<10	<10	<10	<10	<10	43.1
Anthracene	106.7	117.3	20.9	14.8	<10	<10	<10	<10	<10	<10
Fluoranthene	1708.1	1790.7	93.2	92.0	<10	<10	<10	<10	144.0	144.0
Pyrene	1266.7	1381.3	32.0	41.8	<10	<10	<10	<10	108.0	109.0
Benzo[a]anthracene	305.2	438.7	<10	<10	<10	<10	<10	<10	0.0	23.0
Chrysene	731.9	696.0	16.0	17.0	<10	5.3	<10	<10	98.7	66.4
Benzo[b]fluoranthene	851.9	1026.7	39.1	49.0	<10	<10	<10	<10	98.7	102.0
Benzo[k]fluoranthene	380.7	428.0	<10	<10	<10	<10	<10	<10	40.0	32.9
Benzo[a]pyrene	665.2	777.3	<10	<10	<10	<10	<10	<10	<10	<10
Indeno[123cd]pyrene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Dibenzo(a,h)anthracene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Benzo[ghi]perylene	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Total Pesticides	29.0	32.0	1.3	1.2	4.9	10.3	31.9	57.6	<10	<10
Hexachlorobenzene (HCB)	3.6	2.0	1.3	1.2	1.0	0.4	2.2	2.3	<10	<10
DDTs (p,p' DDE)	25.5	30.0	<10	<10	3.9	9.9	29.7	55.3	<10	<10

1. The first two slices were combined (cm 0-2), and the third and fourth slices (2-4 cm), due to insufficient sample mass for analysis.
2. Since samples were combined[1] each analysis covers a range of years. The median age is presented for each of the combined samples.

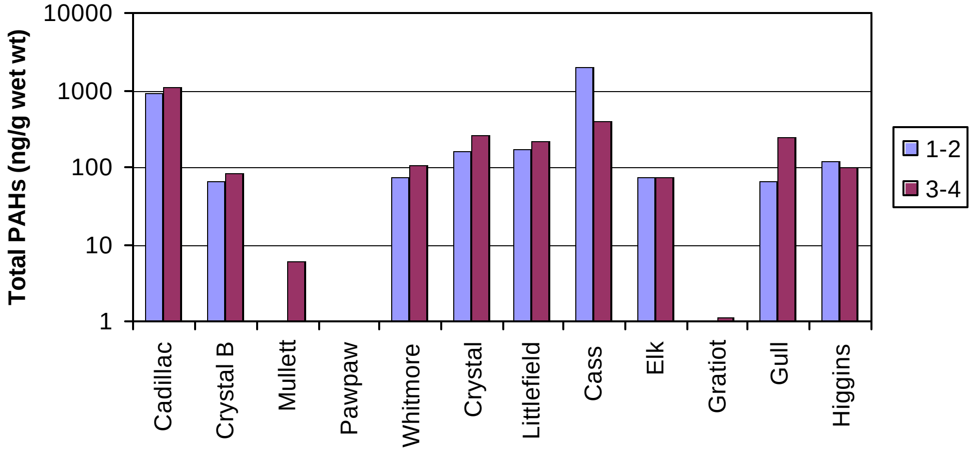


Fig. 3. Concentrations (ng/g wet wt) of total PAHs from the sediments for samples 1-2 (0-2 cm), and samples 3-4 (2-4 cm) for twelve Michigan Lakes. Concentrations are plotted on a log scale.

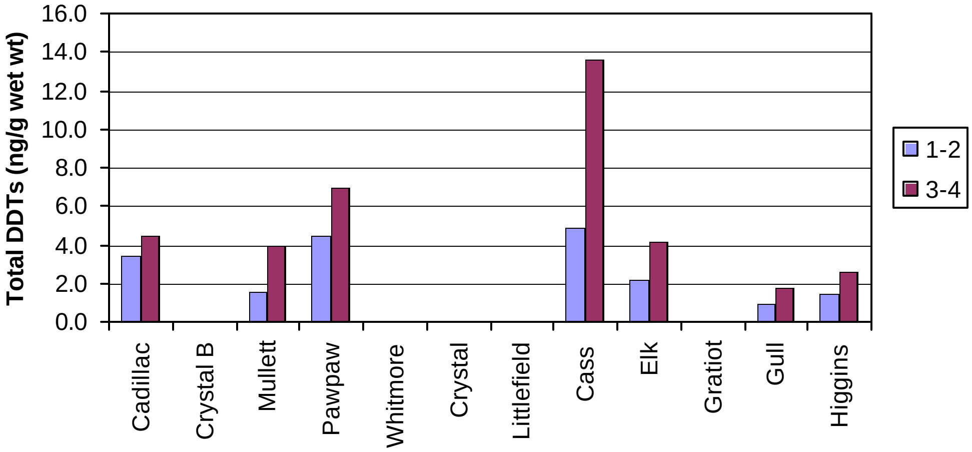


Fig. 4. Concentrations (ng/g wet wt) of total DDTs from the sediments for samples 1-2 (0-2 cm) and samples 3-4 (2-4 cm) for twelve Michigan Lakes.

Total DDTs remain highest in Cass Lake, with Paw Paw, Cadillac, Elk and Mullett Lakes having lower values (Fig. 4). The remainder of the lakes have little or no DDTs present. The concentration of DDTs will be influenced both by the current inputs of DDTs to the lake and by historic inputs. Historically, DDTs were used extensively, but use has decreased significantly over the last three decades. Samples from different lakes are from different ages, dependant on the sedimentation rate. Therefore, Elk Lake, with a low sedimentation rate, represents older sediments, and might be expected to have higher concentrations of DDTs (Simpson et al., 2000). Additionally, the large mixing zone present in Cadillac Lake may cause higher concentrations of DDTs near the surface. All lakes have lower values of DDTs at the surface than in the sample below the surface, indicating that inputs of DDTs to these lakes are declining, as would be expected from the ban of DDT in the United States.

Inorganic chemical sediment chronologies

Many different sources and processes influence the patterns of metal deposition in a sediment core, making it a challenge to interpret the historical records. The multi-element approach, which includes the analysis of more elements than just those of anthropogenic concern, helps provide insight into the history of the lake, and assists in the interpretation of anthropogenic inputs. The first step to understanding multi-element data is grouping the elements that are influenced by similar sources and processes. This reduces the number of elements that must be examined. In order to do this, elements that have similar profiles in the sediment were grouped for each lake. If possible, each group was then placed into a class that represents certain sources and/or processes. Four classes of elements were examined: terrestrial, calcium carbonate, diagenetic, and anthropogenic. The method used to group elements is described below. Then, each of the four classes are examined individually, including a description of the sources / processes influencing that class and the results of the grouping analyses. Finally, the anthropogenic elements are described in depth.

All statistics were performed using SYSTAT 10 (SPSS, 2000). Boxplots were used to identify outliers in the data, and results were analyzed both with and without outliers. Data points were considered to be outliers if they were outside the outer fence as determined by boxplot analysis. The outer fence is defined as:

$$\text{hinge} \pm (3 \times \text{hspread})$$

where the hinge is the first or third quartile, and the hspread is the distance between the hinges (SPSS, 2000).

Elements were grouped by both principal components analysis (Varimax rotation), and factor analysis (iterated principal axis, Varimax rotation). The number of factors chosen was based on Scree plots, percent variance explained by the factor, and ability to interpret the factors (Hair, 1998). Elements were also grouped by hierarchical cluster analysis on both standardized and ranked data. Three distance measures were investigated: Ward’s, average, and single linkage. Clusters were chosen based on the examination of standardized profiles. Cluster analysis was determined to be the most appropriate method for grouping elements, therefore only the results of the cluster analysis will be reported. The three distance measures used, Ward’s, average, and single linkage (Hair, 1998) provided very similar results, therefore only results using Ward’s distance measure will be reported. Similarly, results did not vary if standardized or ranked data were used, therefore results using standardized data will be reported. Table 3 shows how each element is classified for all of the lakes. Elements that did not clearly fit into a group were not classified. The results for each class are described below.

Table 3. Classification of elements into terrestrial (T), carbonate (C), diagenetic (D, D1,D2),and anthropogenic (A, A1, A2). Use of A2 indicates there was more than one group of anthropogenic elements in the lake. Use of D1, D2 notation indicates that there was more then one groups of diagenetic elements in the lake. Unclassified elements did not fit clearly into a group, and elements classified twice appear to be influenced by both classes. A (–) indicates that data were not collected for this element. Lakes include Gratiot (Grat), Elk, Gull, Higgins (Hig), Littlefield (Lit), Crystal M (CrM), Cadillac (Cad), Crystal B (CrB), Mullett (Mul), Paw Paw (Paw), and Whitmore (Whit). OR indicates that outliers were removed.

	Grat	Elk	Elk OR	Gull	Hig	Hig OR	Lit	CrM	Cad	CrB	Mul	Mul OR	Paw	Whit
Ti	T	T	T	T			T		T		T	T	T	T
V	T	T	T	T				T	T	T	T	T	T	T
Cr								T		T	T	T	A	T
Cu	A	A	A	A	A	A	T		A	A	A	A	A	A2
As	A	D	A	A,D2	D1	D	D1	D1	D		D		D2	
Mo		D		D2	D1	D	D1	D2					D2	D
Cd	A	A	A		A	A	A	A	A	A	A	A	A	A1
Pb	A	A	A	A	A	A	A	A	A	A	A	A	A	A1
Al	T	T	T	T	T	T	T	T	T	T	T	T	T	T
Zn	A	A	A	A	A	A		A	A	A	A	A	A	A1
Sr	T	--	--	--	C	C	C	C	C	C	C	C	C	C
Mg	T	T	T	C	T	T	C, T				T	T		
K	D	T	T	T	T	T	T	T		T	--	--	--	--
Mn	D	D		D1	D2		D2	D1	D		D	D		
Ba	D	D	T	C	D2		D2		C	C	D	D		T
Ca	T	C	C	C	C	C	C	C	C	C	C	C	C	C
Fe	A	D	T	D1			D1		D	T	D	D		
U	T	T	T	D2	D1	D	D1	D2	T					D

Terrestrial elements

The first class includes the terrestrial elements, which are those that are influenced by the amount of allocthonous (material from outside the lake) non-organic material entering the lake. Changes in the input of terrestrial materials may be caused by increased erosion by natural (e.g., forest fires) or human processes (e.g., land use changes) (Davis, 1976). Elements that may be primarily influenced by these processes include aluminum, titanium and sometimes iron, potassium, cobalt, nickel, magnesium, sodium, scandium, and the rare earth elements (Boyle et al., 1999; Bruland et al., 1974; Johnson and Nicholls, 1988; Kemp and Thomas, 1976; Kerfoot and Robbins, 1999; Qu et al., 2001; Sanei et al., 2001).

Aluminum is consistently influenced by terrestrial processes for all lakes, and vanadium, titanium, and potassium are often influenced by terrestrial processes (Table 3). Terrestrial processes sometimes influence magnesium, uranium, iron and chromium. Patterns of terrestrial deposition are represented by aluminum, as shown in Figure 5a and 5b. Overall, sediments in Paw Paw Lake have the highest concentration of aluminum, and sediments in Crystal B and Mullett Lakes have the lowest concentrations.

Crystal B Lake has large changes in aluminum concentrations in the sediment, with lower values in the mid-1700s. This is due to a change in the sediment material from dominantly clay to sand. The surfaces of clays are reactive, and tend to have metals associated with them. Sands are less reactive, and therefore this sand layer is depleted in all elements, including aluminum. Generally sand is not present in the deepest portion of a lake because sand grains are larger and heavier then clay, and will settle out of the water column near the shoreline. However, Crystal B Lake is deep and relatively narrow, allowing sand from the shoreline to be transported to the sampling location.

None of the five lakes show patterns similar to Elk and Gull Lakes, with large increase in terrestrial elements in the 1800s due to the logging of lower Michigan (Simpson et al., 2000). Mullett Lake does show an increase in terrestrial elements in the 1900s, and a minor increase from 1965-1975. Terrestrial elements in Whitmore and Cadillac Lakes follow a very similar pattern after 1950, with higher concentrations in the late 1960s and mid-1990s. The causes for the patterns of aluminum deposition in these lakes is unclear, but could be related to land use in the watershed. Additionally, an increase in the amount of organic material or calcium carbonate that is deposited would dilute the concentration of terrestrial elements. Therefore the decrease near the surface of Paw Paw Lake could indicate that there is less erosion occurring around the lake, and less terrestrial material is being brought into the lake, or it could mean that there is a higher production of organic material recently.

Fig. 5a.

Fig 5b. Aluminum current

Calcium carbonate

The second class includes calcium and strontium, which may be influenced by deposition of calcium carbonate. Soils, glacial material, and bedrock in most of the Great Lakes contain abundant limestone ($CaCO_3$). Thus, lakes become enriched in dissolved Ca and HCO_3 that can precipitate in the lake as a consequence of evaporation or photosynthesis (photosynthesis consumes CO_2, which raises the pH of the water). This portion of the sediment tends to have low concentrations of most metals and therefore acts as a diluting phase (Auer et al., 1996). The presence of carbonates may increase the concentration of calcium and strontium, and sometimes magnesium and barium (Auer et al., 1996; Sanei et al., 2001).

In the twelve lakes sampled, calcium consistently follows a pattern unique from the terrestrial elements in all lakes except Gratiot Lake (Table 3). Strontium typically follows the same pattern as calcium, and magnesium and barium sometimes have a similar pattern to calcium as well. Mullet and Crystal B Lakes have the highest concentrations of calcium. Calcium in Crystal B Lake follows a similar overall pattern to aluminum, with low concentrations in the 1700s, and the highest concentrations near the surface (Fig. 6 a,b). Patterns of calcium in Mullett Lake follow the opposite pattern as aluminum, decreasing from the 1800s towards the 1900s, and then increasing again towards the present. The highest concentrations of calcium in Paw Paw Lake sediment occurred in the 1970s, while calcium in Whitmore Lake increases to the present. Concentrations of calcium remain relatively constant in Cadillac Lake.

Diagenesis

A third class includes those elements influenced by diagenesis. Early diagenesis is the alteration of sediment after deposition, and will obscure the depositional record. In the top few centimeters of sediment, there are major geochemical changes that occur. Organic matter is decomposed, which uses the oxygen in the sediment, and changes the sediment from an oxidizing to a reducing environment. This will change the mobility of many metals, and metals may mobilize from the sediment into the porewater (remobilization). For example, those metals that are associated with organic matter in the sediment can be released to the porewater as decomposition progresses. Those metals associated with iron and manganese oxyhydroxides would be released to the porewater when these oxyhydroxides dissolve because of the reducing conditions. Once in the porewater, metals may move from areas of high concentration to lower concentrations through diffusive flux and/or be readsorbed to other sediments phases (Brown et al., 2000; Cooper and Morse, 1998; Douglas and Adeney, 2000; Harrington et al., 1998; McKee et al., 1989; Urban et al., 1990). In particular, arsenic is strongly adsorbed to iron oxyhydroxides, and profiles in the sediment may not reflect the historical record of arsenic deposition. For arsenic, which is influenced by both diagenesis and anthropogenic inputs, it is essential to be able to differentiate patterns caused by diagenesis from those caused by changes in anthropogenic inputs (Harrington et al., 1998). Another complication is that elements respond to changing redox conditions in different manners. While iron oxyhydroxides mobilize in reducing conditions, uranium and molybdenum remobilize in oxidizing environments (Brown et al., 2000). Therefore, it may be possible to have more than one group of diagenetic elements.

Fig 6.a.

Fig 6b.

Arsenic, molybdenum, uranium, iron, manganese and barium are all influenced by diagenesis in the lakes studied, however, it is beyond the scope of this report to examine each of them closely. We will focus on arsenic, because humans have altered the global cycle of arsenic, and it is important to be able to differentiate which patterns of arsenic deposition represent a history of anthropogenic inputs, and which represent diagenetic processes. Additionally, porewater data can provide some insight into the behavior of arsenic.

The geochemical properties of arsenic make its behavior in the environment complex. First, arsenic can strongly adsorb to iron and manganese oxyhydroxides. Iron and manganese oxyhydroxides form and remain stable in oxidizing conditions, but will dissolve under reducing conditions. A cycle can be created where oxidized sediments are deposited on the surface of the sediment, and are slowly buried into a more reduced zone. As the sediments are reduced, the iron and manganese oxyhydroxides dissolve, releasing iron, manganese, and the arsenic associated with these particles into the porewater. Because these elements are not present, or are present in very low concentrations in the porewater of the oxidized zone, iron, manganese and arsenic in the porewater will tend to diffuse upwards towards the oxidized zone. As they reach the oxidized zone, iron and manganese oxyhydroxides again precipitate, scavenging the arsenic out of the porewater. This cycle can cause a layer enriched in iron, manganese and arsenic at the oxic/anoxic boundary. This process is seen in Mullett and Cadillac Lakes, with higher concentrations of arsenic, iron and manganese present near the surface, relative to those of deeper sediments (Fig. 7a,b). Both these lakes have lower concentrations of iron in porewater near the surface, indicating an oxidized environment. Additionally, concentrations of iron in the porewater increase with depth in Mullett Lake, indicating a reducing environment (Appendix A). However, the arsenic peak that occurs in Cadillac Lake in the late 1920s is not seen in iron or manganese, and could be related to anthropogenic inputs. However, it is clear that the arsenic profiles in both of these lakes have been altered by diagenesis, and must be interpreted with care.

While arsenic is often influenced by the geochemical properties of iron and manganese, arsenic is also influenced directly by the reduction / oxidation (redox) state of the sediment. Arsenic may be reduced in anoxic sediments, and, if sulfur is present, may precipitate as a sulfide in reducing conditions. This is the opposite behavior as iron, which precipitates in oxidizing conditions, but is similar to the behavior of uranium and molybdenum (Drever, 1997). Therefore arsenic may be expected to behave in a similar fashion to iron or manganese because it adsorbs to oxyhydroxides, or in a similar fashion to uranium or molybdenum because it has similar redox properties to these elements. In Paw Paw Lake, patterns of arsenic in the sediment are similar to molybdenum, implying that diagenetic processes as well as human inputs are important in determining the pattern of arsenic deposition in this lake. Trends of arsenic and molybdenum also mirror each other in the porewater, giving further credence to this interpretation (Appendix A).

The arsenic profile in Paw Paw Lake is somewhat unusual due to the relatively large changes in concentration over short periods of time. One possibility for this profile can be related to the fact that the area around Paw Paw Lake is heavily agriculture and has been for some time. Arsenic has been used as a pesticide, and it is possible that these changes are related to the application of pesticides in the watershed. More work would have to be done to verify this, but the relatively higher concentrations of arsenic in the lake may indicate this. Arsenic mobility is strongly tied into the oxidation-reduction (redox) state of the environment. If the environment (sediments in the case) go through changes in the redox state then this would alter arsenic concentrations in the sediments. With changing nutrient inputs from agricultural practices, microbial processes most likely change thus causing changes in redox conditions and arsenic mobility.

Thus, the vertical concentration pattern of arsenic in Paw Paw Lake is most likely related to changes in arsenic input to the lake and changes in the biogeochemical conditions in the sediments. Without a detailed analysis (e.g., human perturbations, climate change in the watershed), sorting out the relative importance of these processes is difficult.

On the contrary, patterns of arsenic in the sediment in Whitmore Lake are dissimilar to iron and molybdenum, but similar to typical patterns of human inputs. Concentrations of arsenic increase to the 1970s, and decrease to the present. It is possible that the sediment record in Whitmore Lake is a preserved record of human inputs of arsenic, however, caution must always be used when interpreting arsenic. Patterns of arsenic deposition in Crystal B Lake are not clearly influenced by any one factor, but are most similar to molybdenum.

Fig 7a

Fig 7b.

Anthropogenic Inputs

The final class is the anthropogenic elements. These elements have accumulated in lake sediments due to human actions, and may enter lakes from atmospheric deposition, or from inputs within the watershed. Humans may influence any element, but the geochemical cycles of arsenic, cadmium, copper, chromium, mercury, lead, and zinc have been modified by humans on the global scale (Bruland et al., 1974; Evans and Dillon, 1982; Iskander and Keeney, 1974; Spiethoff and Hemond, 1996). Since the sources of each metal may be different (e.g., copper from copper smelting emissions, or lead from leaded gasoline), anthropogenic elements may follow similar trends or the trends may vary among elements, depending on the dominant sources and processes. Therefore, while elements in the terrestrial class should have very similar profiles, profiles of anthropogenic elements may vary. The profiles of the anthropogenically-influenced elements listed above were examined closely and compared to profiles of terrestrial elements to determine for each lake if deposition of that element was influenced by human activities.

Lead is influenced by human actions in all lakes, while cadmium, copper and zinc are influenced in almost all lakes. Chromium, arsenic, and iron are occasionally dominated by human inputs (Table 3). Additionally, nickel appears to have human sources in Paw Paw Lake. Nickel is not included in the clustering analysis because in many lakes concentrations of nickel are too low to quantify. However, when nickel is added to the Paw Paw Lake dataset, it clusters with lead, chromium, and zinc, indicating that it has anthropogenic sources. It is likely that the signature of the extensive steel industry is being recorded in Paw Paw Lake, which is the closest lake to Gary, IN, and Chicago, IL. Gull Lake, also in the southwest corner of Michigan, shows a similar human influence on chromium inputs. Concentrations of nickel, however, are below quantifiable levels due to the high levels of calcium carbonate in the lake.

There are many ways to evaluate the effects that humans have had on lake sediments, including concentrations and accumulation rates. These contaminants may have toxicological implications for the aquatic life, especially if high concentrations are present in surface sediments. Concentrations reflect both the amount of contaminant entering the lake (from natural and anthropogenic sources) and the amount of total sediment being deposited. High rates of deposition of calcium carbonate or organic carbon will dilute the concentration of the contaminant. Therefore, concentration profiles are most appropriate for evaluating exposure to biota, but accumulation rates are more appropriate to compare rates of contaminant input among lakes. We will first present total concentrations of cadmium, lead, copper and zinc in the sediments, and then discuss the calculation of anthropogenic inputs and compare anthropogenic accumulation rates among lakes. Finally, additional data such as inventories and spatial patterns will be presented.

Concentrations

Overall, sediments from Cadillac and Whitmore Lakes tend to have the highest concentrations of cadmium, copper, lead and zinc. Paw Paw Lake sediments also tend to have high concentrations of these elements compared to Crystal B and Mullett Lakes (Figs 8-15).

8a. Cd 5 lakes

8b Cd 5 lakes current

9. Cd all lakes

10a. Cu 5 lakes

10b. Cu closer scale

10c. Cu 5 lakes current

11. Cu all lakes

12a Pb 5 lakes

12b Pb 5 lakes current

13 Pb all lakes

14a Zn 5 lakes

14b. Zn 5 lakes current

15. Zn all lakes

Cadmium concentrations increased from background levels beginning around 1900 in Crystal B, Cadillac, Mullet, and Whitmore Lakes (Fig. 8 a,b). All lakes had higher values in the 1960s and 70s, with concentrations generally decreasing towards the present. When comparing all lakes sampled, cadmium concentrations in the 1900s are highest in Cadillac and Whitmore Lakes, followed by Higgins Lake (Fig. 9). Crystal B and Paw Paw Lakes have intermediate concentrations, similar to Littlefield, Crystal M, and Gratiot Lakes. Mullett Lake has relatively low concentrations of cadmium in the 1900s compared to the other lakes, with concentrations similar to Elk and Gull Lakes.

The effect of adding copper sulfate to Cadillac Lake is evident in the sediment core, with peak values of copper near 500 mg/kg in Cadillac Lake, almost tenfold higher than the next highest lakes, Paw Paw and Whitmore (Fig. 10 a,b,c). Concentrations of copper are decreasing in Cadillac Lake sediment since the early 1990s, but remain very high. Cadillac Lake has a very deep mixing zone, which will tend to increase the amount of time it will take for concentrations to decrease after the cessation of copper sulfate addition. Sediments from Paw Paw, Whitmore and Mullet Lakes increase in copper concentration in the mid-1940s. While concentrations of copper in Mullet Lake have clearly decreased to the present, concentrations of copper in Paw Paw and Whitmore Lakes do not show a decreasing trend. Copper concentrations in the sediment of Crystal B Lake increase over time from the mid-1700s to the present. Overall, Gratiot Lake has the highest copper concentrations after Cadillac Lake, due to its location in the copper rich Keweenaw peninsula (Fig. 11). Paw Paw and Whitmore Lakes have copper concentrations much higher then all lakes beside Gratiot and Cadillac. Elk Lake has the lowest copper sediment concentrations.

Lead shows a consistent pattern of increasing concentrations from the mid-1800s to the 1970s, with concentrations decreasing to the present (Fig.12 a,b). The reduction of lead from the 1970s to the present has been seen in lakes throughout North America, and is attributed to the removal of lead from gasoline (Eisenreich et al., 1986; Evans et al., 1986). Sediments in Whitmore and Cadillac Lakes have the highest lead concentrations of all the lakes in the 1900s. Sediments in Mullett and Crystal B Lakes have low concentrations, similar to Elk and Gratiot Lakes (Fig. 13). Paw Paw Lake has moderately high sediment concentrations, similar to Gull Lake.

Concentrations of zinc generally increase from the mid 1800s to the 1960s and 70s, and decrease to the present (Fig. 14 a,b). Zinc concentrations in the sediments of Crystal B Lake do not follow this pattern, but rather increase gradually to the surface. Cadillac and Whitmore Lakes have the highest sediment concentrations of zinc in the 1900s compared to all lakes (Fig. 15). Sediments in Paw Paw Lake also have relatively high concentrations.

While high concentrations of some contaminants may exist in sediments deposited in the 1960s and 70s, the concentrations in the surface sediments are of more concern. We have averaged the top three samples, 1.5 cm, to represent the surface samples. Three samples were averaged to reduce the possible effects of one anomalous sample. These concentrations were compared among lakes, and compared to sediment quality guidelines (MacDonald et al., 2000). MacDonald et al. define a threshold effect concentration (TEC) and a probable effect concentration (PEC). The TEC is the concentration below which harmful effects are unlikely to be observed, while the PEC is the concentration above which harmful effects are likely to be observed.

Arsenic concentrations are highest in surface sediments of Cass and Elk Lakes, followed by Paw Paw, Whitmore and Cadillac Lakes (Table 4, Fig. 16a). These lakes, as well as Littlefield and Higgins Lakes, have surface sediment concentrations greater than the TEC, but no lakes have concentrations that exceed the PEC. Crystal B and Mullet Lakes have the lowest surface concentrations of arsenic.

Cadillac and Whitmore Lakes have the highest surface sediment concentrations of cadmium, followed by Higgins and Crystal B Lakes (Table 4, Fig 16a). All four of these lakes exceed the TEC, the concentration below which adverse effects are unlikely to occur, but do not exceed the PEC. Gull, Elk and Cass Lakes have the lowest values.

Lead surface sediment concentrations follow a similar pattern to cadmium, with Cadillac and Whitmore Lakes having the highest sediment concentrations, followed by Higgins Lake. Gull, Mullett and Elk Lakes have the lowest concentrations (Table 4, Fig. 16a). Eight of the thirteen lakes exceed the TEC (Cass, Gratiot, Higgins, Crystal M, Cadillac, Crystal B, Paw Paw and Whitmore Lakes), and Cadillac and Whitmore Lakes also exceed the PEC. At concentration levels greater then the PEC there are likely to be harmful effects on sediment-dwelling

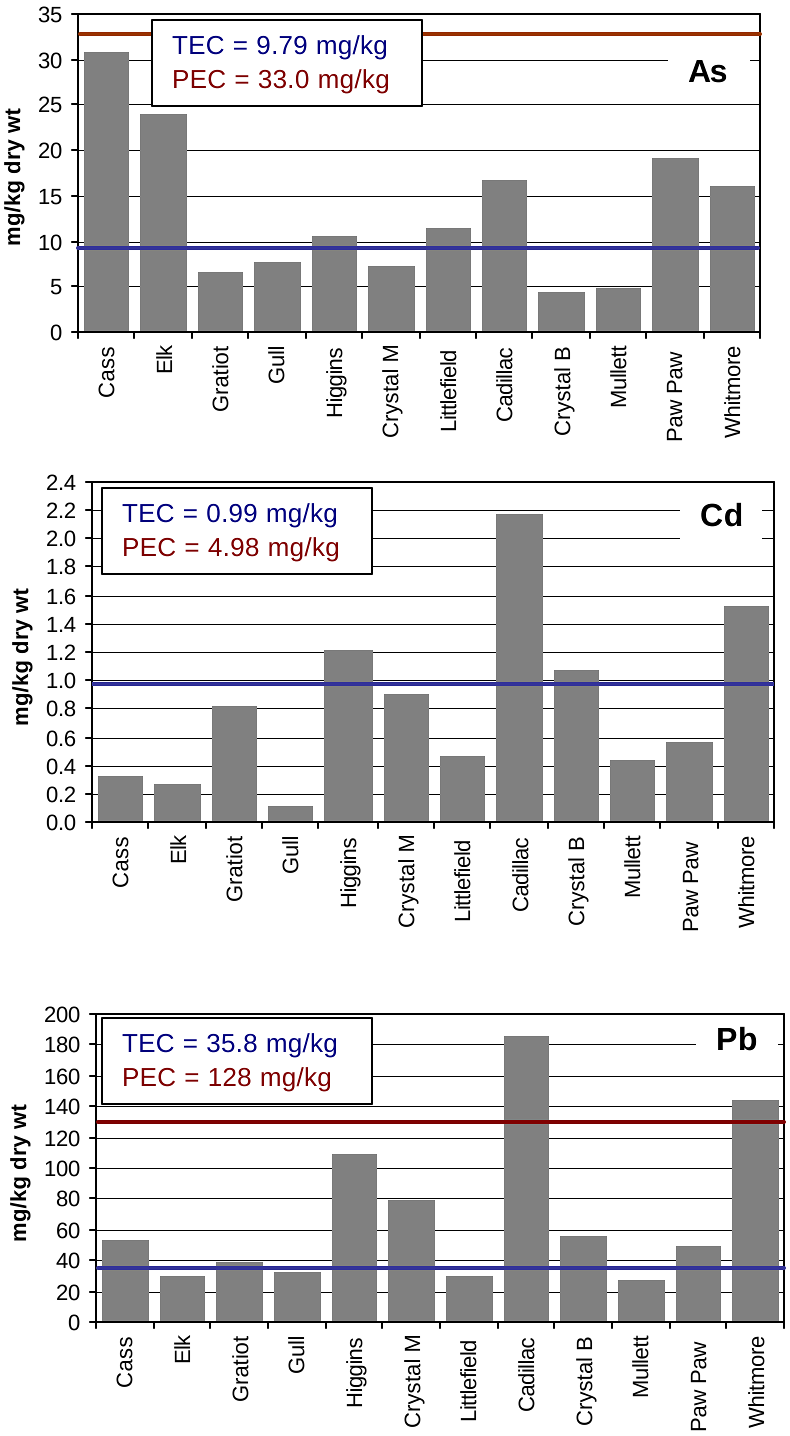


Fig. 16a. Surface (1.5 cm) concentrations (mg/kg dry wt) for arsenic (As), cadmium (Cd), and lead (Pb) in twelve Michigan lakes. The lower blue line indicates the TEC, the upper red line indicates the PEC. The PEC is not shown for cadmium.

organisms (MacDonald et al., 2000).

Although copper sulfate is no longer being added to Cadillac Lake, surface sediment concentrations are still highly elevated, and are 3.6 times the PEC (Table 4, Fig. 16b). Gratiot, Paw Paw and Whitmore Lakes have high copper concentrations compared to all lakes besides Cadillac. These lakes exceed the TEC for copper, but remain well below the PEC. Elk Lake has the lowest copper surface concentrations.

Cadillac, Whitmore and Paw Paw Lakes have the highest zinc surface sediment concentrations (Table 4, Fig. 16b). These three lakes, as well as Higgins Lake, exceed the TEC. No lakes exceed the PEC for zinc. Elk, Gull and Littlefield Lakes have the lowest zinc surface concentrations.

Overall, Cadillac, Whitmore and Paw Paw Lakes tend to have the highest surface sediment concentrations of contaminants, followed by Higgins Lake. Cadillac and Whitmore Lake sediments exceed TEC values in all elements, and PEC values for lead (Table 4). Cadillac Lake sediments also exceed the PEC values for lead. Paw Paw and Higgins Lake sediments exceed TEC values in all elements but one (cadmium and copper respectively). Mullett Lake and Gull sediments are the only to not exceed TEC values in any element, but Elk and Crystal B Lake sediments have low concentrations in many of the metals.

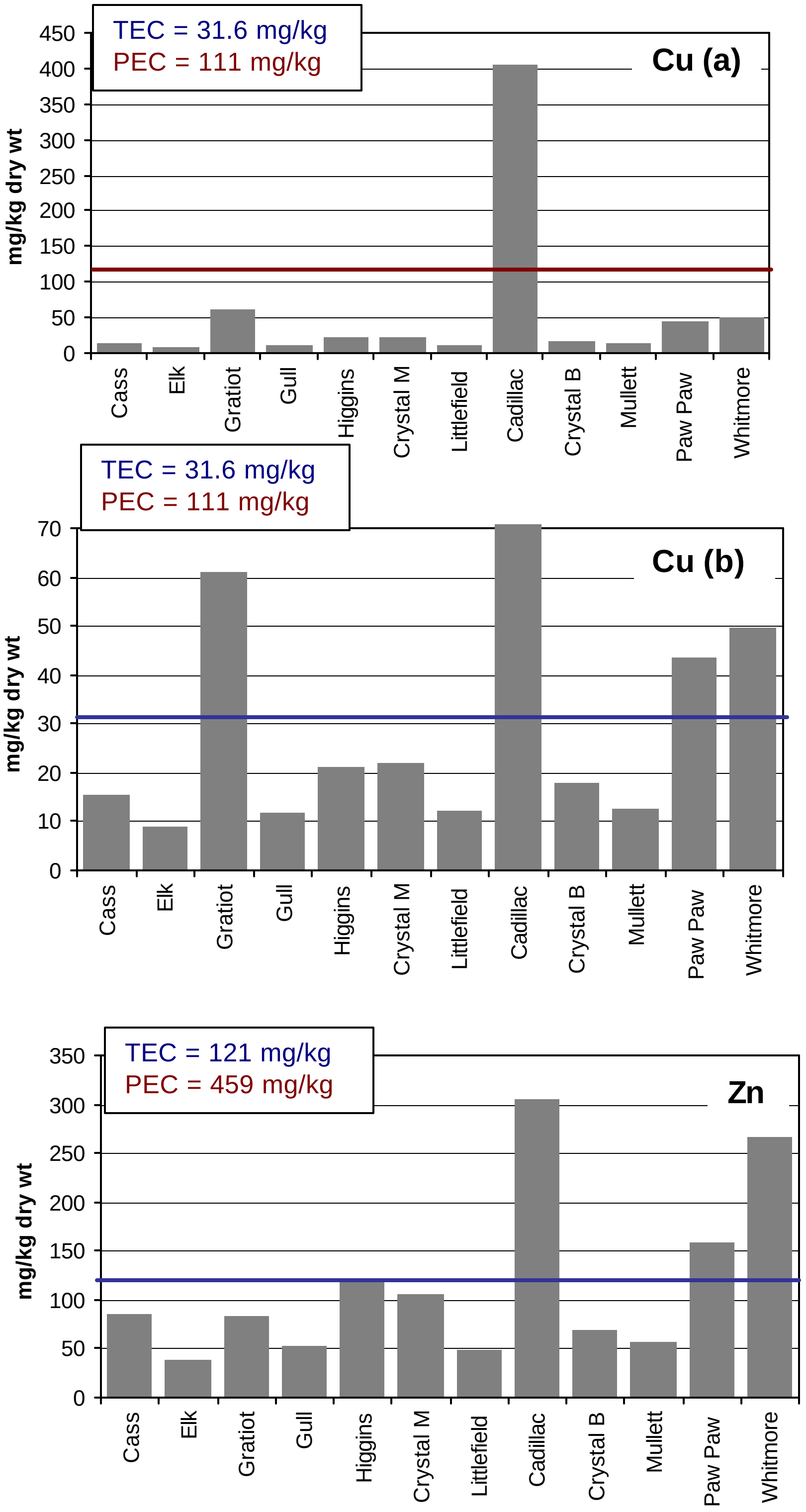


Fig. 16b. Surface (1.5 cm) concentrations (mg/kg dry wt) for copper (Cu a,b), and zinc (Zn) in twelve Michigan lakes. Copper is graphed at two different scales. The lower blue line indicates the TEC, the upper red line indicates the PEC. The PEC is not shown for Cd (b) or Zn, the TEC is not shown for Cu (a).

Table 4. Surface (1.5 cm) concentrations (mg/kg) of five elements for thirteen lakes in Michigan, threshold effect concentrations (TEC) and probable effect concentrations (PEC) (MacDonald et al., 2000). Italics indicates values greater than TEC, bold indicates concentrations greater than PEC.

mg/kg	As	Cd	Cu	Pb	Zn
Cass	*30.76*	0.32	15.35	*53.73*	85.39
Elk	*23.94*	0.27	8.77	29.92	38.41
Gratiot	6.64	0.82	*60.95*	*39.53*	82.44
Gull	7.64	0.12	11.63	32.42	52.37
Higgins	*10.48*	*1.21*	21.05	*109.14*	*122.12*
Crystal M	7.32	0.90	21.94	*78.88*	106.48
Littlefield	*11.51*	0.47	12.16	30.14	49.02
Cadillac	*16.81*	*2.17*	**404.16**	**185.36**	*265.71*
Crystal B	4.36	*1.07*	18.04	*56.09*	106.72
Mullett	4.87	0.44	12.72	26.64	57.85
Paw Paw	*19.16*	0.57	*43.75*	*49.74*	*151.77*
Whitmore	*16.07*	*1.53*	*49.65*	**143.90**	*229.00*
TEC	9.79	0.99	31.6	35.8	121
PEC	33.0	4.98	111	128	459

Anthropogenic accumulation rates

The total concentration data described above have important implications on bottom-dwelling organisms, however, they do not provide insight into how much of the element is present due to human actions. For example, Gratiot Lake has high copper concentrations even in deep sediments because the lake is located in an area that is naturally rich in copper. Therefore, in this section we shall present focusing-corrected anthropogenic accumulation rates. The rationale and calculations will be presented first, and then the results for cadmium, copper, lead and zinc.

Determining focusing corrected anthropogenic accumulation rates

The first step in calculating anthropogenic accumulation rates is determining anthropogenic concentrations. Although elements such as lead and cadmium have many human sources, they are also present in sediment naturally, primarily due to terrestrial inputs. For this study, the watershed correction technique was used to differentiate natural and anthropogenic sources.

The watershed correction technique is based on the idea that there are two major sources of sediment in a lake: terrestrial inputs from the watershed, and within lake production (organic and carbonate). Terrestrial inputs will tend to have higher natural concentrations of metals than within lake production, and changes in the proportions of these two sources can cause differences in chemical concentration trends, even if there is no change in human inputs. This technique thus assumes that the concentration of a metal (e.g., lead) remains the same in the terrestrial inputs, but the amount of terrestrial input may vary over time. Since the concentrations of elements are assumed to remain the same in the terrestrial inputs, it follows that the natural ratios of elements remain the same throughout the core. The ratio of an anthropogenic element (e.g., lead), and an element not influenced by direct human inputs (e.g., aluminum, iron or scandium) is determined in the pre-anthropogenic sediments, (Bruland et al., 1974; Koelmans, 1998; Tuncer et al., 2001) and the background concentration of the anthropogenic element is calculated separately for each depth using the equation:

$$\frac{M_{BG}}{T_{BG}} \times T_S = M_S$$

Where M_{BG} and T_{BG} are the concentrations of the anthropogenic metal of interest and the terrestrial element respectively in pre-anthropogenic sediments, M_S and T_S are the concentration of the anthropogenic and terrestrial metal in the sample of interest. We use aluminum as the terrestrial element.

Accumulation rates are calculated from the anthropogenic concentrations using:

$$\text{Anthropogenic accumulation rate } (\mu g/m^2/y) = \text{anthro conc (mg/kg) x mass sedimentation rate } (g/m^2/y)$$

The mass sedimentation rate is taken from the dating model used for that particular lake. The advantage of using accumulation rates rather than concentrations is twofold. First, within one lake, the concentration of an element coming in at a constant rate may change, if there are changes in the input rates of other portions of the sediment. For example, if lead is being deposited from the atmosphere at a constant rate, but the rate of calcium carbonate deposition increases, the concentration of lead will go down, even though the rate of input remained the same. Secondly, this same problem occurs not just within one core, but also among lakes. Therefore the use of accumulation rates allows us to compare data over space and time. The disadvantage of this technique is that any errors in the calculation of sedimentation rates from ^{210}Pb data will be propagated to the accumulation rates.

To account for different amounts of focusing that occurs among lakes, the anthropogenic accumulation rate is divided by the focusing factor. The rationale and calculation of the focusing factor was described above in the ^{210}Pb section.

Focusing corrected anthropogenic accumulation rates: cadmium, copper, lead and zinc

Some difficulties were encountered in the determination of anthropogenic inputs. Sediment cores taken from Whitmore and Paw Paw Lakes were not deep enough to reach background sediments (oldest sections are 1887 and 1923, respectively). To estimate background concentrations, the concentrations of two major sediment components, aluminum and calcium, were compared to those of other lakes. For both Paw Paw and Whitmore Lakes, Higgins Lake had the most similar sediment chemistry. Therefore the background metal: aluminum ratio from Higgins Lake was used to calculate anthropogenic inputs. However, the copper profile in Whitmore Lake does appear to reach constant low concentrations in lower portion of the core in the late 1800s (Fig. 10a.). This is reasonable because other lakes approach or reach background concentrations by the late 1800s, and therefore the Cu:Al ratio of the older sediment in Whitmore Lake was used. This method results in lower anthropogenic accumulation rates than using the Cu:Al ratio from Higgins Lake, and may underestimate the human inputs. All anthropogenic accumulation rates from Paw Paw and Whitmore Lakes should be interpreted with care, as there could be considerable error in this estimation technique. Cadmium and copper are particularly sensitive to the estimation technique used, while total concentrations of lead and zinc are high enough above background that small changes in background estimation change the final results very little.

Sediment cores from Cadillac Lake do not reach pre-1800 dates, however, concentrations in the oldest sediment collected have relatively constant low values. These concentrations near the bottom of the core were used as background values. These concentrations are somewhat higher than most other lakes, and it is possible that anthropogenic values have been underestimated.

As discussed above, the sediment core from Crystal B Lake has changes in the type of sediment, and large shifts in the inputs of terrestrial materials. The use of the constant background technique is not feasible, because elements such as copper do not remain constant in the deeper portion of the core, but rather follow a similar pattern as aluminum (Fig. 5a). Ideally, the use of the watershed correction technique would account for the shifts in sediment type. However, this technique assumes that the type of terrestrial material entering the lake remains the same over time, and therefore that the natural metal:aluminum ratio does not change. It is clear that in Crystal Lake the type of terrestrial material entering the lake has not remained the same over time, and therefore we cannot assume that the metal:aluminum ratio remains the same. To test the validity of the method, the metal:aluminum ratios of sediments older than 1731 were averaged, and used as the background ratio. The section of the core includes a range of aluminum values, and represents shifting sediment types. Ideally, the anthropogenic concentration would be zero for each sample in the background section of the core. Concentrations are not zero, however, because there is always some variation in ratios representing both error and natural variability. Therefore anthropogenic concentrations in the background area include some slightly negative and slightly positive values. These numbers should be small compared to the anthropogenic concentrations in the upper portion of the core. If they vary significantly, this indicates that the natural metal:aluminum ratio is not remaining constant and cannot be used to determine human inputs. For Crystal B Lake, using the average metal:aluminum ratio from sediments older than 1731 provides reasonable data for lead, copper, and cadmium, but not for zinc. Therefore zinc anthropogenic inputs were not calculated for Crystal B Lake.

In Mullett Lake, copper, cadmium, and lead have relatively constant concentrations at depth, and it was possible to calculate anthropogenic inputs. However, there are significant variations in zinc concentrations in sediments older than 1800, and it was not possible to calculate anthropogenic inputs.

Overall, Whitmore and Paw Paw Lakes have the highest anthropogenic accumulation rates of the five lakes. In Cadillac and Crystal B Lakes, the total sedimentation rate increases to the surface, causing an increase in anthropogenic accumulation rates even if concentrations are decreasing.

Both Whitmore and Mullett Lakes have broad cadmium peaks, with cadmium accumulation rates decreasing from the late 1960s to the present (Fig. 17a). The peak in cadmium in Crystal B Lake is similar to the shape of the peak in Crystal M Lake, except displaced downward in the core (Fig. 17b). This is possibly due to dating errors. Whitmore Lake has the highest anthropogenic accumulation rate among all the lakes, but Cadillac Lake has the highest accumulation rate at the surface (most recent deposition). Accumulation rates of cadmium in Cadillac Lake peak in the late 1980s, but then continue to increase to the present due to an increase in total mass sedimentation rate.

Cadillac Lake has, by far, the highest copper accumulation rates, followed by Paw Paw and Whitmore Lakes (Fig. 18 a,b). Whitmore Lake has a peak in copper accumulation rates in 1974 that is very similar to Gull Lake. However, Whitmore Lake has a second peak in 1990 that is not present in Gull Lake. Mullett and Crystal B Lakes have relatively low accumulation rates, with Elk Lake having the lowest accumulation rates.

Whitmore and Paw Paw Lakes show the typical lead profile, with the highest accumulation rates in the mid-1970s and a decrease to the present (Fig. 19 a,b). Whitmore Lake has the highest accumulation rates of lead, while Paw Paw Lake has accumulation rates similar to Gull Lake.

Zinc accumulation rates also generally increase until the 1970s and decrease to the present. Whitmore, Paw Paw and Gull Lakes have the highest zinc accumulation rates in the 1970s, but these rates decrease to the present (Fig. 20 a,b). Accumulation rates for zinc in Cadillac Lake are increasing to the present.

Fig 17a

Fig 17b

Fig 18a

Fig 18b

Fig 18c

19a

19b

20a

20b

Spatial analysis of anthropogenic inventories

Examination of spatial patterns of data can begin to lend insight into whether sources for chemicals are local or regional. The dominant regional source is atmospheric deposition, while local sources include those within a lake's watershed (e.g., sewage, or storm water runoff). If regional sources are dominant for a contaminant, then that contaminant should have a spatial pattern relating to a major source. For example, if atmospheric deposition is the major source of a contaminant, it might have a decreasing south to north trend due to the major industrial and population centers in the south (e.g., Chicago, IL, Gary IN, Detroit, MI.) If local sources are dominant, then there should be no spatial pattern, since the amount of contaminant in each lake will be dependant on features of that watershed.

We examined spatial patterns of anthropogenic inventories for cadmium, copper, lead and zinc. An anthropogenic inventory is the total mass of a contaminant per unit area due to human inputs. This value was calculated by multiplying the anthropogenic concentration (mg/kg, calculation described above) times the dry mass (g/cm^2) of each sediment slice, and then summing these values for the entire core (µg/cm^2) (Simpson et al., 2000). These inventories were then examined spatially.

Sediment cores from Whitmore and Paw Paw Lakes were not deep enough to reach background values, therefore it was not possible to calculate true inventories for these lakes. However, in Whitmore Lake, because concentration profiles of cadmium, copper, lead and zinc are all approaching background concentrations (as estimated from Higgins Lake, Figs. 8a, 9a, 10b, 11a), we felt that inventories calculated from the available data would provide reasonable estimations. The calculated inventories for Whitmore Lake will be underestimates of the true inventory, as human inputs before 1887 (oldest section in the collected core) are not included. However, this should be a minor portion of the entire inventory. In Paw Paw Lake the oldest section of the core is younger than in Whitmore Lake (1923), and estimates of inventories would have greater error. Therefore, in Paw Paw Lake, an anthropogenic inventory was only estimated for lead. The record of lead inputs is very similar among lakes where most of the mass of lead is input in the mid-1900s. Profiles of cadmium, copper and zinc are much less consistent among lakes, and we felt that estimation of these elements from Paw Paw Lake was not appropriate. The calculated inventory of lead in Paw Paw Lake is an underestimation of the actual value, and is reported here for comparative purposes only.

Lead and zinc both show regional patterns of decreasing inventories from south to north (Fig. 21). Whitmore Lake is higher than expected, but while this lake is slightly north of Gull Lake, it is also located in the eastern part of the state, near Detroit (Fig. 1). The focusing factor of Littlefield Lake was estimated (Yohn et al., 2001), which may account for the lower than anticipated inventory. This indicates that both lead and zinc may be influenced by regional inputs, and cadmium and copper are more influenced by local inputs. The influence of the addition of copper sulfate is again seen clearly in Cadillac Lake, which has a copper inventory much higher than all other lakes. Gratiot Lake, which has relatively low inventories of lead, cadmium and zinc, has the third highest inventory for copper. This is likely due to the extensive copper mining and smelting in the area. Whitmore Lake has the highest inventories of cadmium, lead and zinc, and the second highest for copper.

fig21

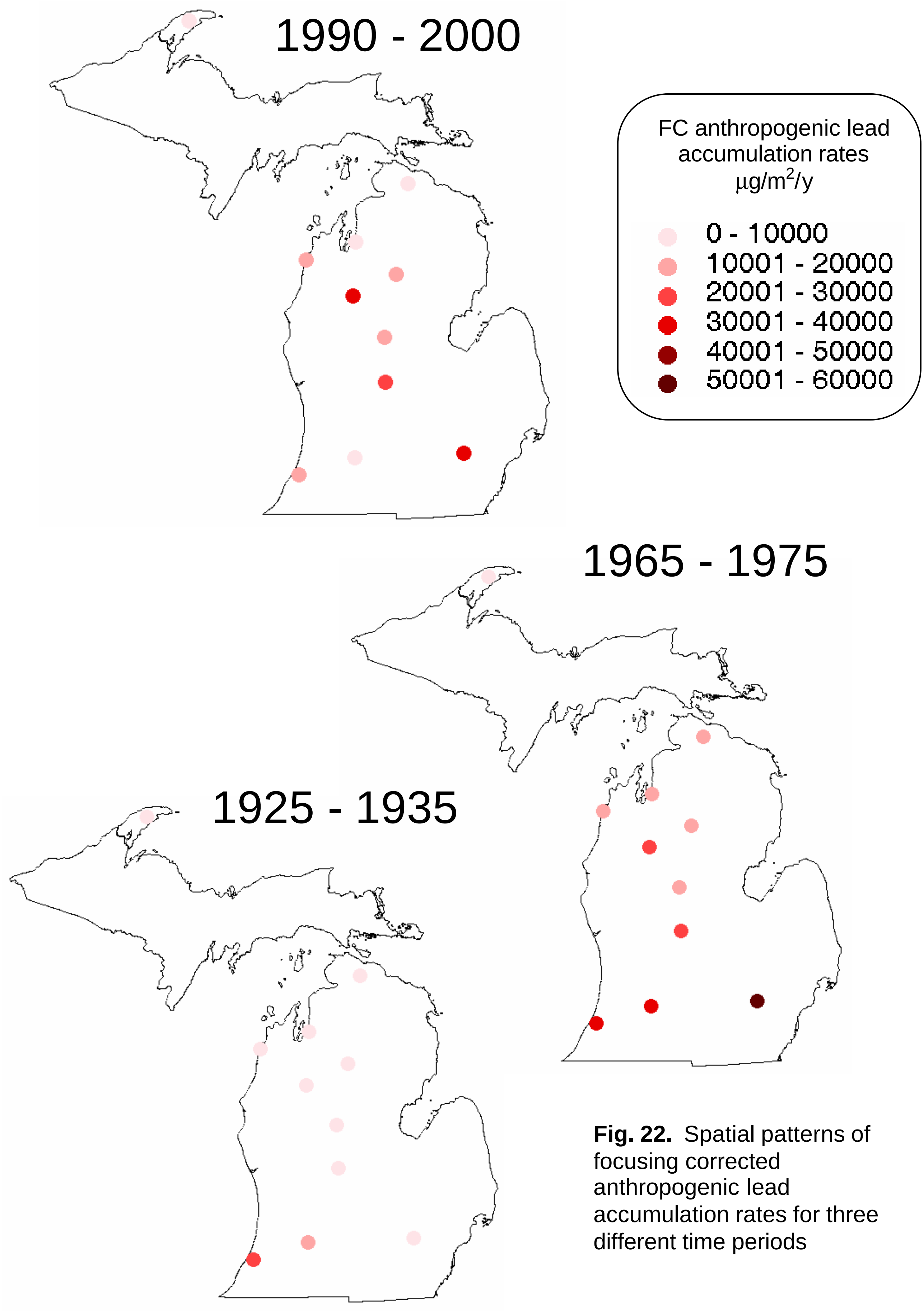


Fig. 22. Spatial patterns of focusing corrected anthropogenic lead accumulation rates for three different time periods

The spatial of pattern of lead is not unexpected in Michigan. Many studies have found that the atmosphere is an important source of lead to the environment (Eisenreich et al., 1986; Evans et al., 1986), and in particular, lead from gasoline is a major source (Callender and Rice, 2000; Graney et al., 1995). Coal burning and ore smelting was also an important source of lead to the atmosphere, particularly in the early 1900s. Lead was phased out of gasoline in the 1970s, and concentrations of lead in the sediment have consistently decreased since then. To investigate if atmospheric lead is still an important source to lakes in Michigan, we examined spatial patterns of anthropogenic accumulation rates over time. Anthropogenic accumulation rates were averaged from 1990-2000, from 1975-1965, and 1925-1935, and plotted using ArcView (ESRI, 1998)(Fig. 22).

Anthropogenic accumulation rates in the 1970s show the same spatial pattern as the total inventories, decreasing from the south to north, with Whitmore Lake having the highest average accumulation rate (Fig. 22). A similar pattern is seen in the 1930s, except that accumulation rate in Whitmore Lake is now lower then those in Gull and Paw Paw Lakes (Fig. 22). It appears that in the 1930s the extensive coal burning and ore smelting that occurred in the highly industrialized regions to the southwest of Michigan were a more important source than Detroit. Current patterns of accumulation rates are much different however. While the northernmost lake (Gratiot Lake) still has the lowest accumulation rate, the south to north decreasing trend is not as obvious. This indicates that sources of lead are moving from regional atmospheric sources to more local sources. Future reports will investigate the influence of features of the watershed (e.g., population, land use), on human inputs of lead and other contaminants to Michigan lakes.

Recommendations of a lake monitoring strategy

The intent of monitoring is to be able to detect change from when the last sample was taken. Change can be in the concentration of a chemical or a change in the trend of the environmental loading of a chemical. In the first case only the very surface sediment sample would need to be taken. But given the complexities of lake dynamics (e.g., bioturbation) a single sample would not be informative. What is more important is the change in the trend of the chemical inputs. The challenge is to be able to determine current trends. One surface sample will not reveal a trend. One might consider a minimum of four samples that reflect new sediment input from the last sampling as necessary to define a trend.

Our current sampling protocols involves taking 0.5 cm samples from the top sediments. Therefore, the accumulation of 2.0 cm of new sediment would be needed to obtain the four samples. The time to deposited 2.0 cm of sediment can be determined from the sedimentation rate (Table 5).

Table 5. Minimum number of years needed to deposit approximately 2 cm of new sediment for seven inland lakes in Michigan. * Littlefield estimated

Cass	Elk	Gratiot	Gull	Higgins	Crystal M
1 y	10 y	2 y	4 y	6 y	3 y
Cadillac	Crystal B	Mullett	Paw Paw	Whitmore	Littlefield*
2 y	4 y	3 y	1 y	1 y	5 y

Another important consideration is the quality of the core. Littlefield Lake has a disturbed record, and cannot be dated. If this lake were resampled, ^{210}Pb dating could not be used to determine the depth of new deposition. It would be possible to match element profiles to differentiate the depth of new deposition. However, unless there are particular contaminant concerns, resampling this lake is not recommended.

An overall monitoring strategy should include:

1. Lakes of concern: lakes with increasing levels of contaminants to the surface, or concentrations of contaminants higher than most other Michigan lakes
2. Background lakes: lakes with low concentrations of contaminants with few point sources in the watershed. These lakes would provide background data on atmospheric deposition and provide a comparison for the lakes of concern. Ideally, these lakes would be spatially dispersed throughout Michigan.

It is not appropriate to make final recommendations on which lakes to monitor until all the preliminary sampling is done, however, some of the lakes may be classified as lakes of concern or background lakes. Classifying a lake as “of concern” is not an evaluation of the toxicity of the sediments, but rather a comparison to other Michigan lakes in this study.

The lakes that have been most affected by anthropogenic activities are classified as lakes of concern. Cass Lake has clearly been influenced by human activities, and has relatively high concentrations of anthropogenic elements near the surface. Concentrations of anthropogenic elements are also higher than most lakes in Crystal M, Whitmore, Paw Paw and Cadillac Lakes. Of the lakes sampled, these four lakes show the greatest impact from human actions.

Elk Lake has consistently low concentrations of contaminants. Gratiot and Mullett Lakes also have low anthropogenic accumulation rates. These three lakes appear to be the “cleanest” of the lakes sampled.

After all the preliminary lakes are sampled, it will be possible to determine the lakes with the greatest issues of concern. It will also be possible to identify background lakes, which will serve as monitors of contaminants entering lakes with few known point sources.

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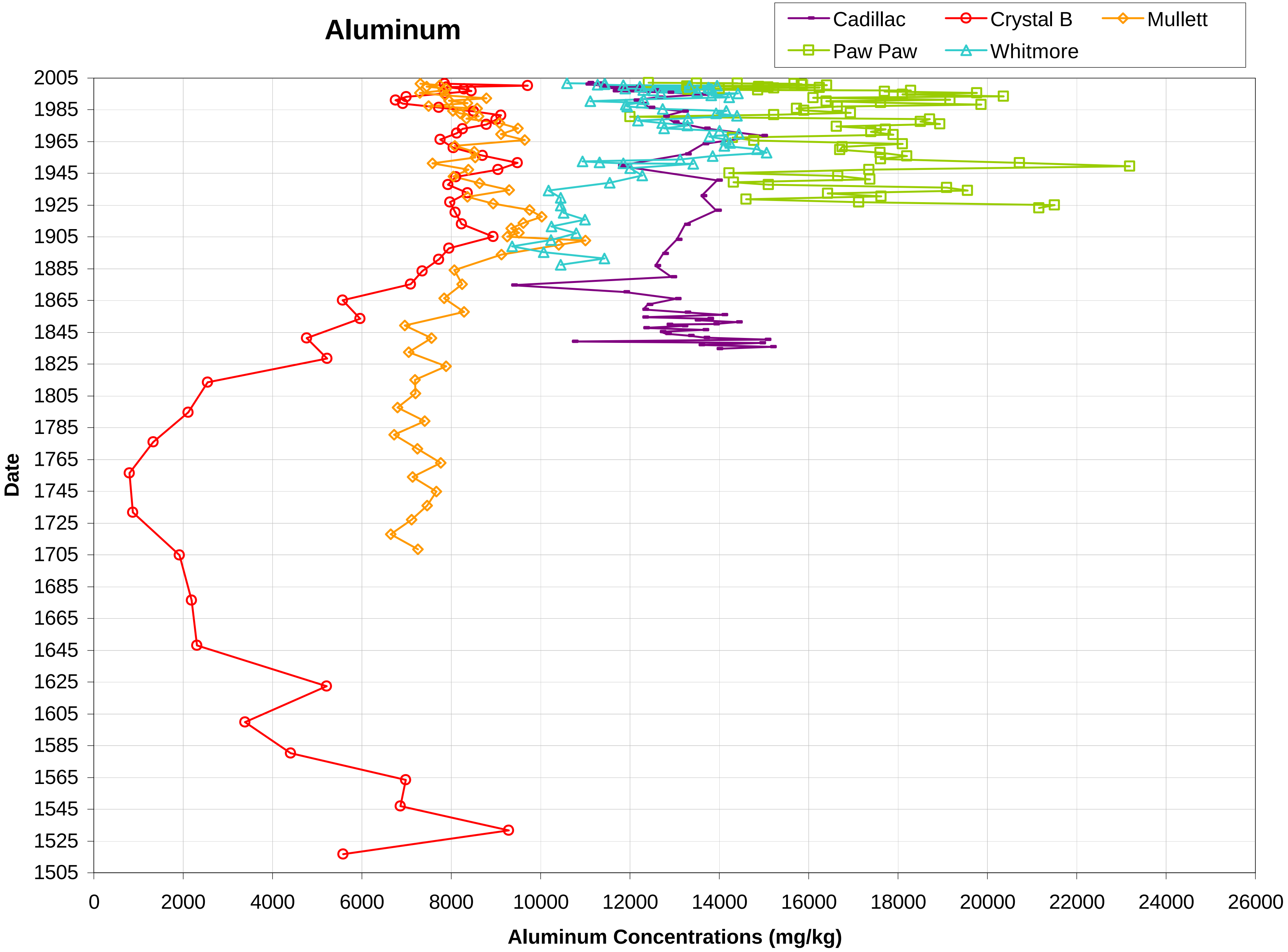

Fig. 5a. Concentrations (mg/kg dry wt) of aluminum in five Michigan lakes.

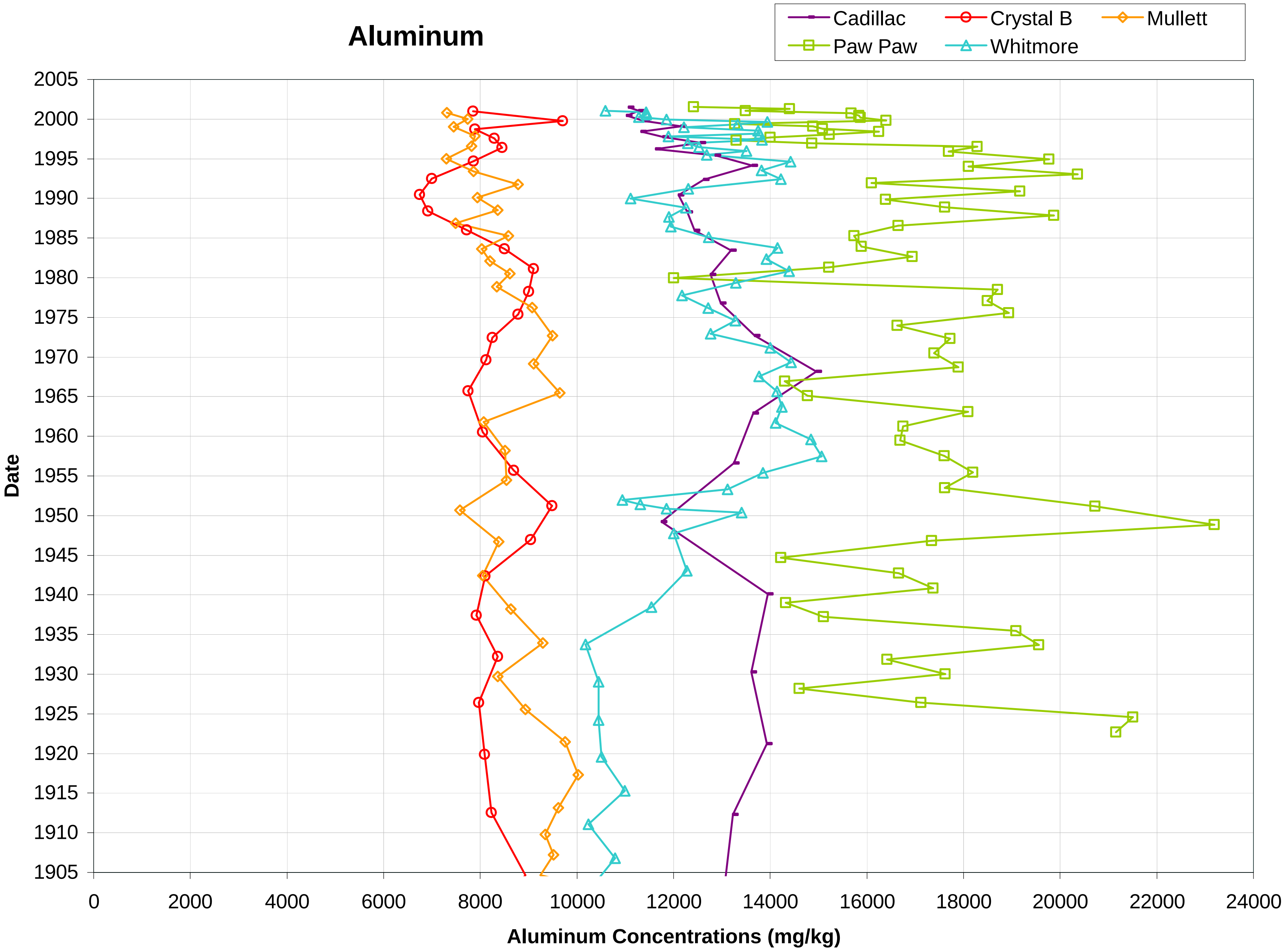

Fig. 5b. Concentrations (mg/kg dry wt) of aluminum in five Michigan lakes since 1905.

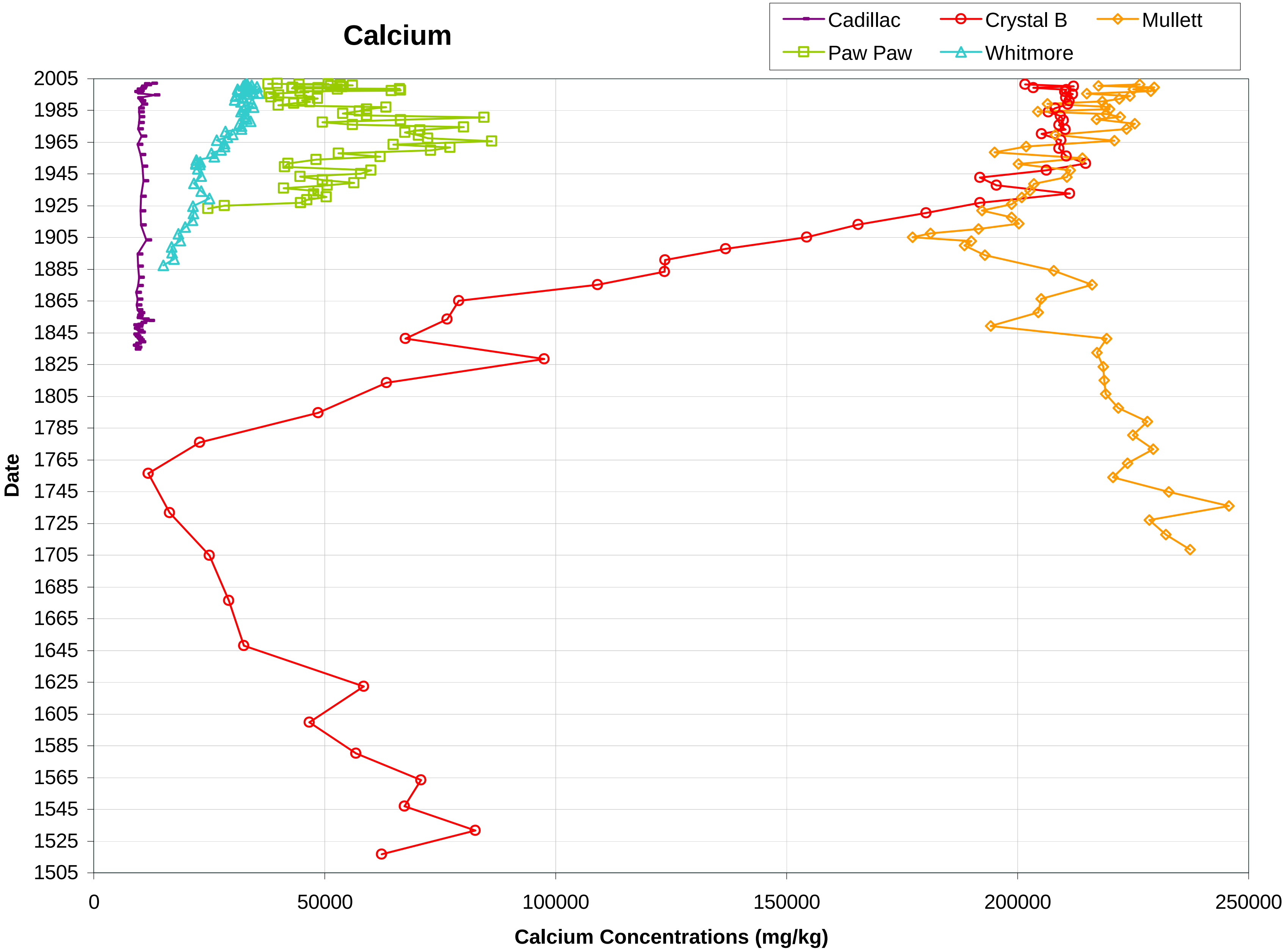

Fig. 6a. Concentrations (mg/kg dry wt) of calcium in five Michigan lakes.

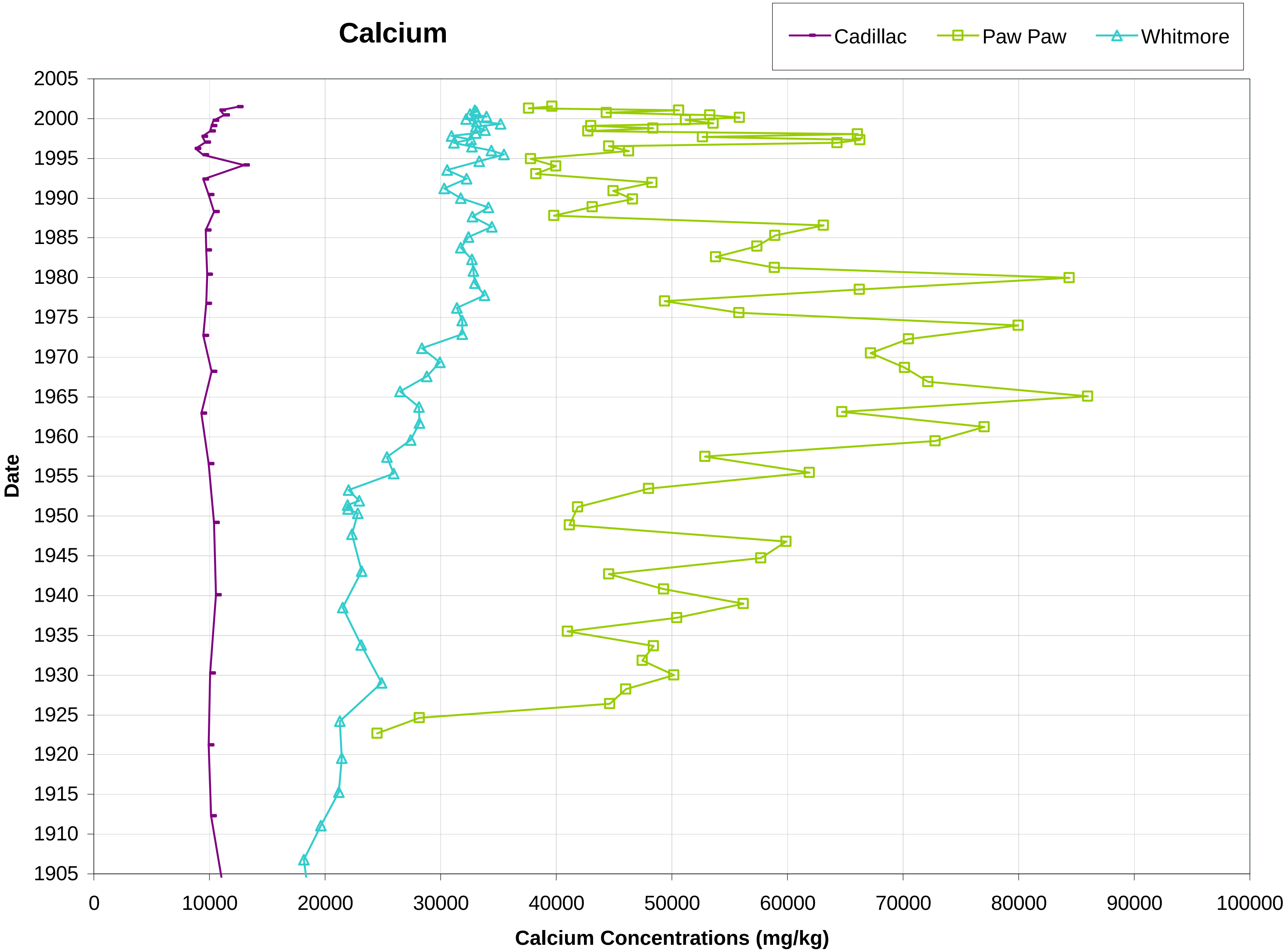

Fig. 6b. Concentrations (mg/kg dry wt) of calcium in three Michigan lakes since 1905. Note change in scale of x-axis.

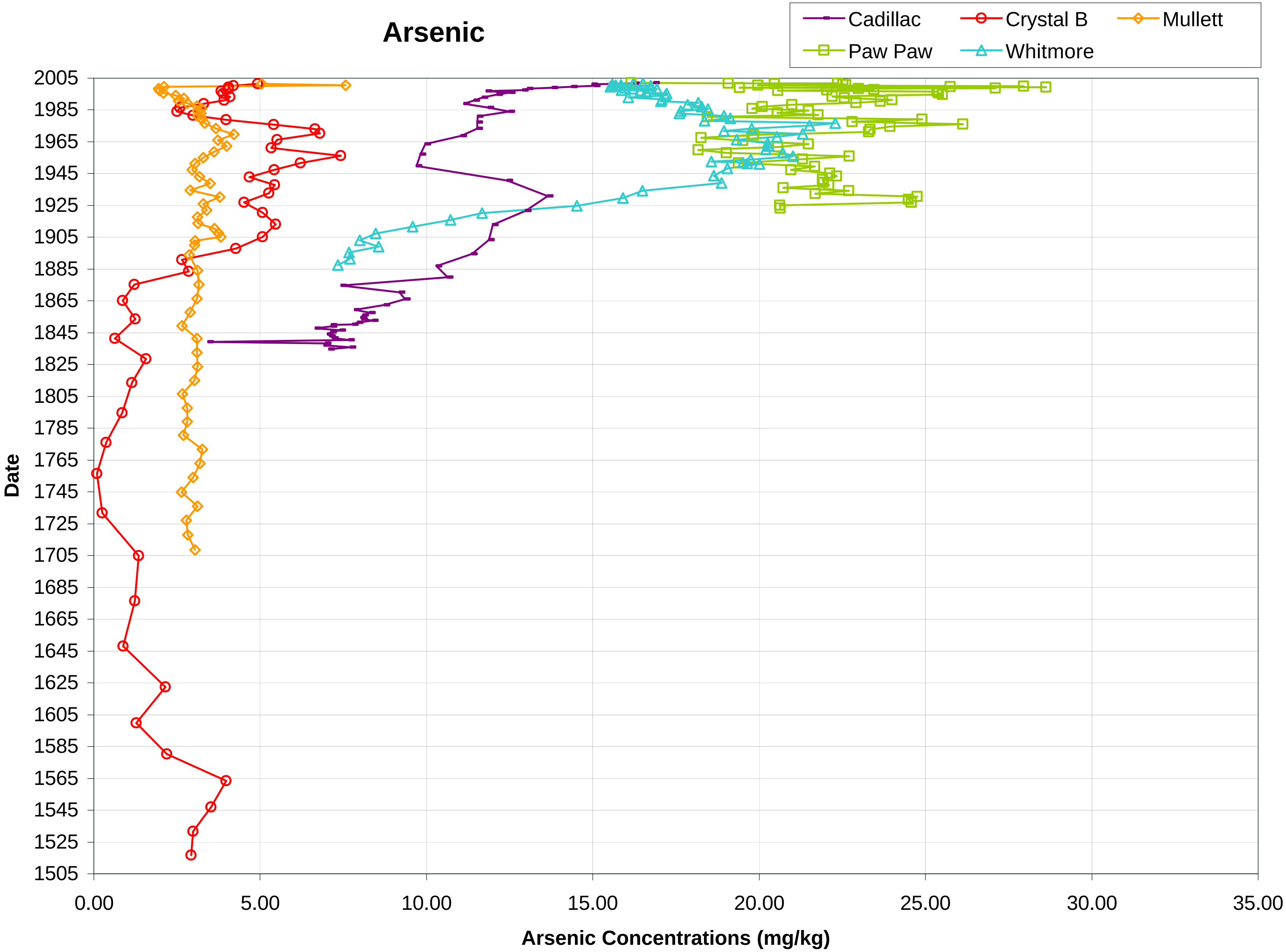

Fig. 7a. Concentrations (mg/kg dry wt) of arsenic in five Michigan lakes.

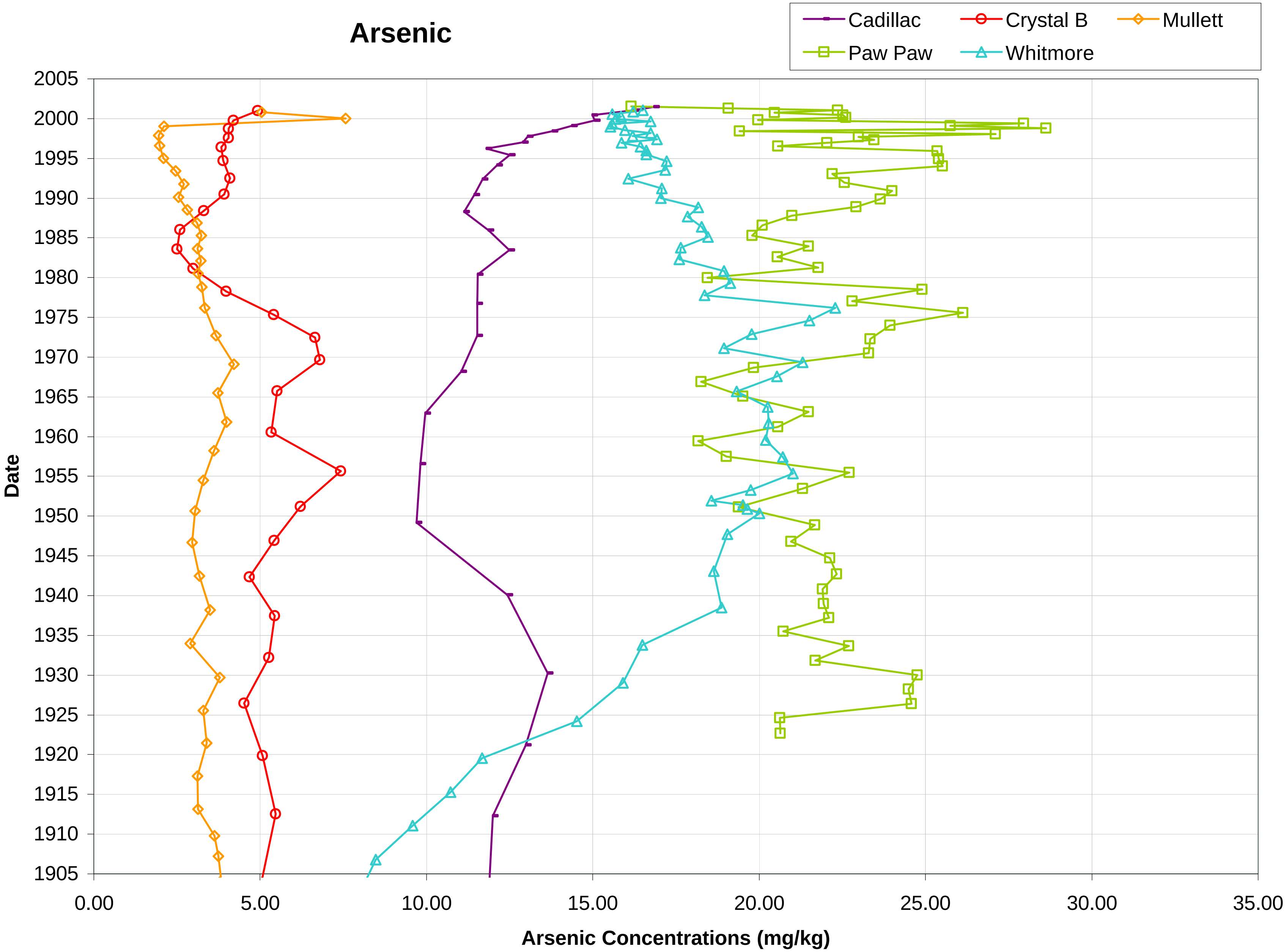

Fig. 7b. Concentrations (mg/kg dry wt) of arsenic in five Michigan lakes since 1905.

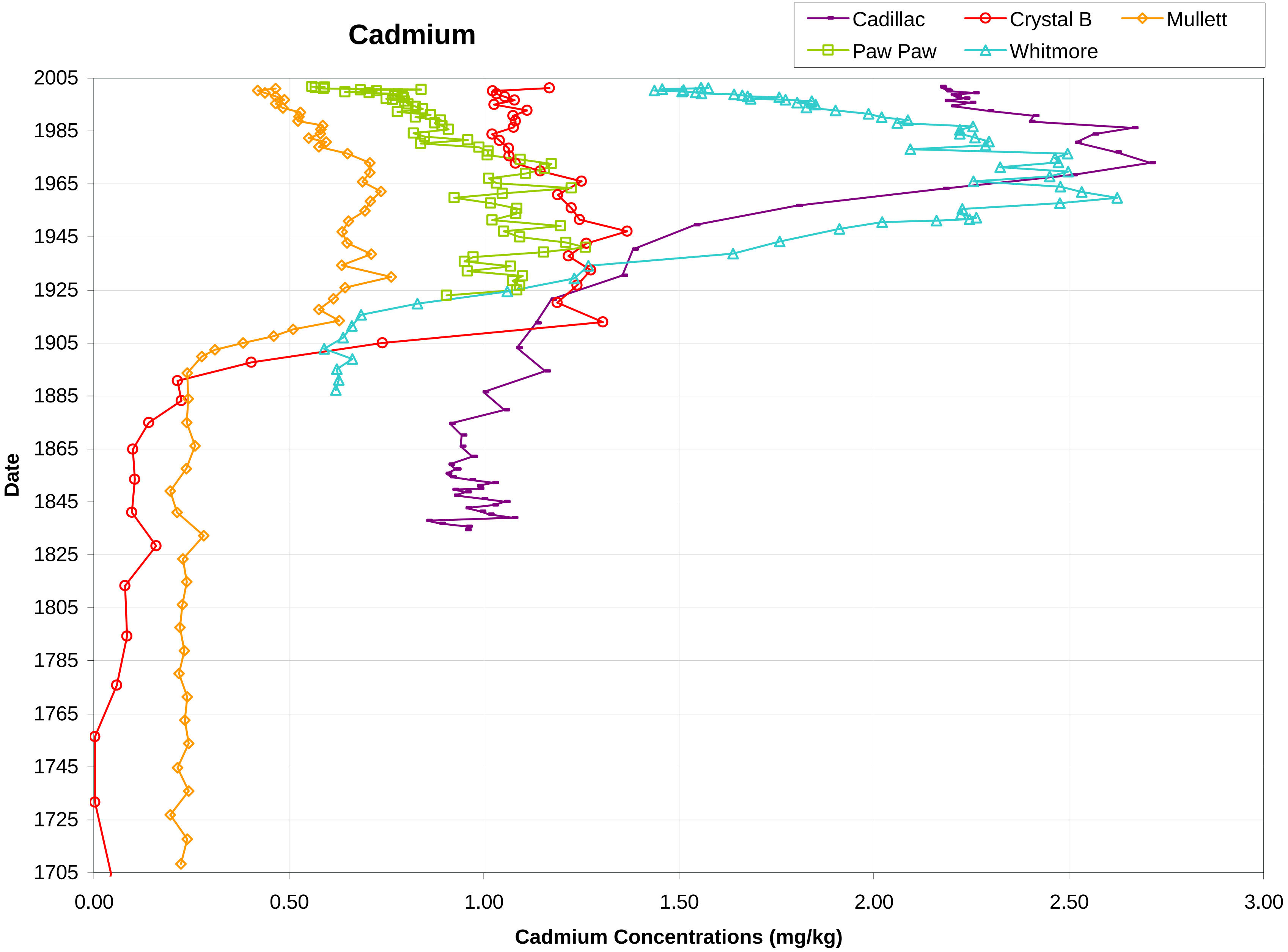

Fig. 8a. Concentrations (mg/kg dry wt) of cadmium in five Michigan lakes.

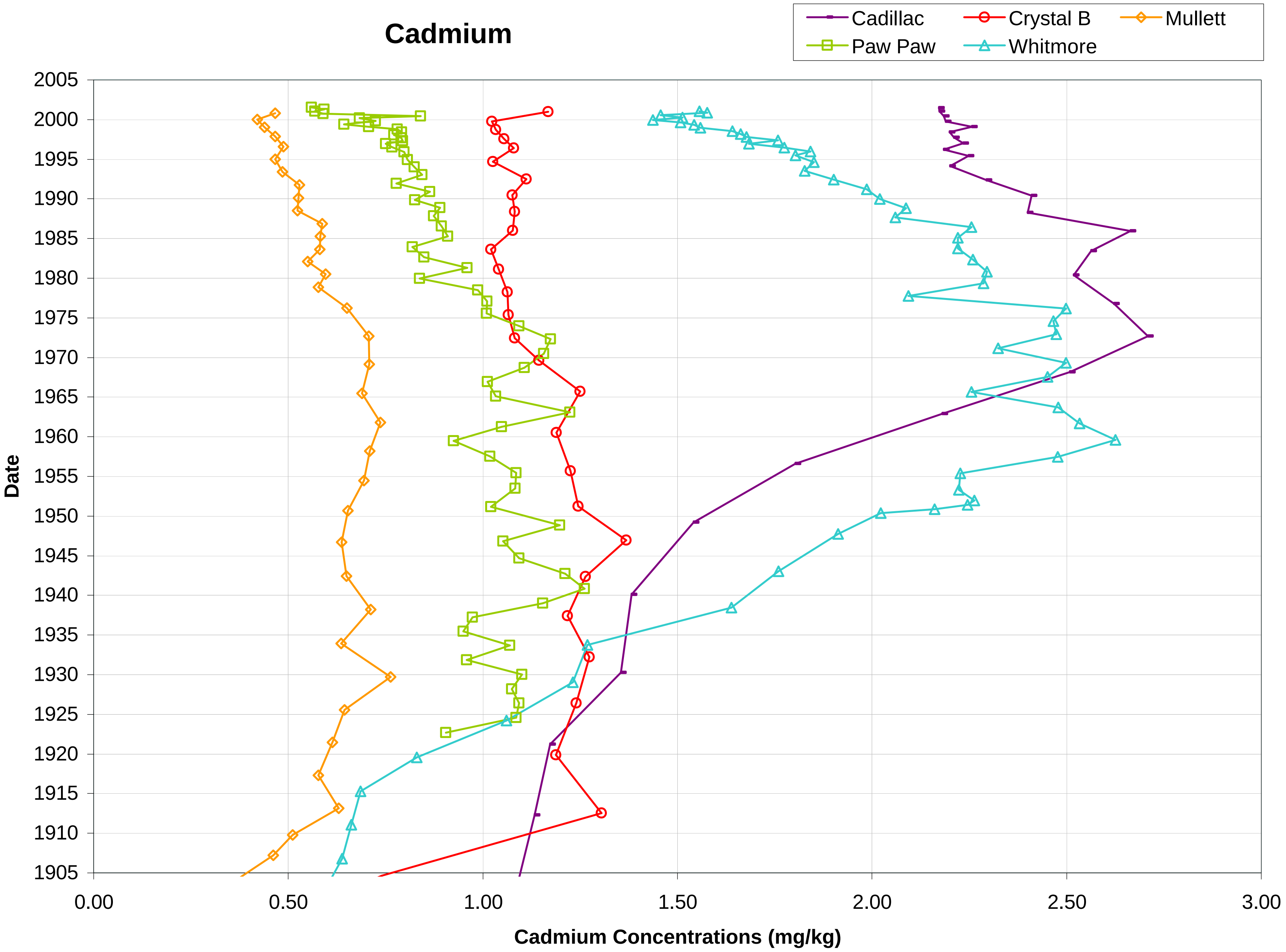

Fig. 8b. Concentrations (mg/kg dry wt) of cadmium in five Michigan lakes since 1905.

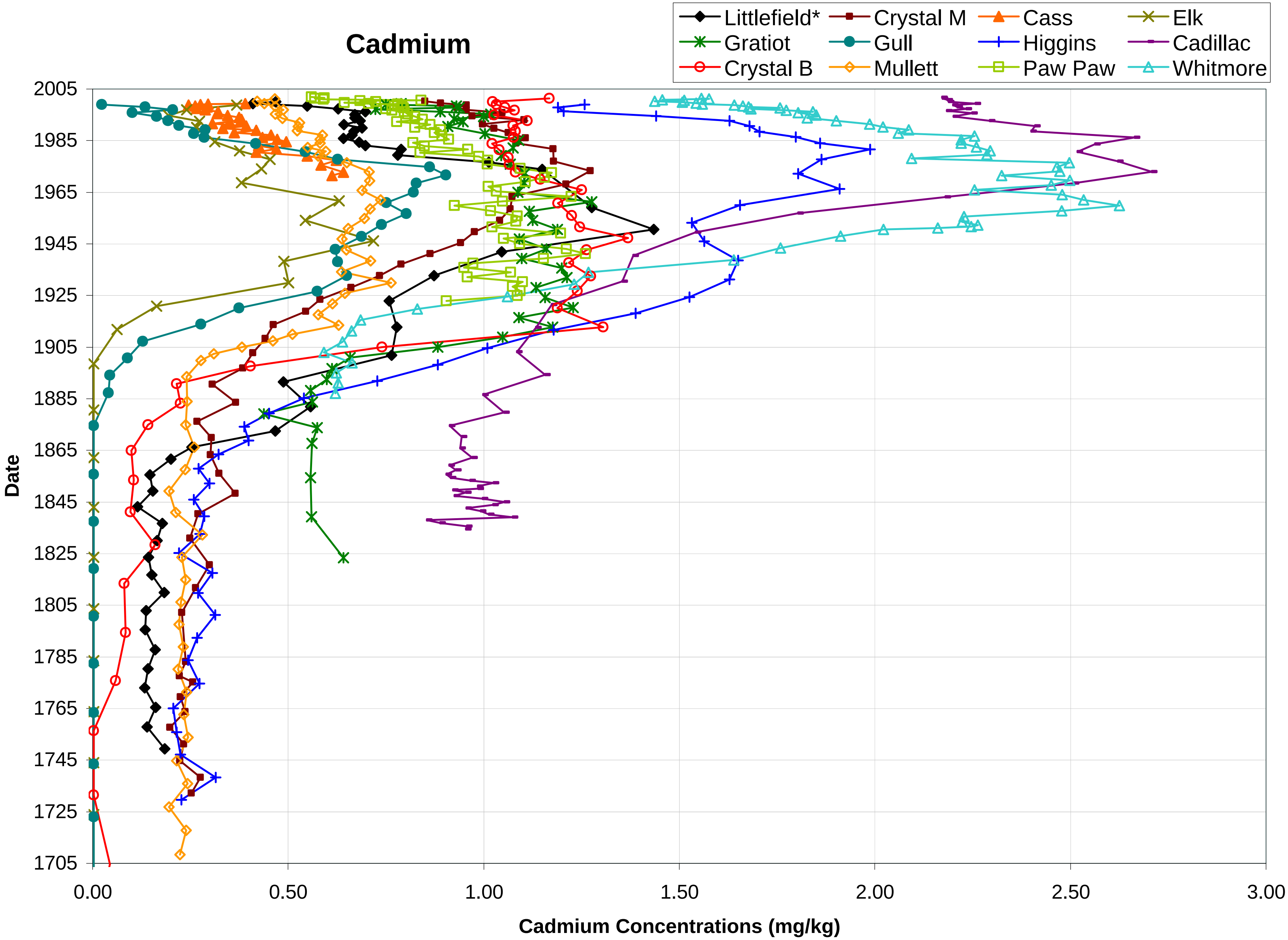

Fig. 9. Concentrations (mg/kg dry wt) of cadmium in twelve Michigan lakes. *Dates for Littlefield Lake are estimations.

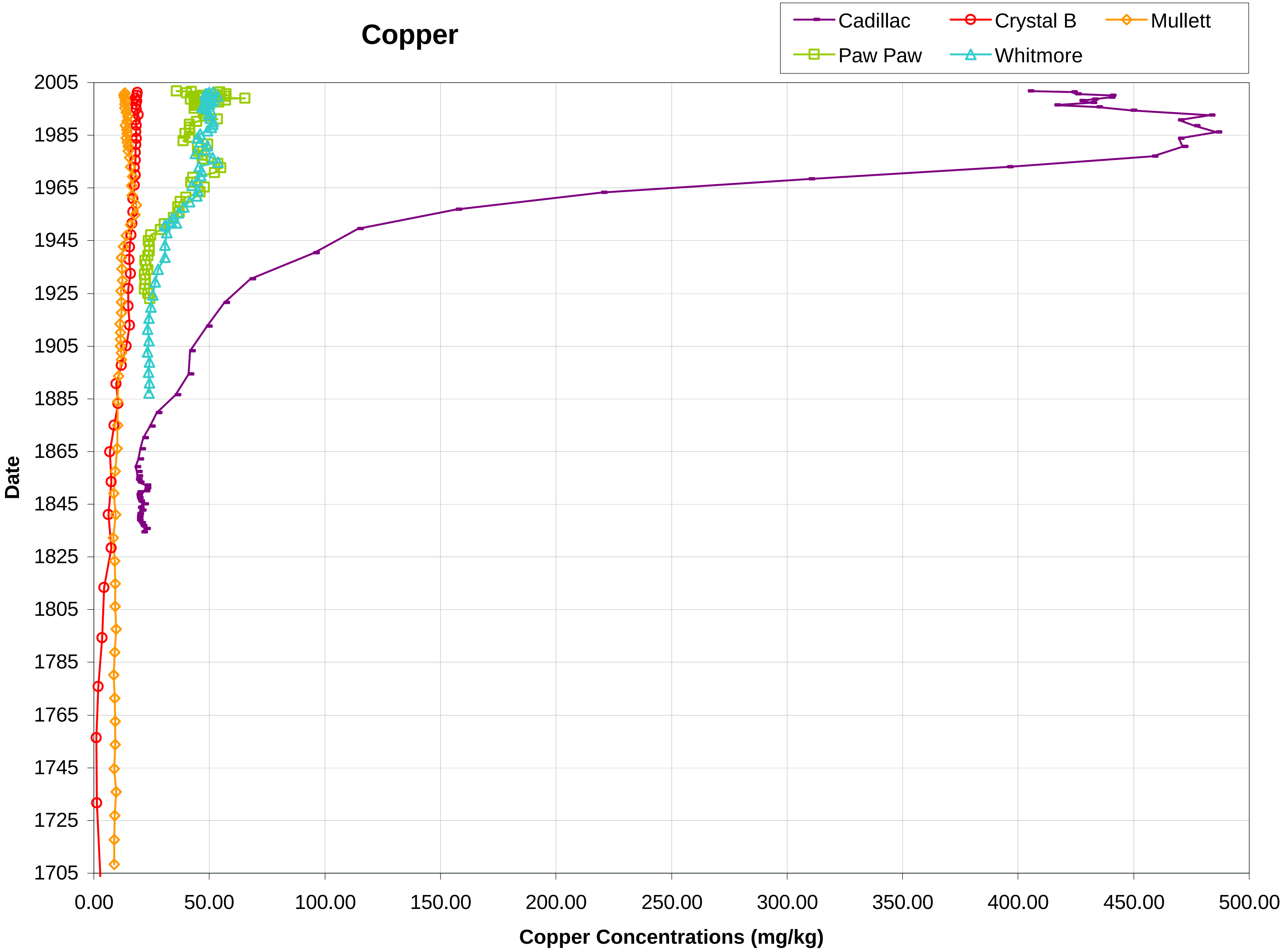

Fig. 10a. Concentrations (mg/kg dry wt) of copper in five Michigan lakes.

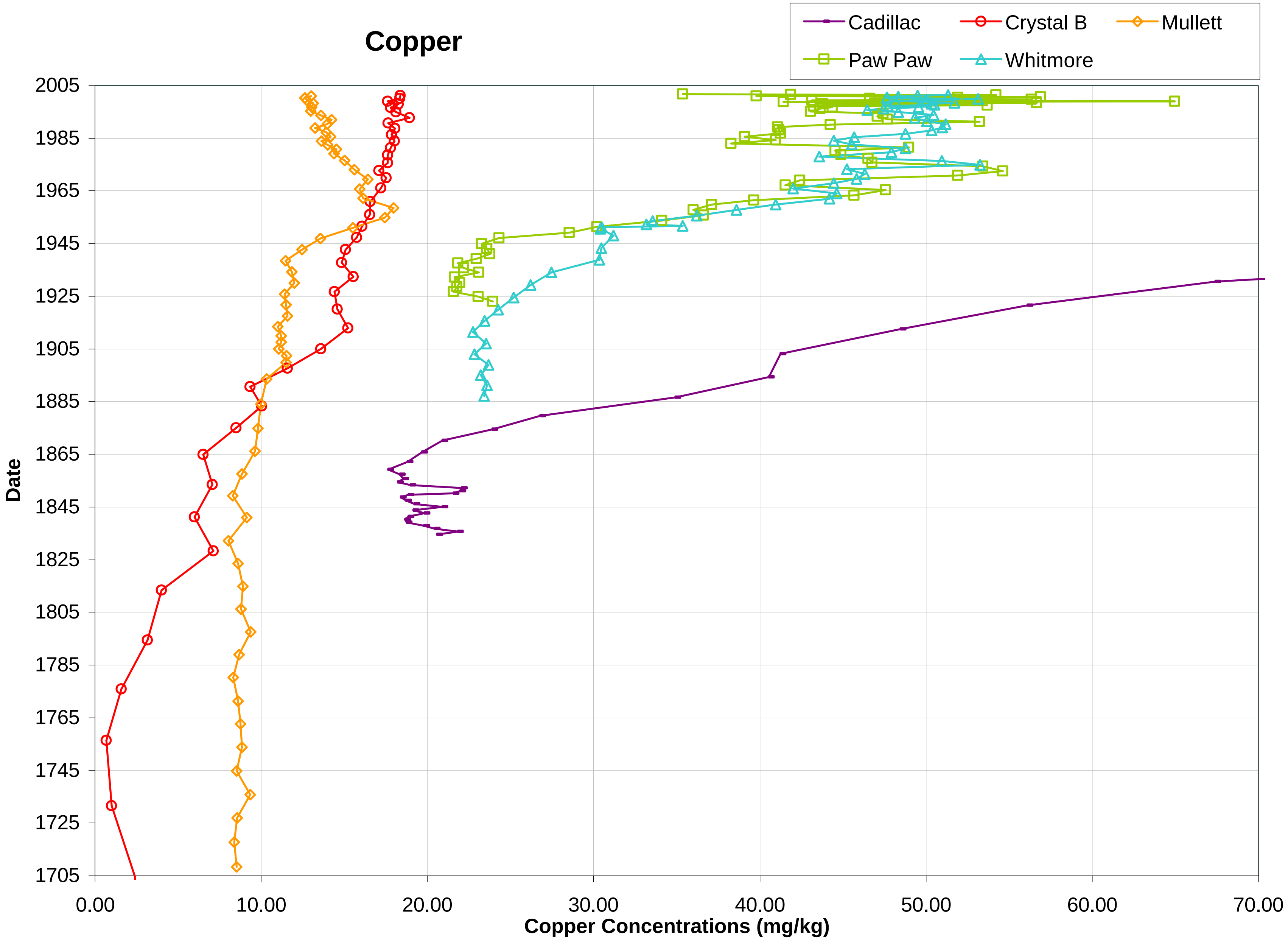

Fig. 10b. Concentrations (mg/kg dry wt) of copper in five Michigan lakes, similar to Fig. 10a, with x-axis scale changed to better show profiles of Crystal B, Mullett, Paw Paw and Whitmore Lakes.

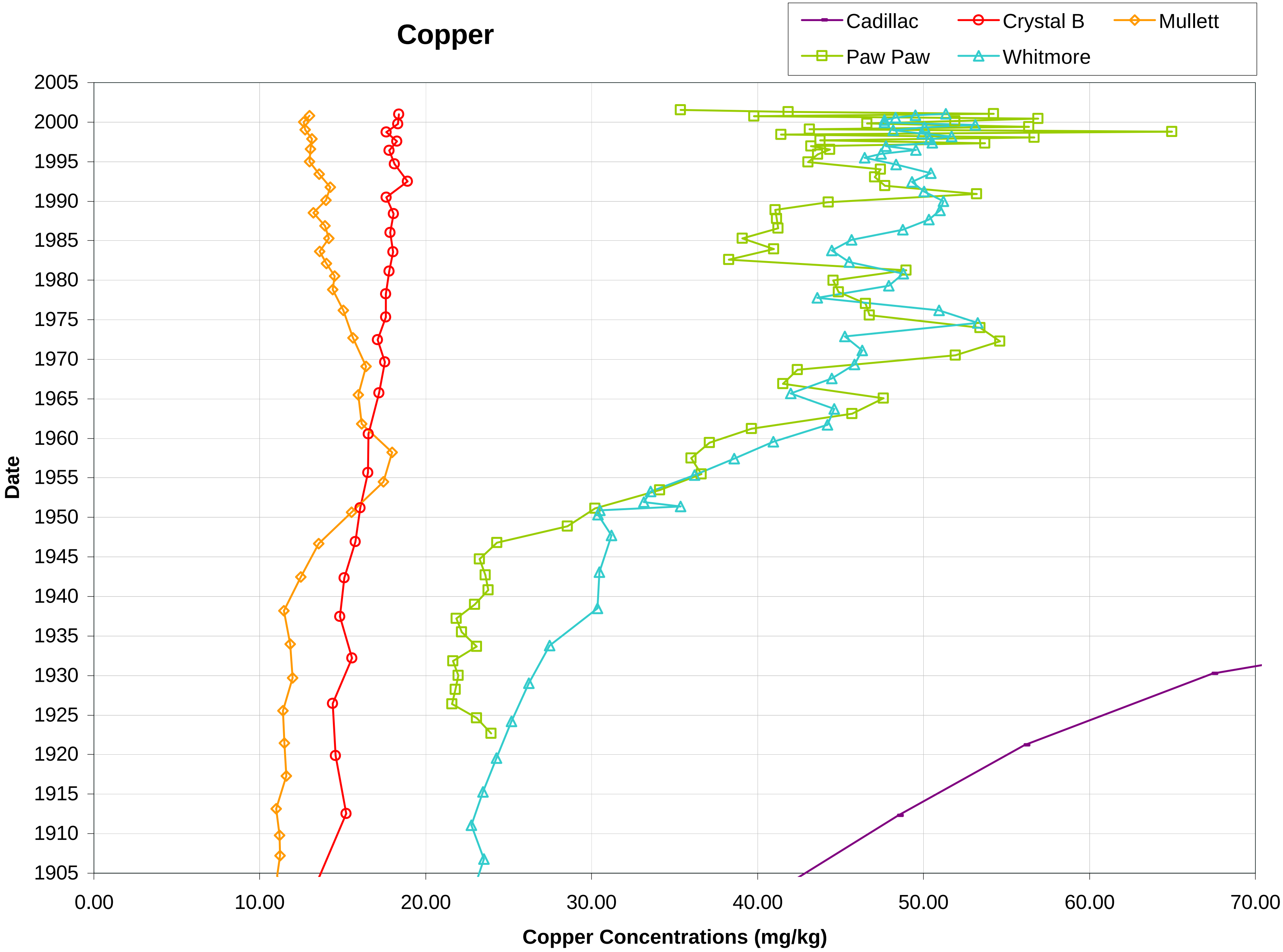

Fig. 10c. Concentrations (mg/kg dry wt) of copper in five Michigan lakes since 1905.

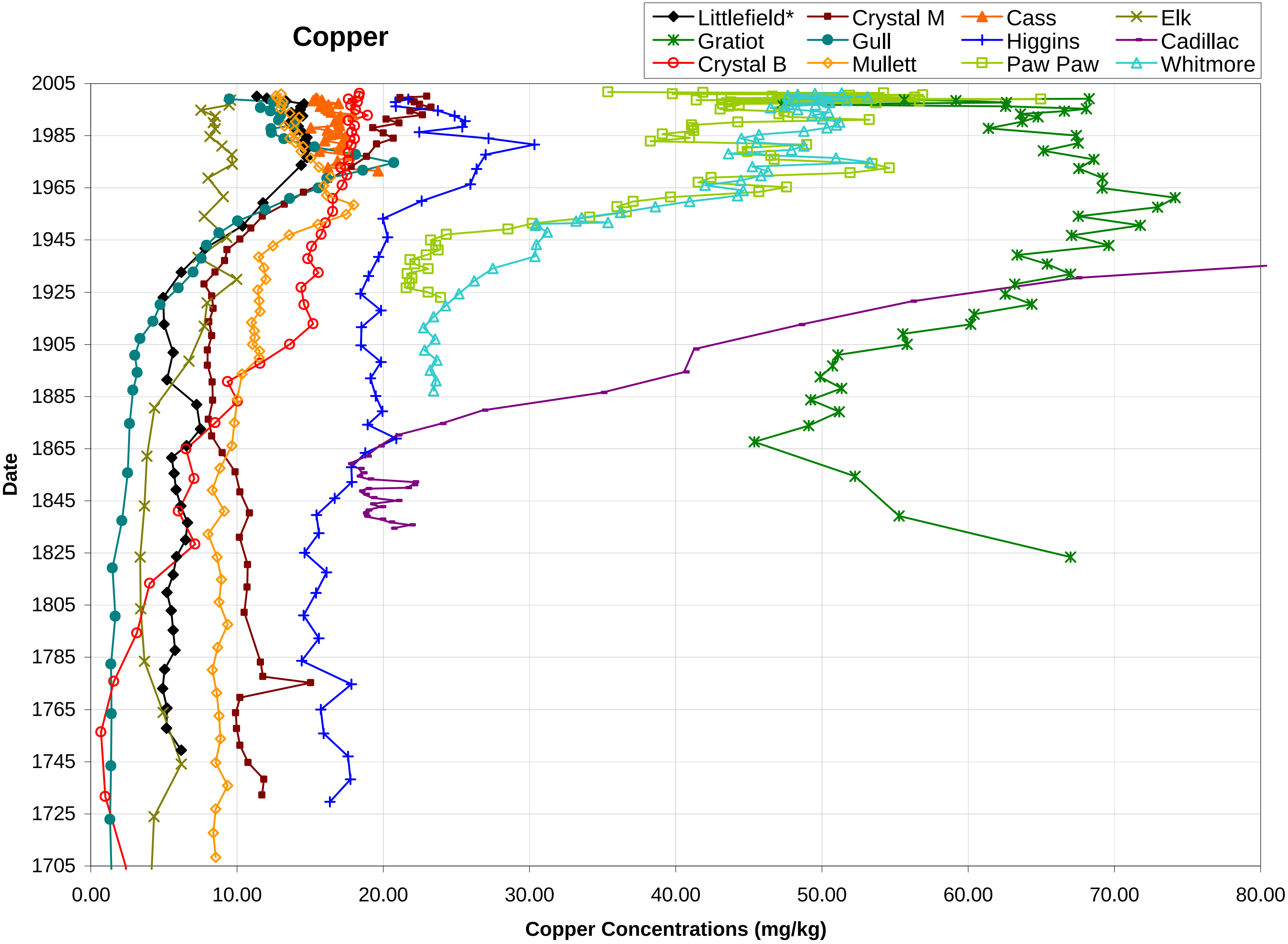

Fig. 11. Concentrations (mg/kg dry wt) of cadmium in twelve Michigan lakes. *Dates for Littlefield Lake are estimations.

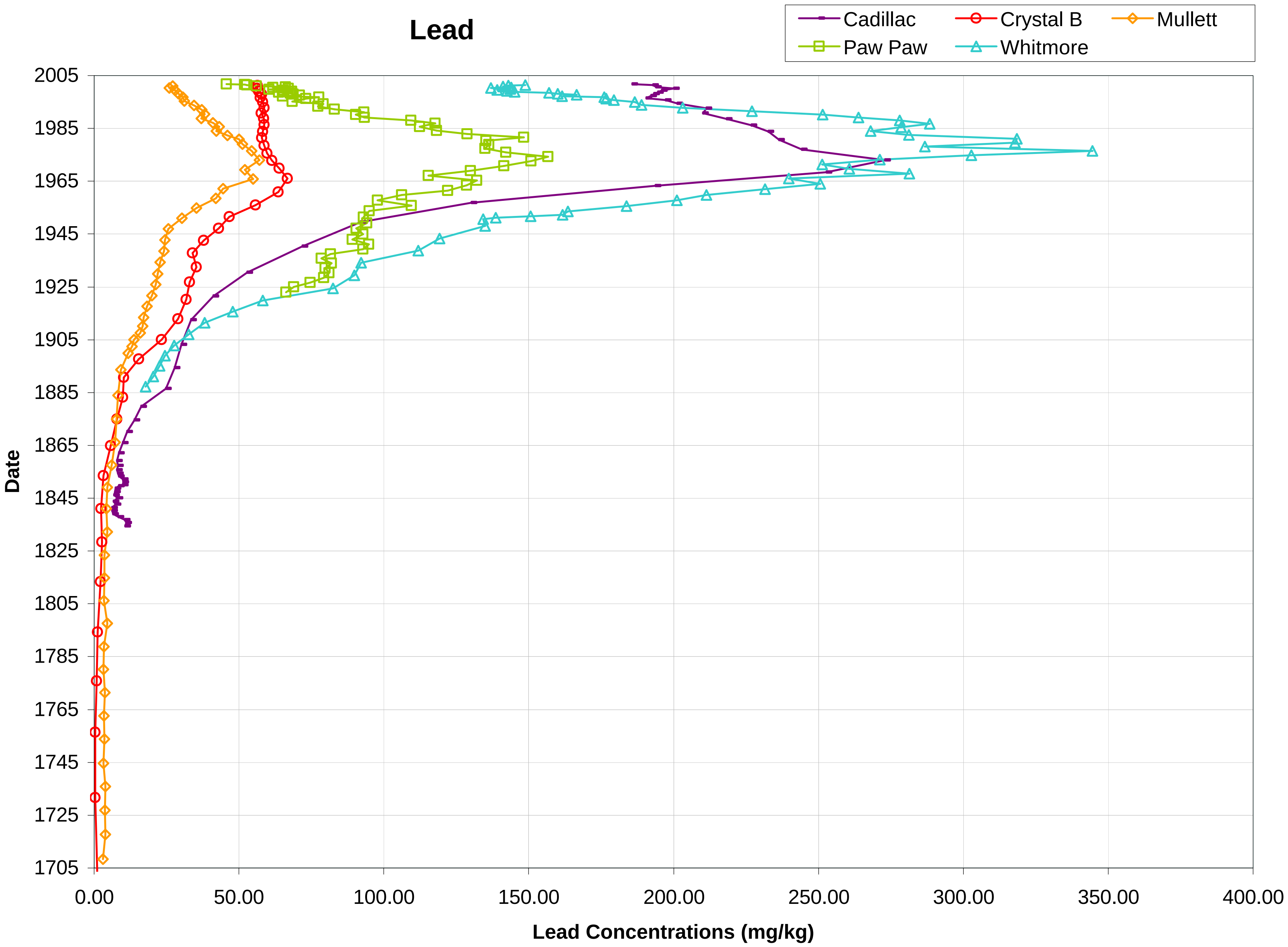

Fig. 12a. Concentrations (mg/kg dry wt) of lead in five Michigan lakes.

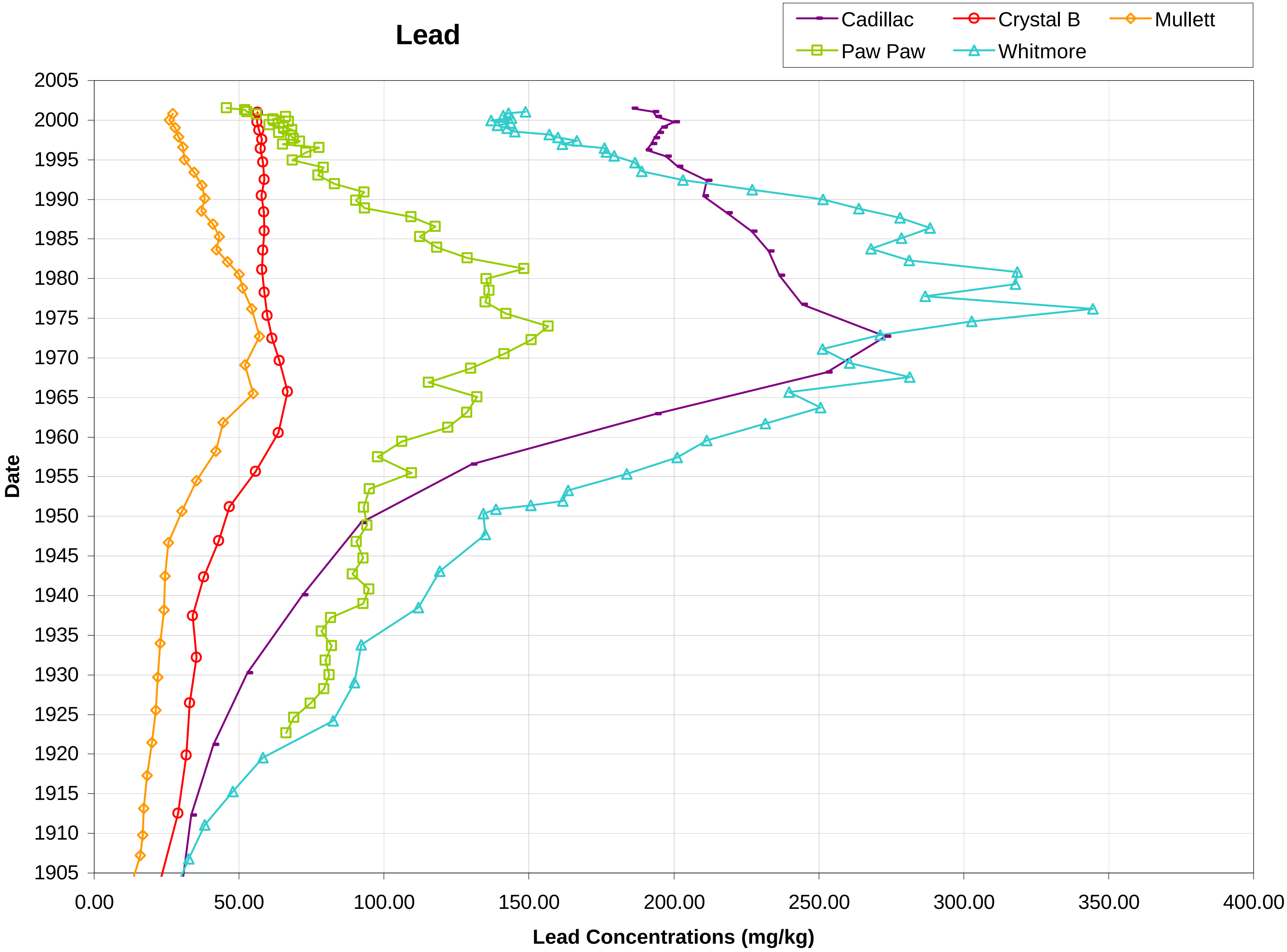

Fig. 12b. Concentrations (mg/kg dry wt) of lead in five Michigan lakes since 1905.

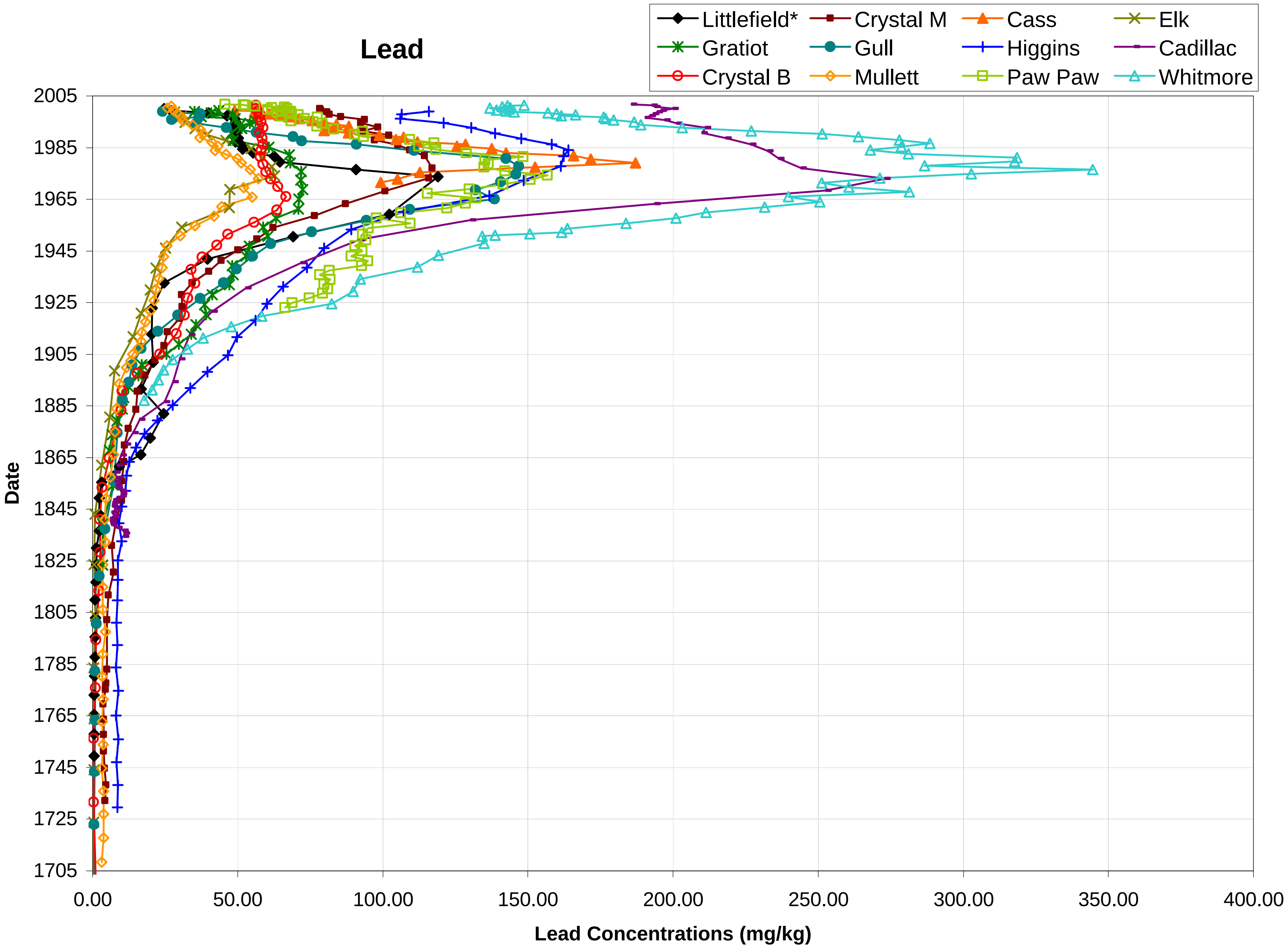

Fig. 13. Concentrations (mg/kg dry wt) of lead in twelve Michigan lakes. *Dates for Littlefield Lake are estimations.

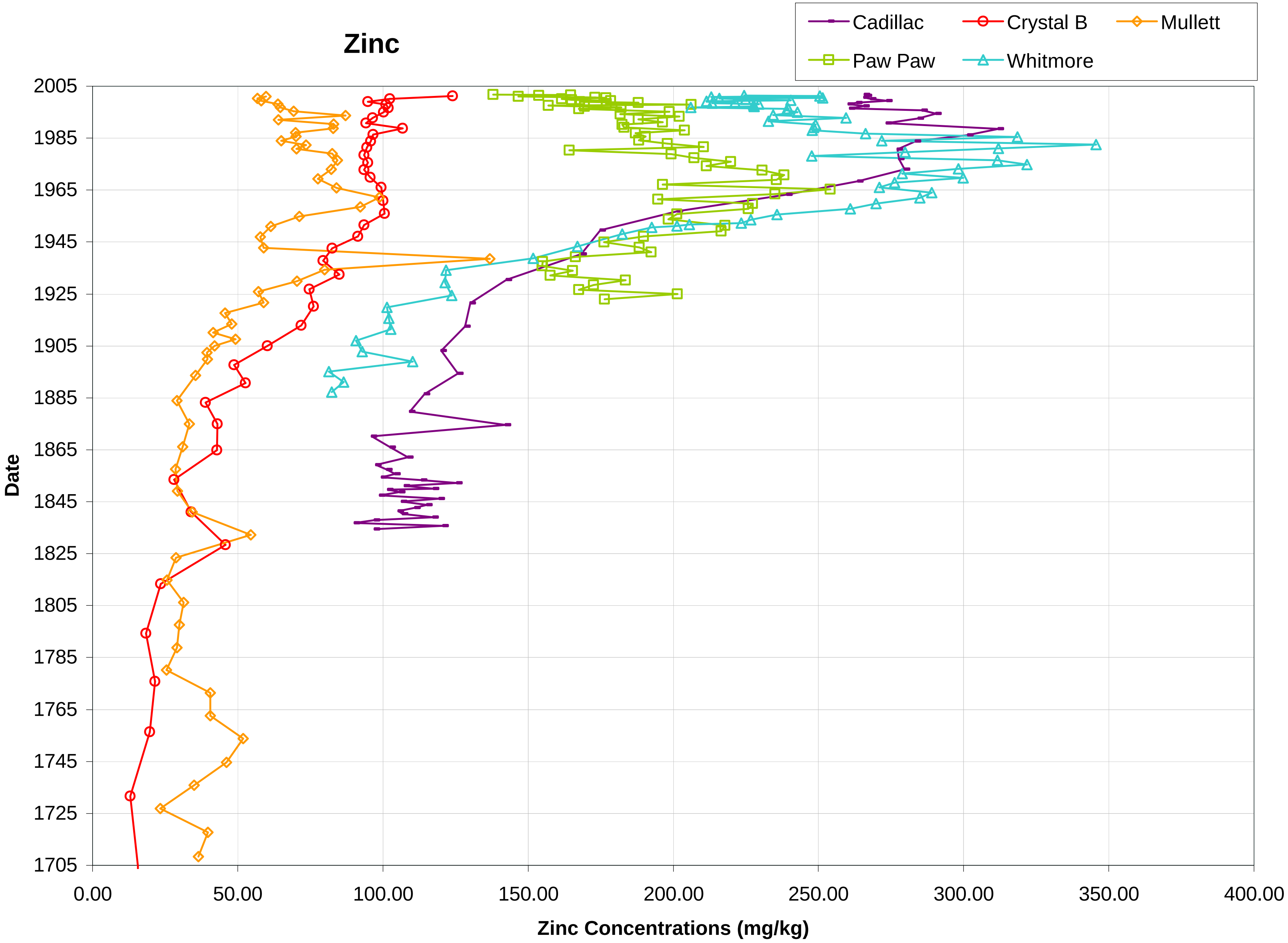

Fig. 14a. Concentrations (mg/kg dry wt) of zinc in five Michigan lakes.

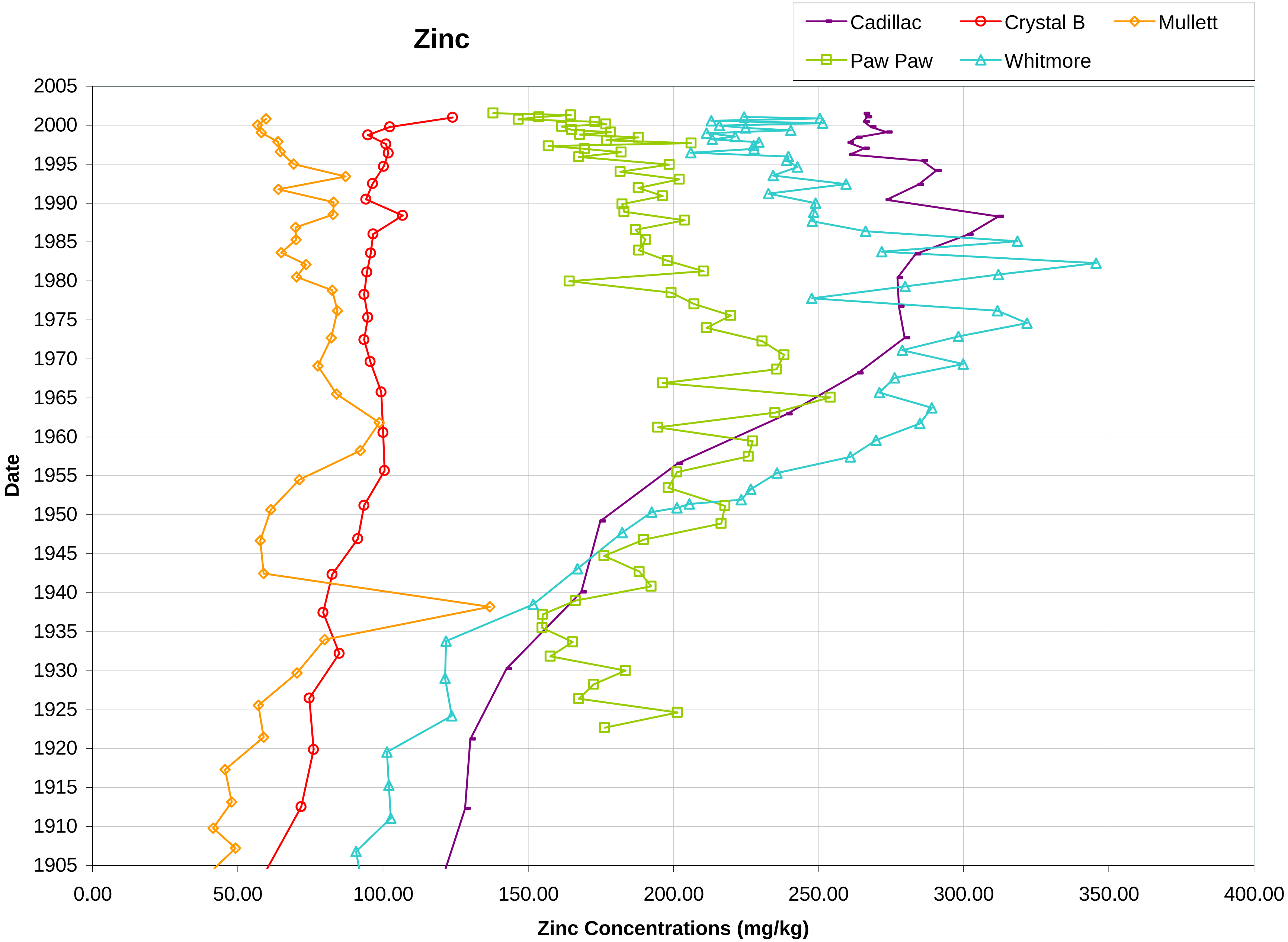

Fig. 14b. Concentrations (mg/kg dry wt) of zinc in five Michigan lakes since 1905.

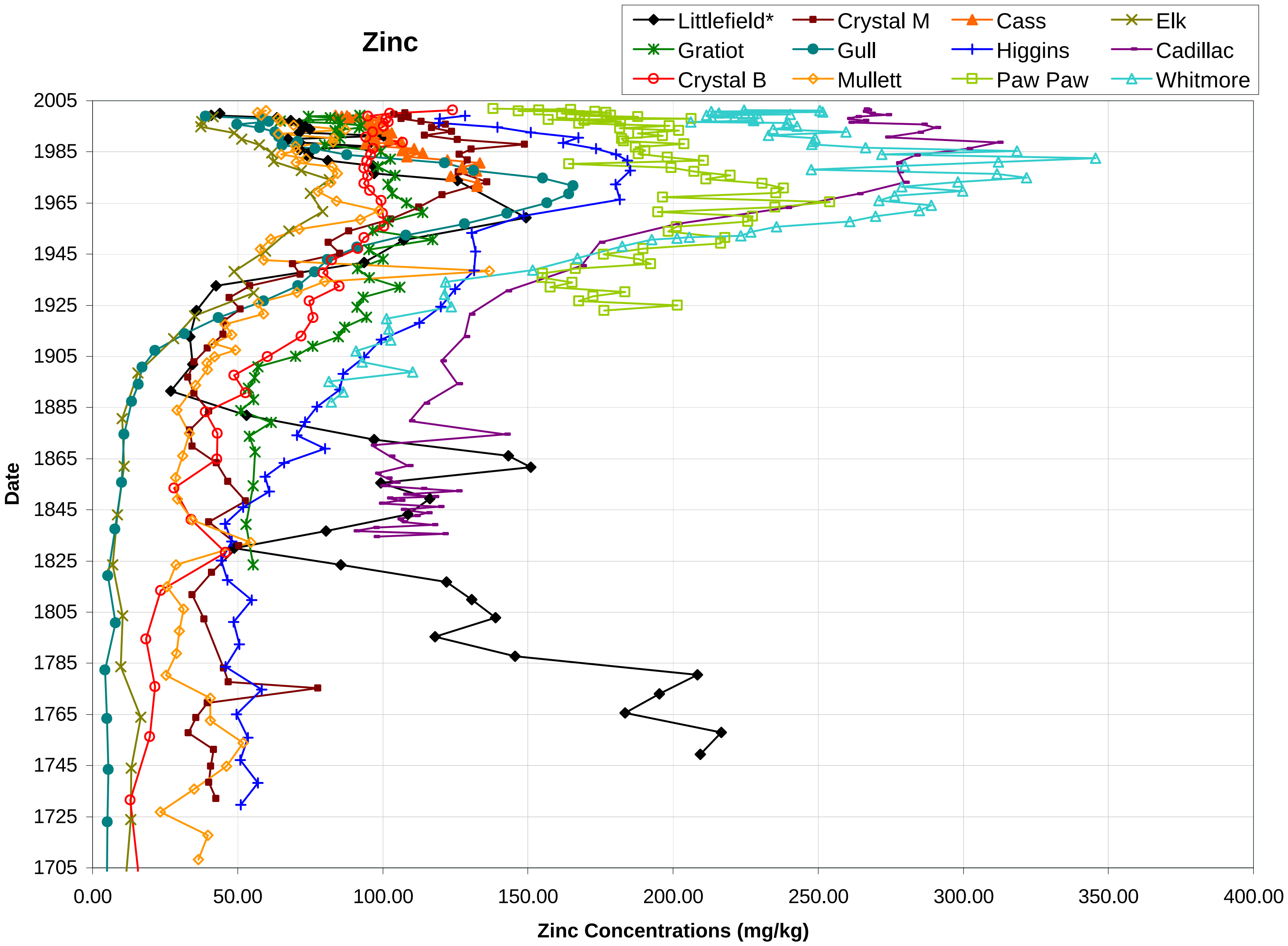

Fig. 15. Concentrations (mg/kg dry wt) of zinc in twelve Michigan lakes. *Dates for Littlefield Lake are estimations.

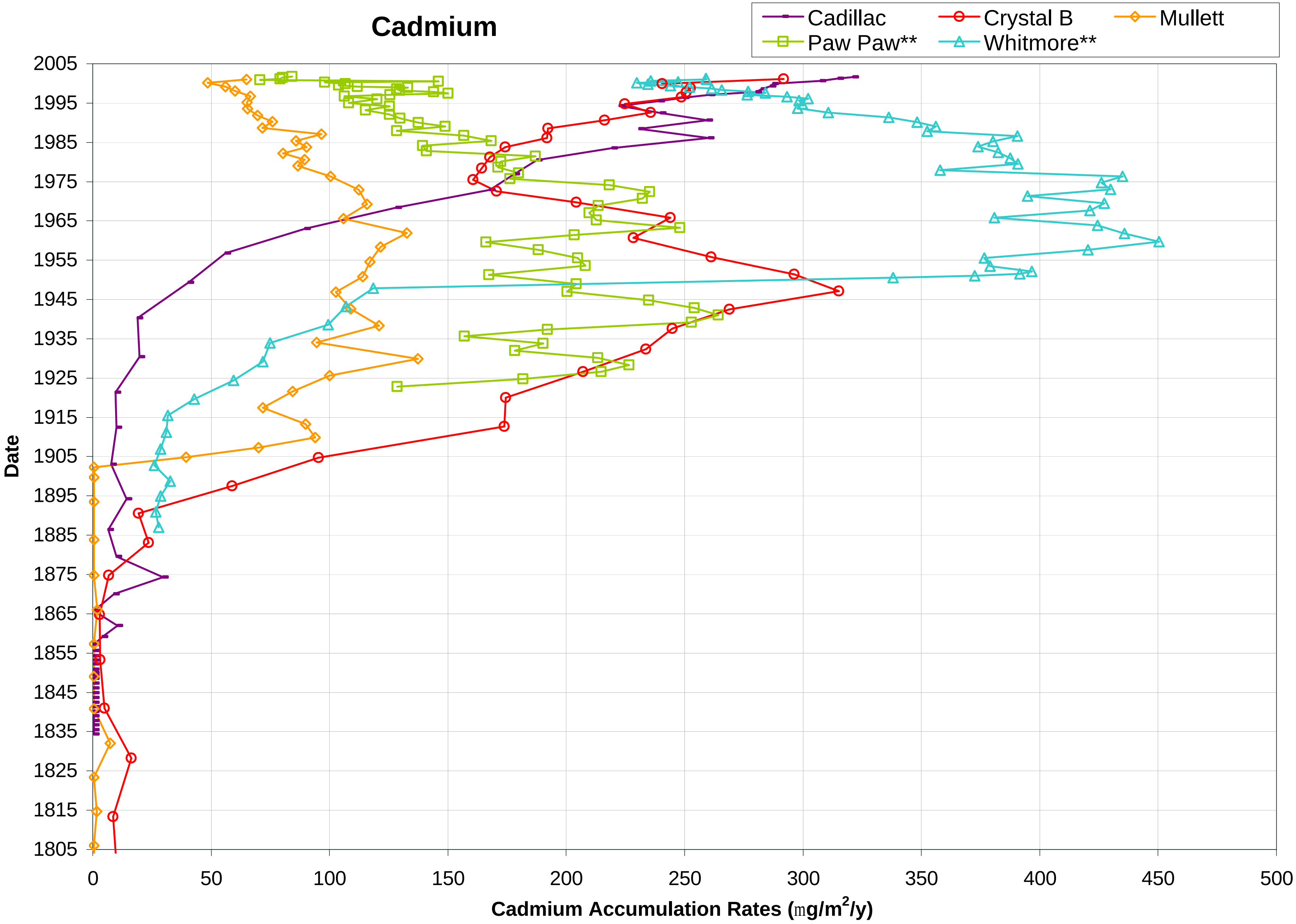

Fig. 17a. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of cadmium in five Michigan lakes. **Background values for Whitmore and Paw Paw Lakes are estimated.

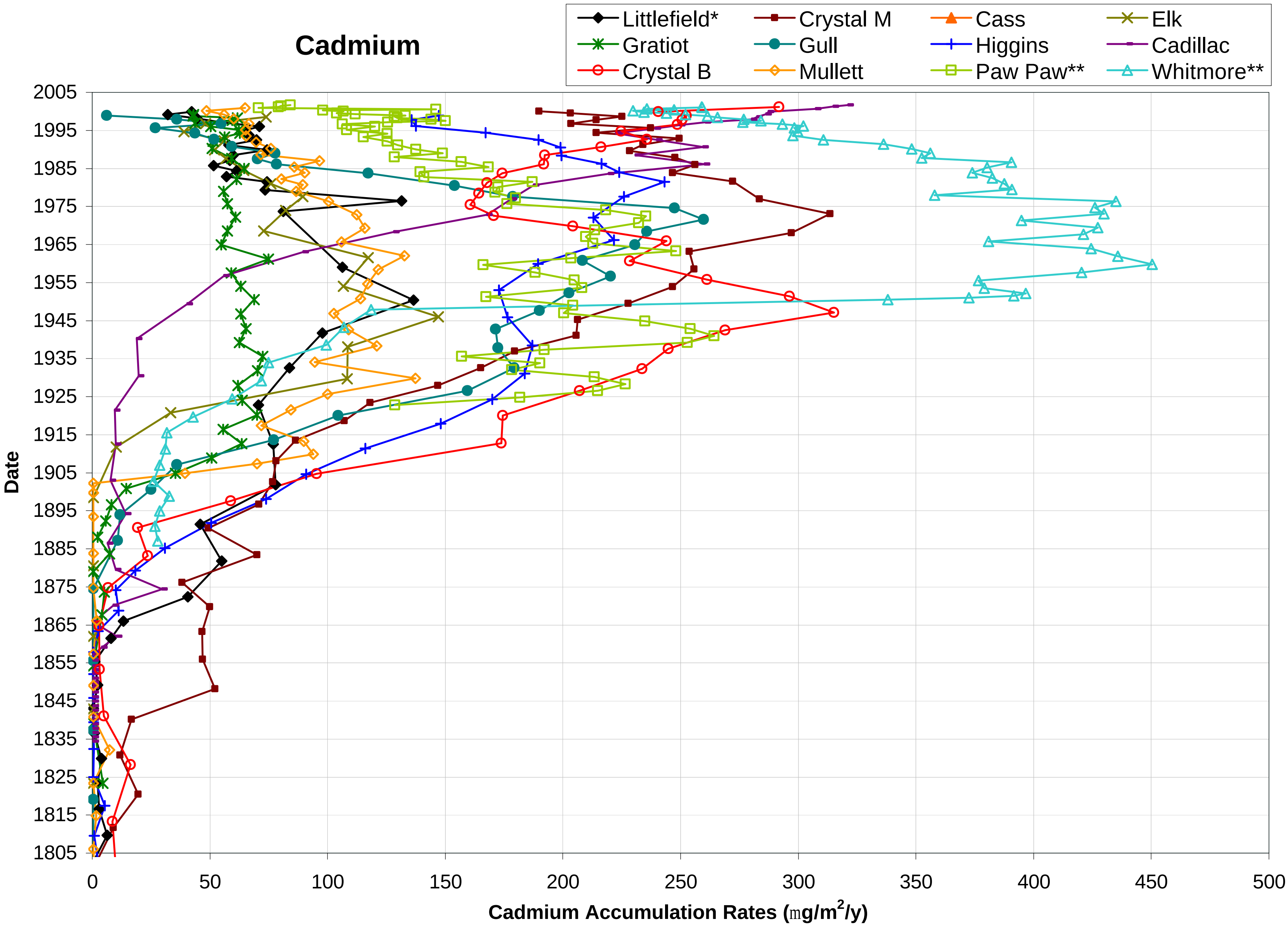

Fig. 17b. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of cadmium in twelve Michigan lakes. *Dates for Littlefield Lake are estimations. **Background values for Whitmore and Paw Paw Lakes are estimated.

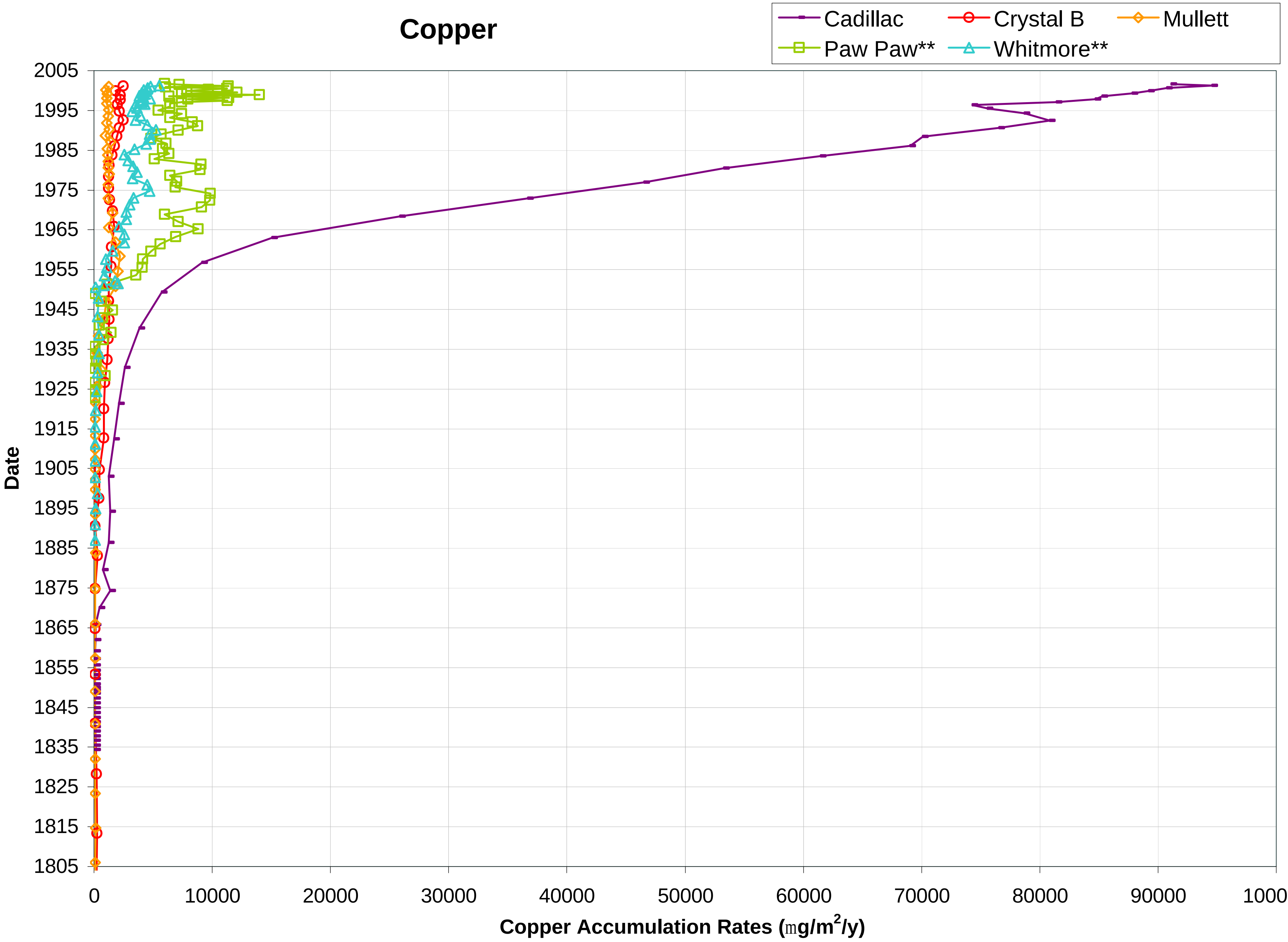

Fig. 18a. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of copper in five Michigan lakes. **Background values for Whitmore and Paw Paw Lakes are estimated.

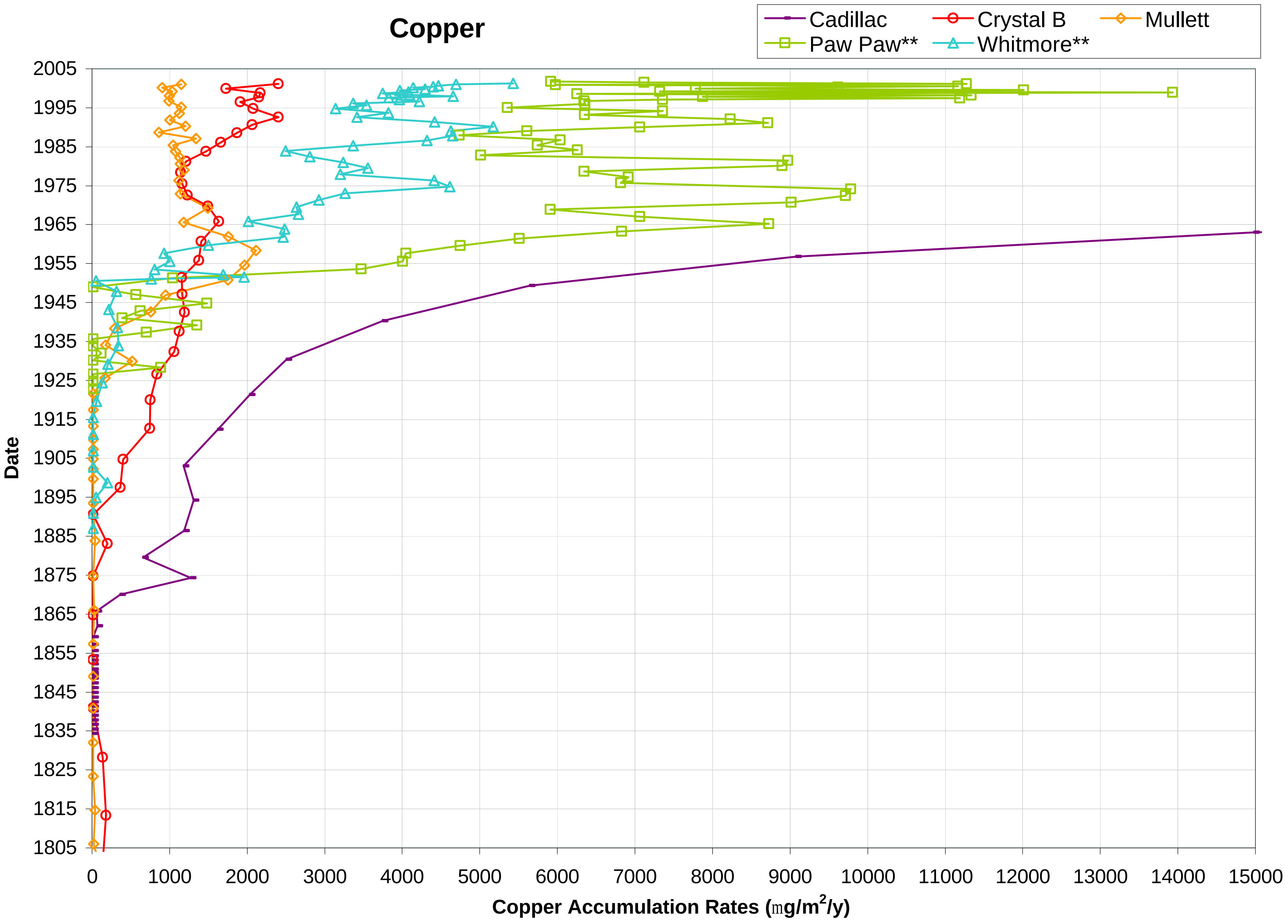

Fig. 18b. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of copper in five Michigan lakes, similar to Fig. 18a, with x-axis changed. **Background values for Whitmore and Paw Paw Lakes are estimated.

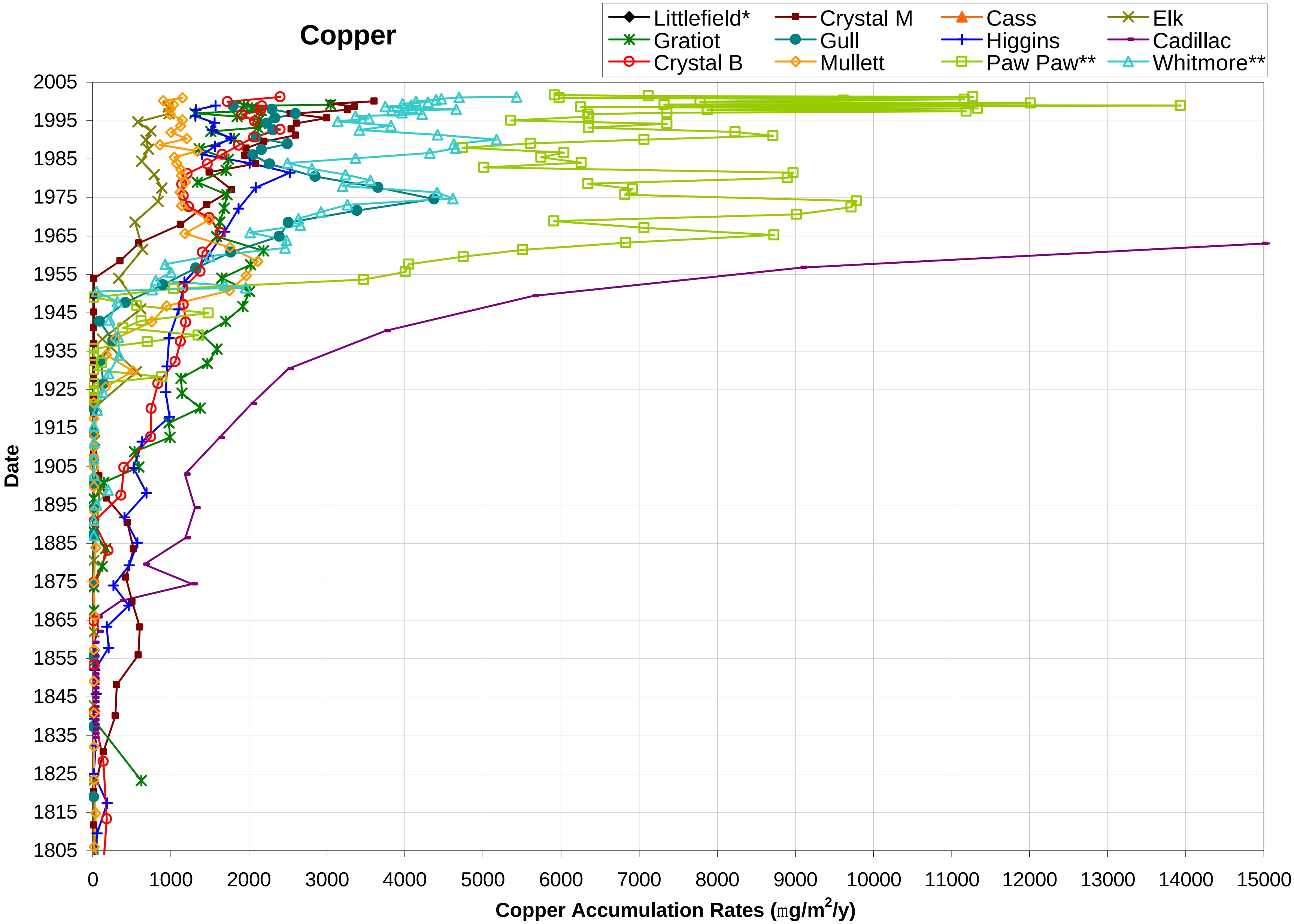

Fig. 18c. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of copper in twelve Michigan lakes. *Dates for Littlefield Lake are estimations. **Background values for Whitmore and Paw Paw Lakes are estimated.

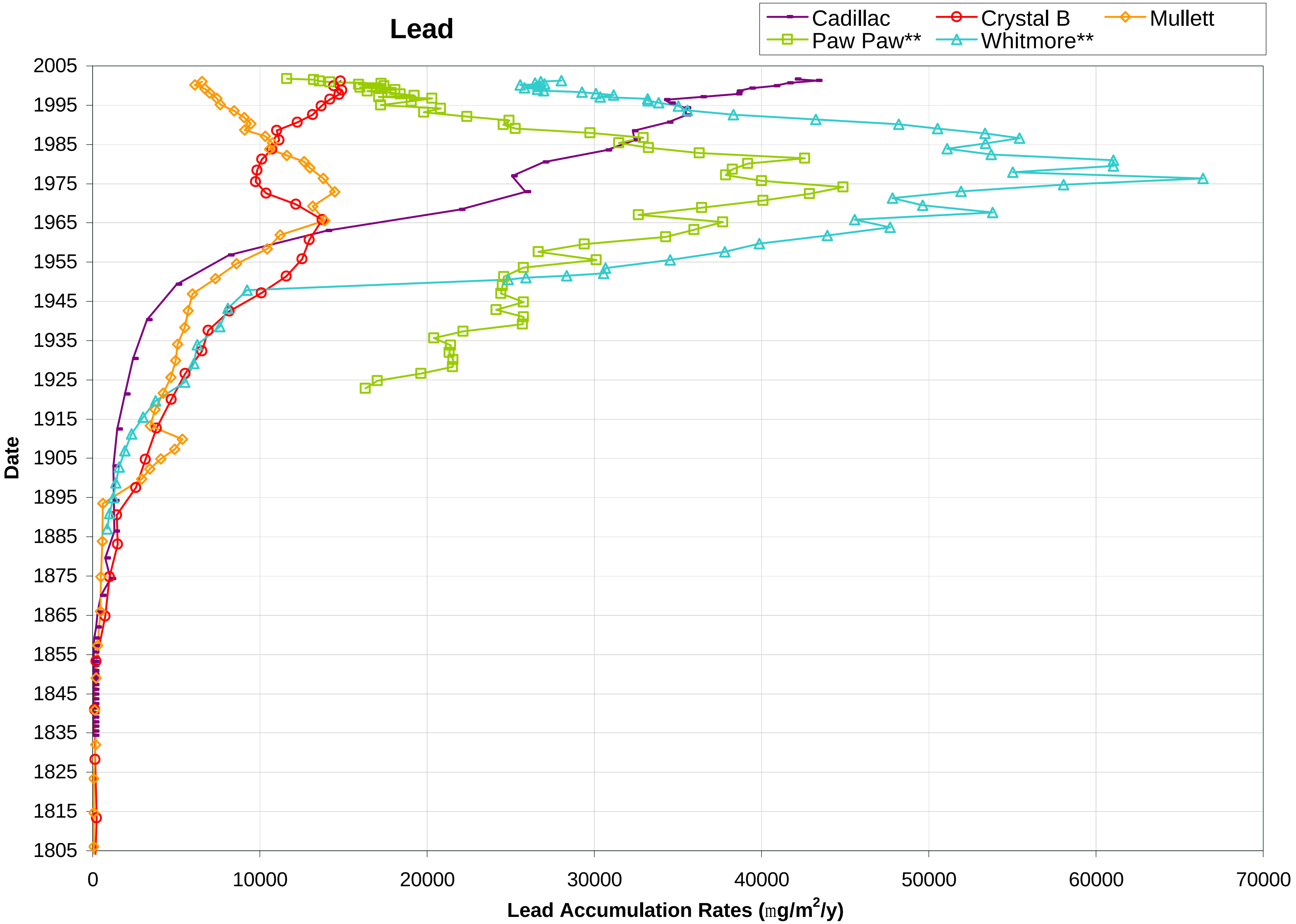

Fig. 19a. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of lead in five Michigan lakes. **Background values for Whitmore and Paw Paw Lakes are estimated.

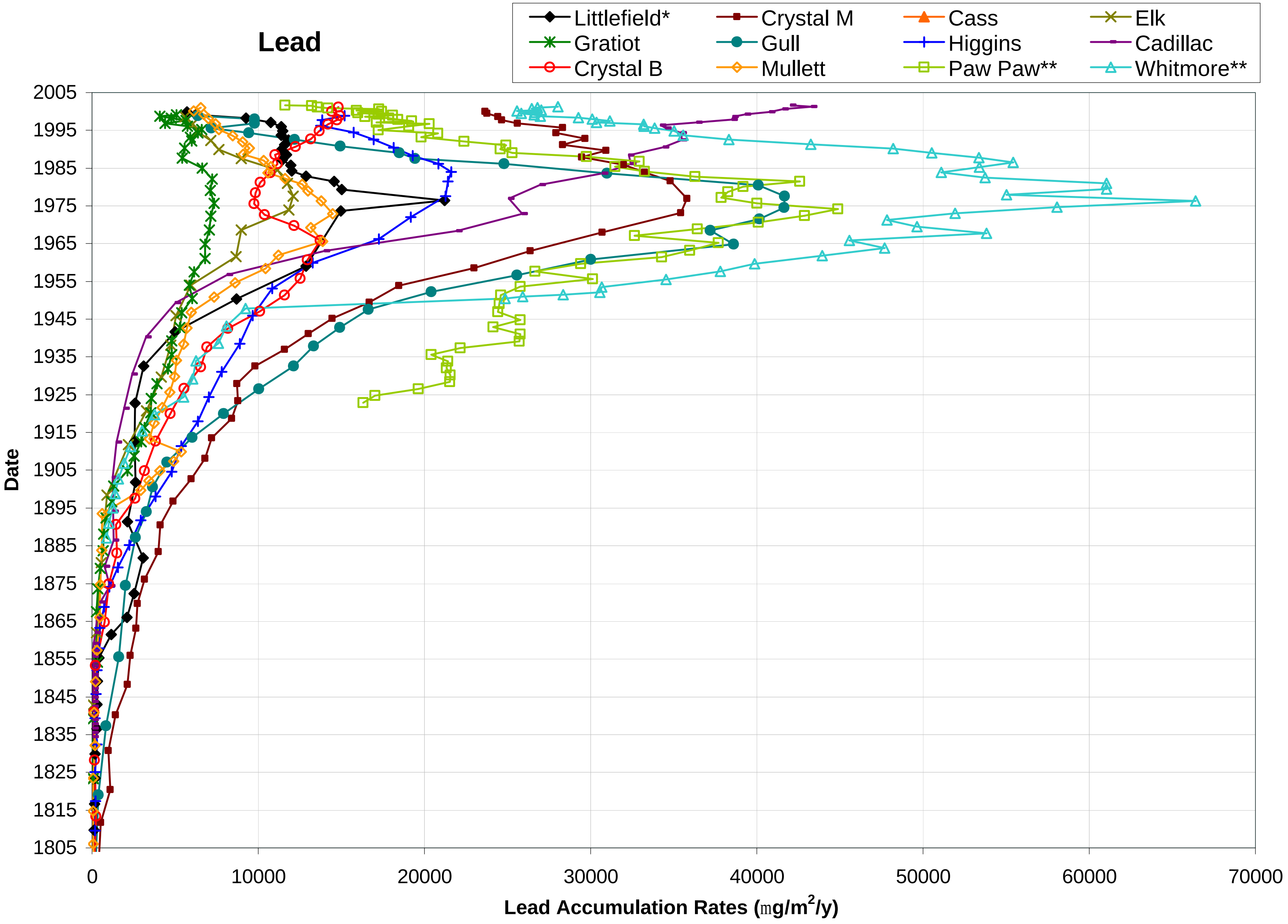

Fig. 19b. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of lead in twelve Michigan lakes. *Dates for Littlefield Lake are estimations. **Background values for Whitmore and Paw Paw Lakes are estimated.

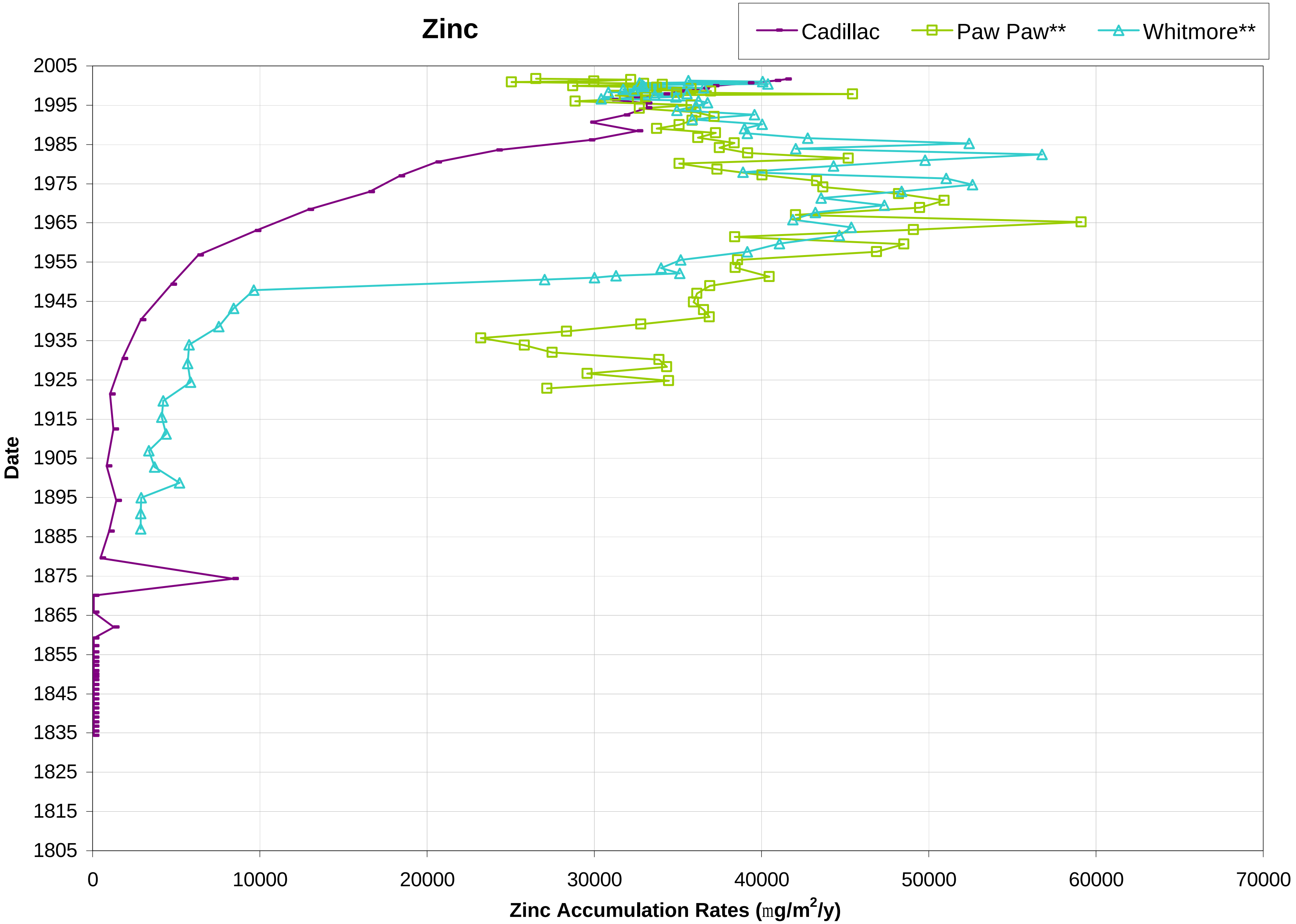

Fig. 20a. Focusing corrected anthropogenic accumulation rates (µg/m^2/y) of zinc in three Michigan lakes. Anthropogenic accumulation rates could not be calculated for Crystal B and Mullett Lakes. **Background values for Whitmore and Paw Paw Lakes are estimated.

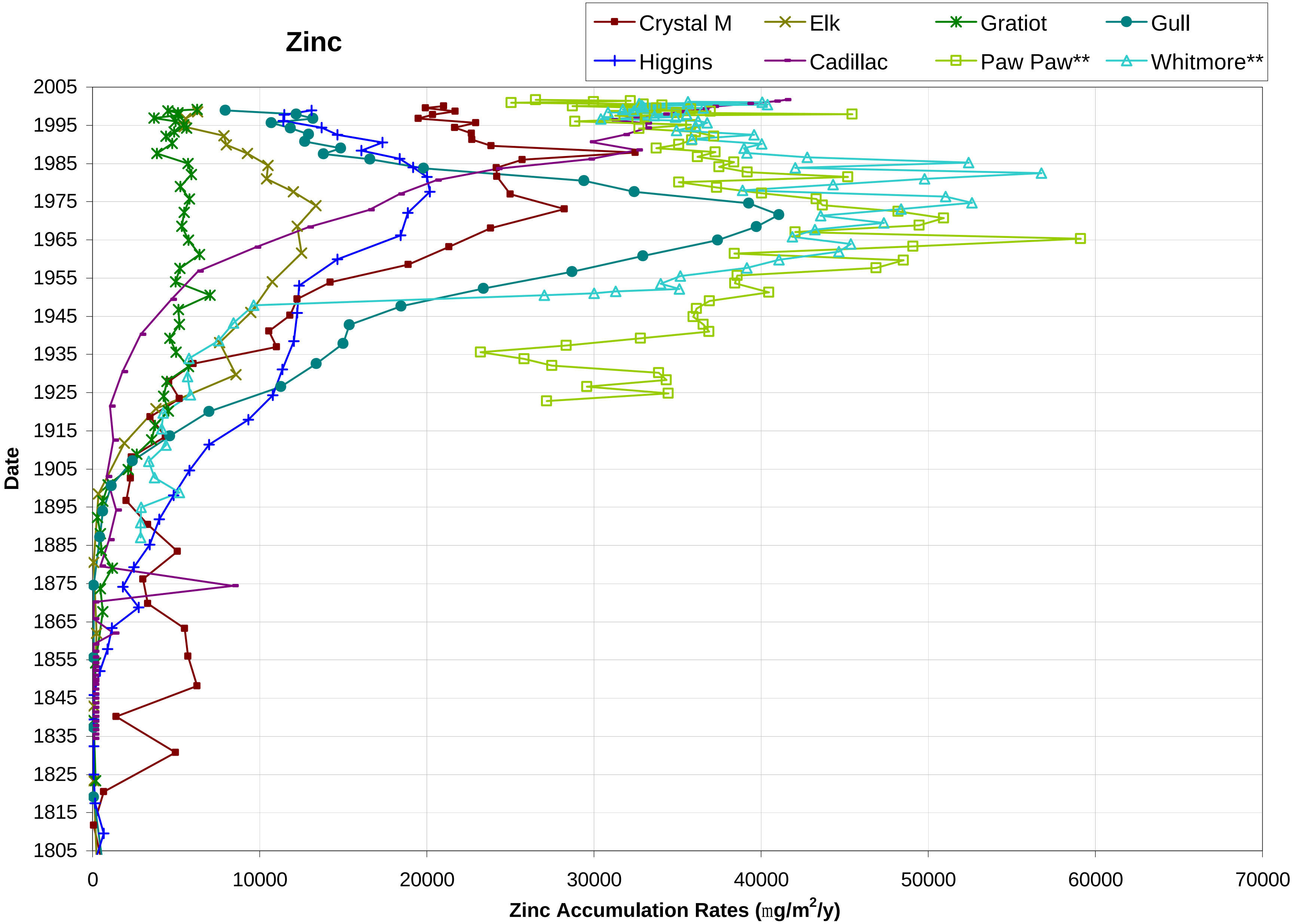

Fig. 20b. Focusing corrected anthropogenic accumulation rates (μg/m^2/y) of zinc in eight Michigan lakes. Anthropogenic accumulation rates could not be calculated for several lakes. *Dates for Littlefield Lake are estimations. **Background values for Whitmore and Paw Paw Lakes

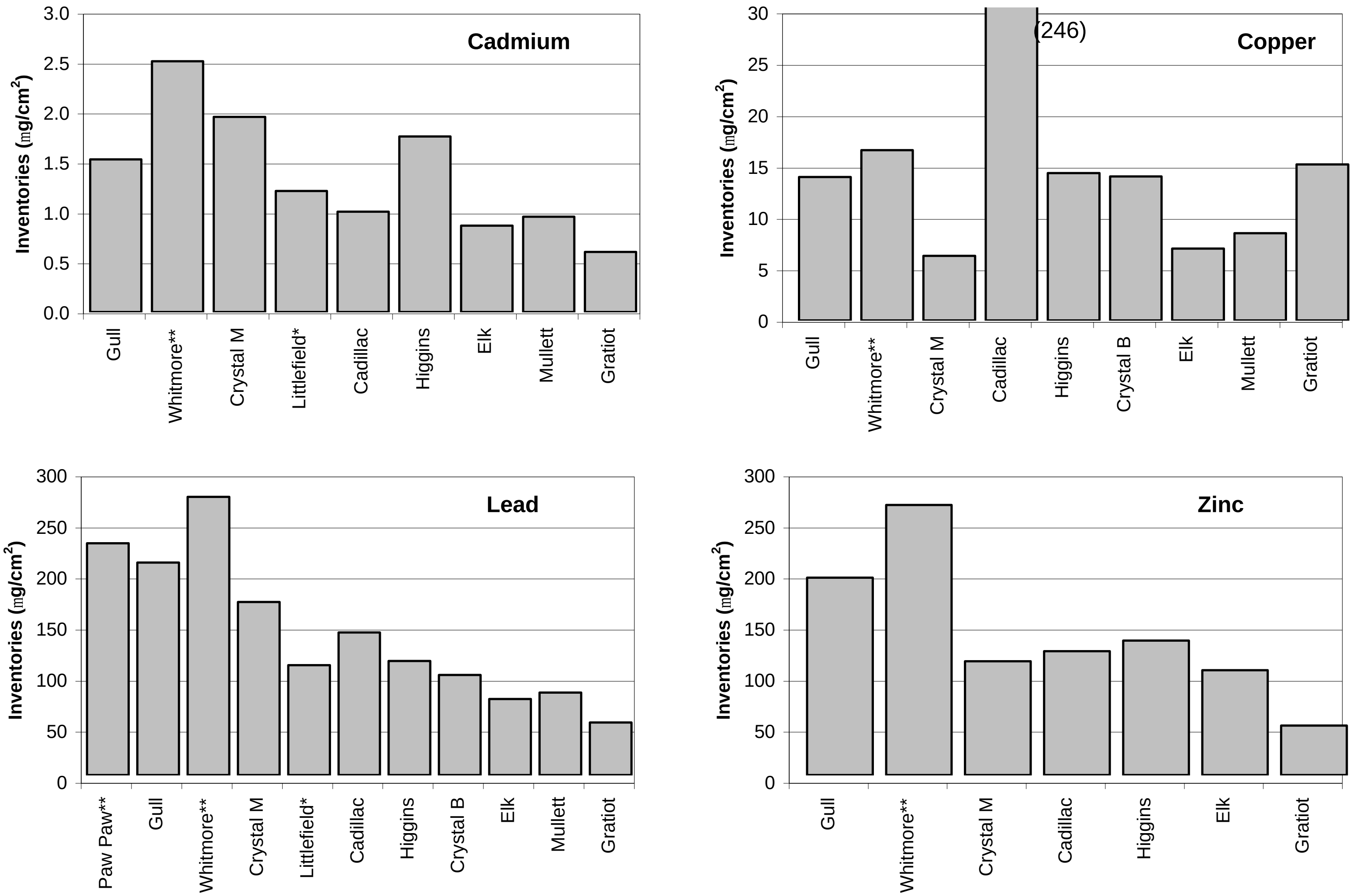

Fig. 21. Focusing corrected, watershed corrected anthropogenic inventories for four metals in Michigan Lakes. The inventory of copper in Cadillac Lake is 246 μg/cm^2, which is greater then the scale of the graph. *Focusing factor for Littlefield Lake was estimated.
** Background values for Paw Paw and Whitmore Lakes were estimated.