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TRACE-ELEMENT GEOCHEMISTRY OF PISTON CORES FROM WESTERN MICHIGAN COASTAL LAKES

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ABSTRACT

Thirty-four cores from 100 to 320 cm in length from western Michigan coastal lakes were analyzed for Cr, Cu, Zn, Mn, per cent volatile material, and sediment size. Lakes included in the study were Spring Lake, White Lake, Muskegon Lake, and Lake Macatawa representing areas of high and low industrial development. Industrialization is indicated by increases in Cr, Cu, and Zn concentrations toward the tops of most cores. Various industrial events of known time and origin can be correlated between cores and are used to establish sediment accumulation rates. Sedimentation rates vary between lakes and average from 1.1 to 3.0 cm/year.

Natural background concentrations of trace elements vary between core locations and within a given core and are apparently altered slightly by natural phenomena. Relative background concentrations of Cr, Cu, and Zn compare favorably with those of other areas. Enrichment of Cr, Cu, and Zn and changes in relative proportions of these elements reflect contamination by aerosols and/or industrial effluent. Aerosol contamination levels for the region are reflected by trace-metal enrichment within near-surface sediments collected from Spring Lake, which has no industry.

Interpretation of trace-element enrichment zones within sediment cores is dependent upon establishment of background levels for specific locations, determination of relative aerosol concentrations for the region, and sediment analysis of cores.

RÉSUMÉ

Trente-quatre carottes de 100 à 320 cm de longueur provenant des lacs côtiers de l'ouest de l'état du Michigan ont été analysées pour leur contenu en Cr, Cu, Zn, Mn, leur pourcentage de matériel volatile et leur dimension sédimentaire. Les lacs qui ont fait partie de l'étude sont les lacs Spring, White, Muskegon et Macatawa pour leur représentation des régions à fort et pauvre développement industriel. L'industrialisation se manifeste par une augmentation du Cr, Cu et des concentrations de Zn aux alentours des surfaces de la majorité des carottes. Divers événements industriels de temps et d'origine connus peuvent être apparentés aux carottes et sont utilisés pour établir les taux d'accumulation des sédiments. Les taux de sédimentation varient selon les lacs et ont une moyenne de 1.1 à 3.0 cm par année.

Les concentrations de fond naturelles des traces d'éléments varient selon la location des carottes et à l'intérieur même d'une carotte et sont apparemment légèrement transformées par des phénomènes naturels. Les concentrations de fond relatives de Cr, Cu et de Zn se comparent favorablement avec celles des autres régions. L'enrichissement de Cr, Cu et Zn et des changements relativement proportionnés de ces éléments sont une indication de la contamination par les aérosols et/ou par des effluents industriels. Les niveaux de contamination de la région par les aérosols sont représentés par l'enrichissement de traces de métaux à l'intérieur des sédiments presque superficiels ramassés du lac Spring, où il n'y a pas d'industrie.

L'interprétation des zones d'enrichissement d'éléments de trace à l'intérieur des carottes de sédiments dépend de l'établissement de niveaux de fond en des lieux spécifiques, de la détermination des concentrations relatives d'aérosols dans la région et de l'analyse sédimentaire des carottes.

(Traduit par le journal)

INTRODUCTION

Lake Macatawa, Spring Lake, Muskegon Lake and White Lake are all coastal inland lakes located along the southeastern shore of Lake Michigan (Fig. 1). A total of 34 piston cores ranging from 100 to 320 cm in length was taken from these lakes and analyzed for trace concentrations of Cr, Cu, Zn and Mn, per cent volatile material and sediment texture. Associated studies were done of the pollen and diatom assemblages in some cores (Fowke 1975; Dunning *et al.* 1975).

The purpose of the study was to use trace-element geochemistry as a chronologic tool for locating natural background as well as agricultural and industrial horizons within the sediment column. Correlation of trace-element horizons with known agricultural and industrial events enabled determination of average sedimentation rates for post-settlement periods in the various lakes.

TECHNIQUES

Sediment cores were taken with a modified piston corer from the Hope College Vessel *Hope I*. Each core was described, x-radiographed

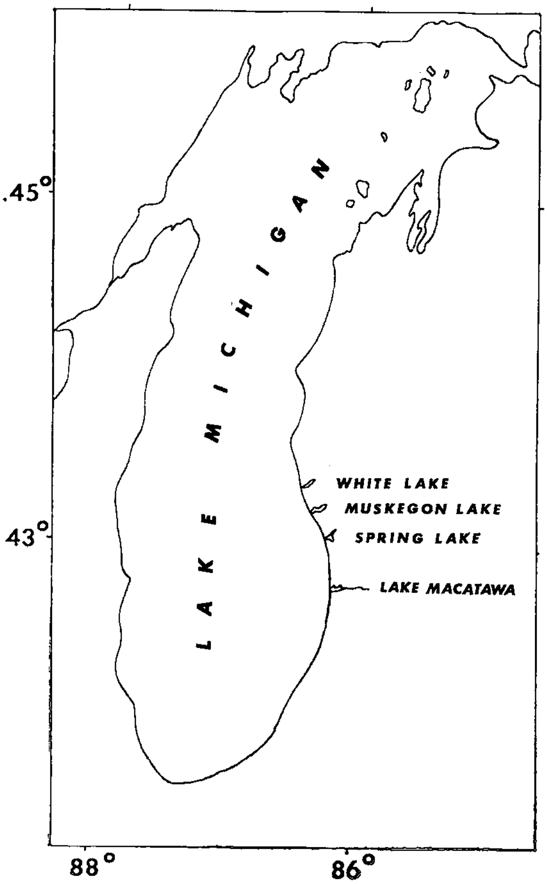

FIG. 1. Location of Lake Macatawa, Spring Lake, Muskegon Lake and White Lake.

to check for disturbed sections, split longitudinally and sampled at 10 cm intervals.

The technique used in preparation of samples was devised by Dr. David Klein of the Hope College Chemistry Department. One gram samples were treated with 0.5 ml commercial Clorox and 2.5 ml of 50% reagent strength nitric acid. The sample was heated until the reaction was completed and then centrifuged to remove the insoluble residue. The solution was diluted to a 50 ml volume with deionized water to yield a 2% concentration. Samples were analyzed with a Perkin Elmer Model 303 Atomic Absorption Spectrophotometer. The percentage of volatile material comprising each sample was determined by calculating the weight loss after combustion at 550 to 600°C for one hour.

DISCUSSION

Background concentrations of the four elements studied were found near the bottoms of some cores taken from each lake. These precontamination levels were defined by low concentrations of Cr, Cu, and Zn, generally less than 100 ppm, whereas naturally-high Mn concentrations ranged from 150 to 700 ppm. Natural background concentrations of Cr, Cu and Zn were consistent in that, in most cases, Cu was more abundant than Cr and Zn was the most abundant of the three.

Natural background levels of all four elements vary between lakes and within any given core. Manganese is naturally abundant and its concentration, along with that of the volatile material and the texture of the sediments, is largely controlled by the energy regime of the depositional environment. Figure 2 shows that Mn concentrations and per cent organics, as estimated from the volatile concentrations, are low in sandy, high-energy areas and are relatively higher in the low-energy, muddy areas. The levels of Cr, Cu, and Zn are also influenced in the same manner, but this phenomenon is not so apparent due to contamination and the lesser natural concentrations.

Development within the four lake basins ranges from that of a highly agricultural and industrial Lake Macatawa basin to that of Spring Lake whose natural setting has been altered only slightly. Using trace-element concentrations, the natural background, as well

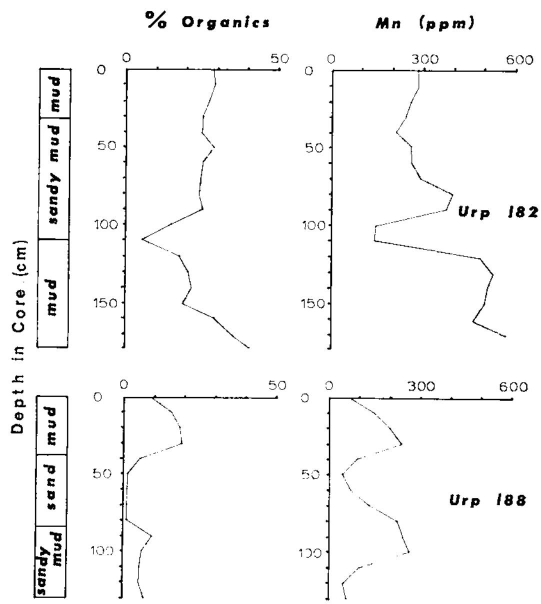

FIG. 2. Correlation between sediment texture, per cent organics, and Mn concentrations in selected cores from Lake Macatawa.

as agricultural and industrial horizons, were identified in sediment cores. An agricultural horizon was only observed in Lake Macatawa deposits. Cores from all of the lakes can be subdivided into background and contaminated layers (Fig. 3).

The near-natural condition of Spring Lake is seen in Core Sp 17 (Fig. 4) as background is reached only 10 cm below the surface. Between 10 cm and the surface Cr, Cu and Zn increase significantly, probably as a result of aerosol contamination by the Consumers Power plant along the Grand River (Klein, personal communication). An average sedimentation rate of less than 0.5 cm/yr. was determined for core Sp 17. Core Sp 19 is contaminated to a depth of 40 cm, indicating a somewhat higher rate of sedimentation (1.0 cm/yr). This core was taken closer to the source of the suspected pollutant and closer to the Grand River

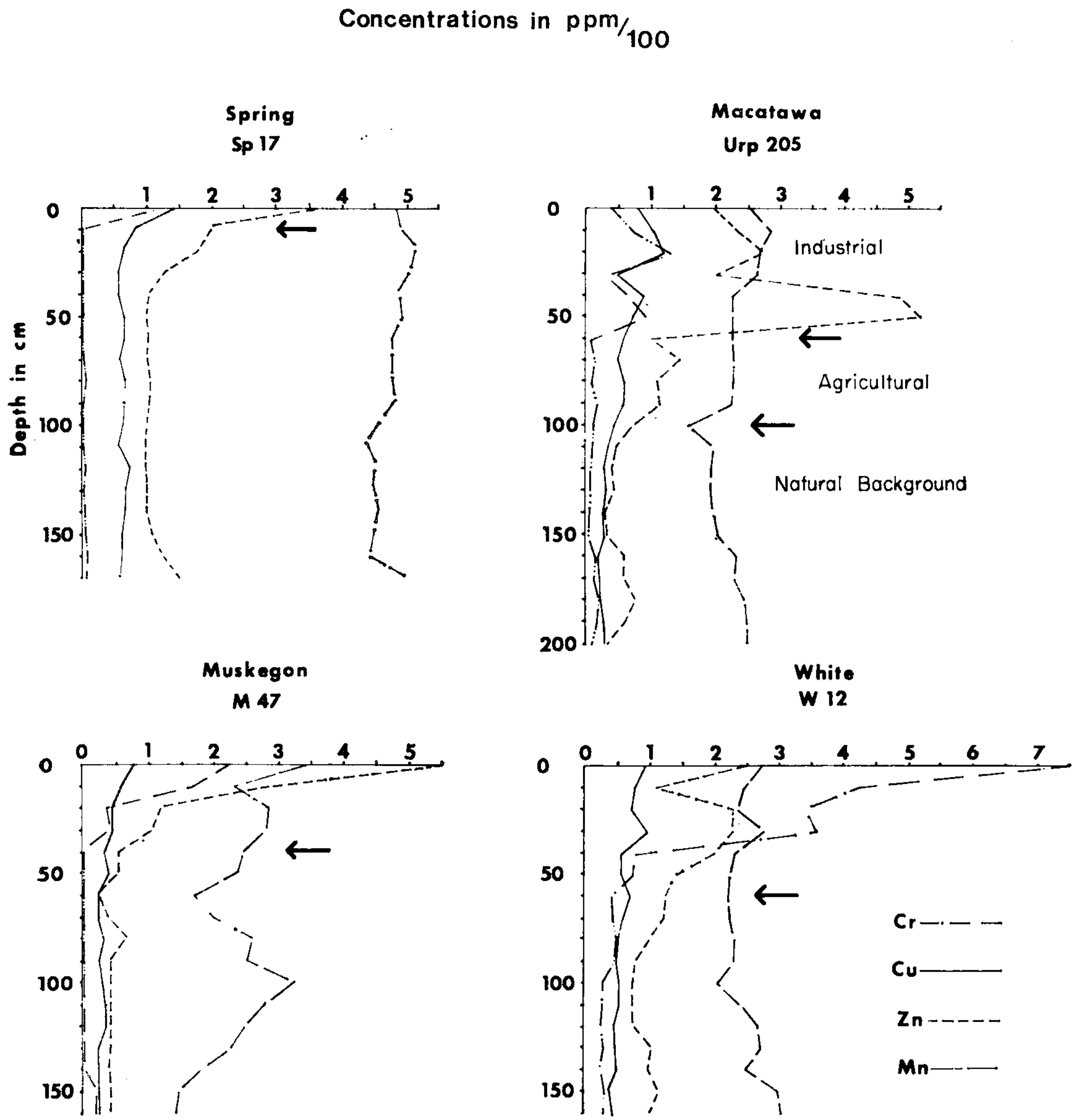

FIG. 3. Selected cores from Spring Lake, Lake Macatawa, Muskegon Lake and White Lake showing natural background, agricultural (Urp 205) and industrial horizons. Arrows indicate natural background industrial and agricultural horizons.

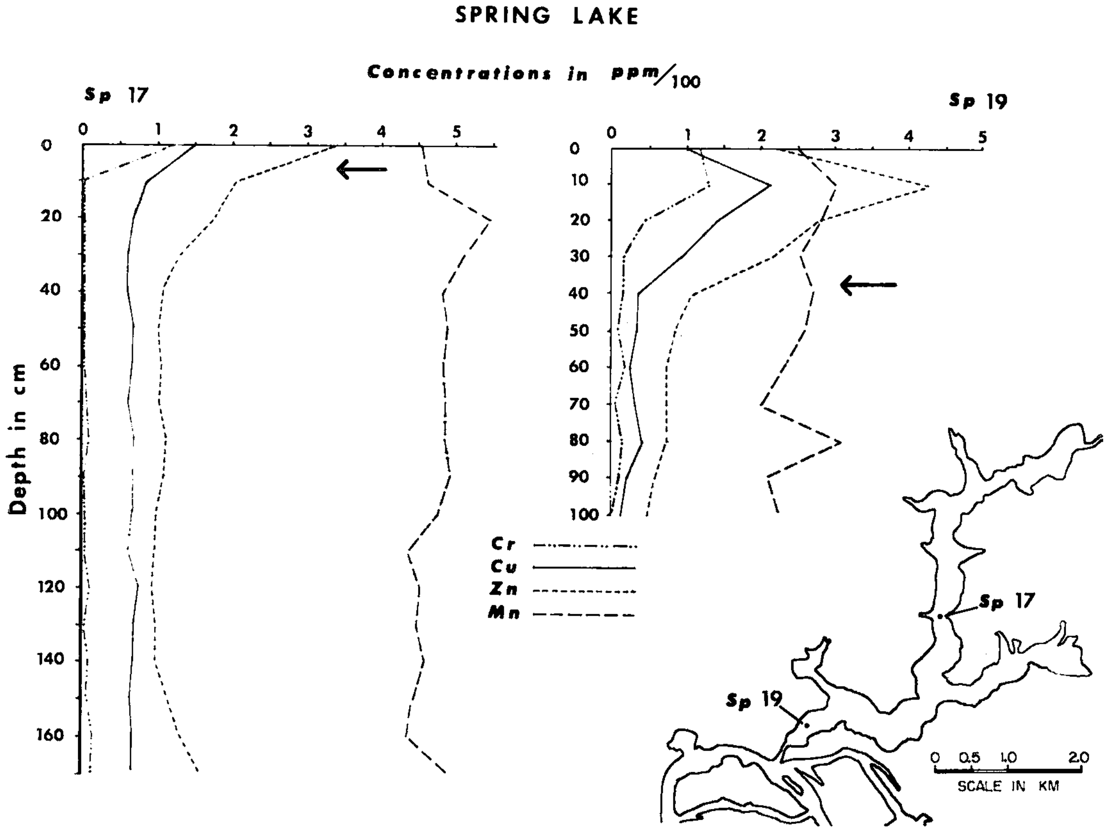

FIG. 4. Spring Lake; core locations and trace-element concentrations versus depth in core in cm. Arrow indicates industrial horizon.

from which it may receive some sediments and/or contaminants. Water-quality information for the Grand River is not available, however, and its principle direction of flow is past, rather than into the lake.

Muskegon Lake, like White Lake and Spring Lake, has very little agriculture in its drainage basin. There is, however, significant industry located near the lake including a power plant, foundry and refineries. Enrichment of trace elements in the top 90 cm of core M 49 and the top 40 cm of core M 47 (Fig. 5) results from industrialization. The average sedimentation rate in the area of core M 49 is in excess of 2.5 cm/yr., and in the area of core M 47 a rate of approximately 1.0 cm/yr. was determined. This is a substantial difference within a small area of the lake.

White Lake is similar to Muskegon Lake in that it receives effluents from several industries, and its drainage basin consists predominantly of sandy deposits. Cores W 08 and W 01 were taken in areas some distance from industrial sites (Fig. 6). Core W 12 was taken near Hooker Chemical Company which began operation in 1953. This event can be correlated with a sharp increase in Cr and Zn in the upper 60 cm of the core, from which an average sedimentation rate of 3.0 cm/yr. was determined. The Whitehall Leather Company began using dichromate salts in its tanning process in 1944. Cr contamination is evident in the upper 30 cm of core W 09 and concentrations of more than 1900 ppm occur at the surface. Using this core, a sedimentation rate of 1.0 cm/yr. was established for this area.

Core W 08 was taken slightly more than 1.5 km from core W 09 and shows essentially no enrichment of Cr and Zn, indicating that these particular trace elements were not transported far from the point of introduction. Core W 01, located in the extreme western portion of the lake (Fig. 6) is enriched in Zn near the surface. These concentrations are higher than measured anywhere else in White Lake, and as yet the source is not identified.

Lake Macatawa was the most extensively studied of the four lakes. In all, 23 piston cores taken from this lake were analyzed for their trace-element geochemistry. Lake Macatawa is highly industrialized like White Lake and Muskegon Lake, and about 65% of its drainage basin is presently used for agriculture. Consequently, an agricultural horizon is seen below the industrial horizon. The introduction of Cu, and particularly Zn, into the lake as a result of the use of pesticides and fertilizers (Hesse & Evans 1972) can be seen at about 100 cm in core Urp 205 (Fig. 7) and follows a significant down-core change in the ambrosia/vesticulate pollen ratio (Fowke 1975). The change from primarily vesiculate to primarily ambrosia indicates replacement of woodlands around the lake by clearings, presumably farmland, sometime near the turn of the century. Further enrichment of Cr, Cu, and Zn at approximately 60 cm in core Urp 205 represents the industrial period which began about 40 years ago.

Core Urp 195, taken in the eastern portion of the lake near the former effluent discharge of Holland Suco (Fig. 8) shows industrial contamination throughout its 150 cm length. From this core a sedimentation rate of greater than 3.5 cm/yr. for this area was computed. Sedimentation rates from other cores in this area were as high as 5.3 cm/yr. and generally de-

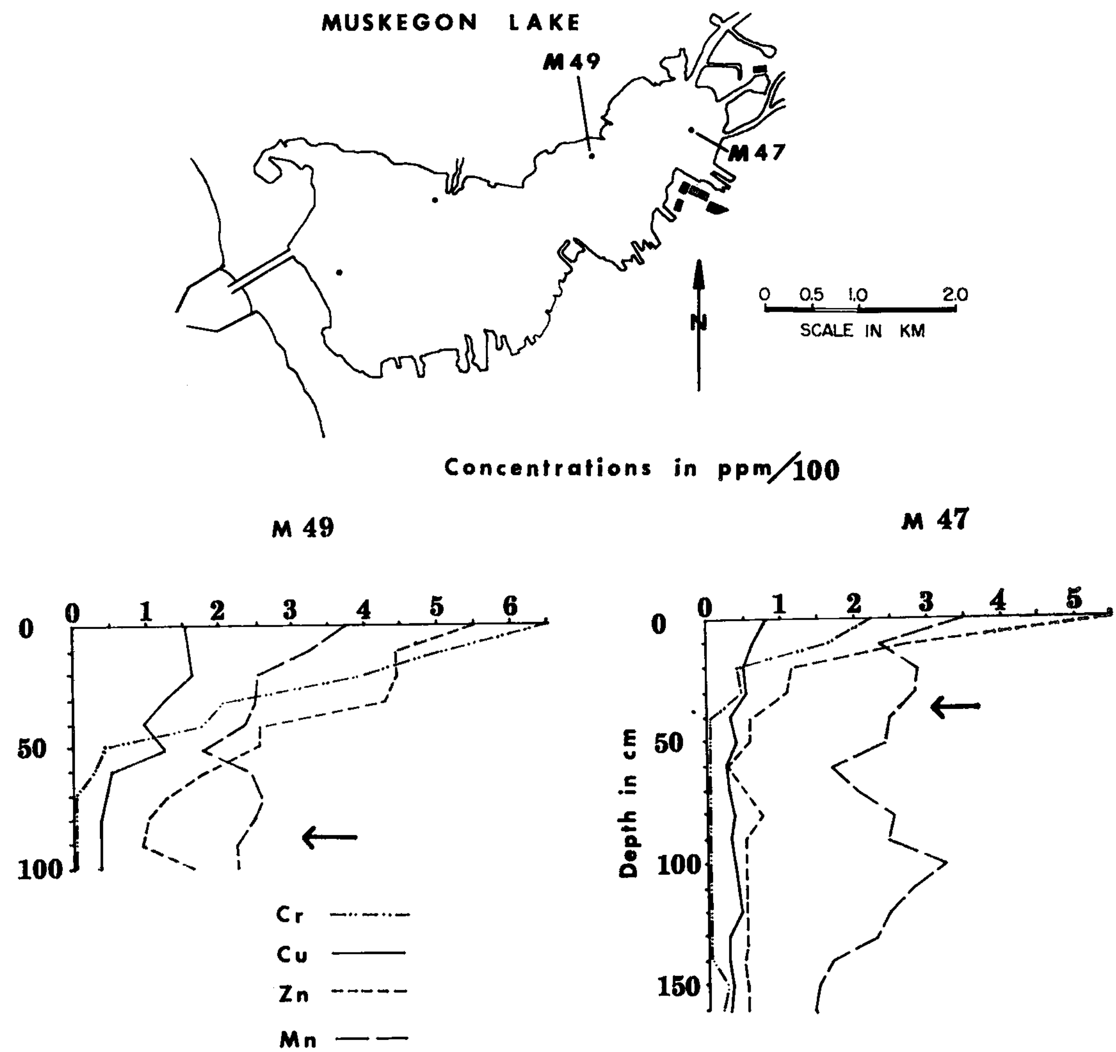

FIG. 5. Muskegon Lake; core locations and trace-element concentrations versus depth in core in cm for selected cores. Arrow indicates industrial horizons.

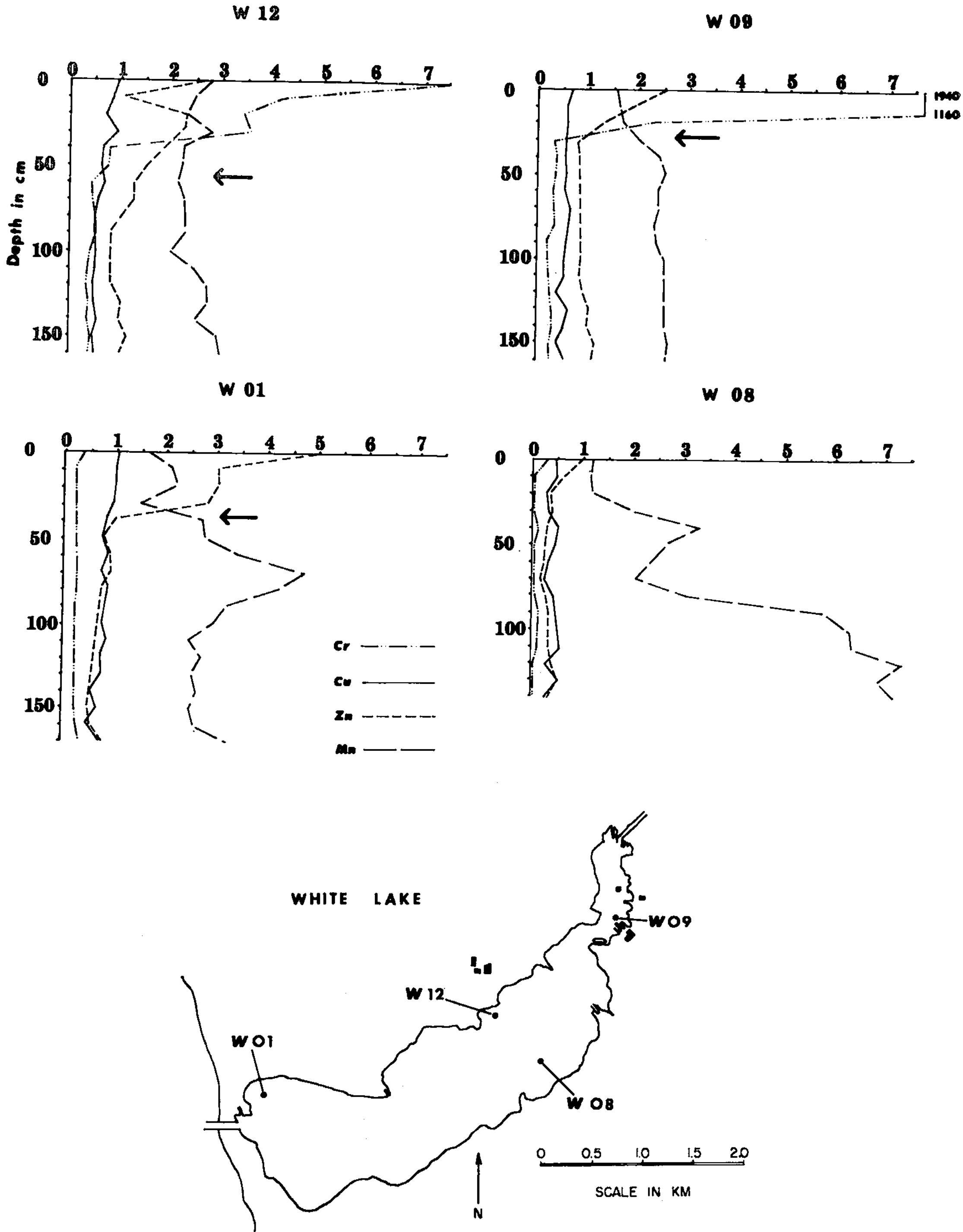

FIG. 6. White Lake; core locations and trace-element concentrations versus depth in core in cm. Arrow indicates industrial horizon.

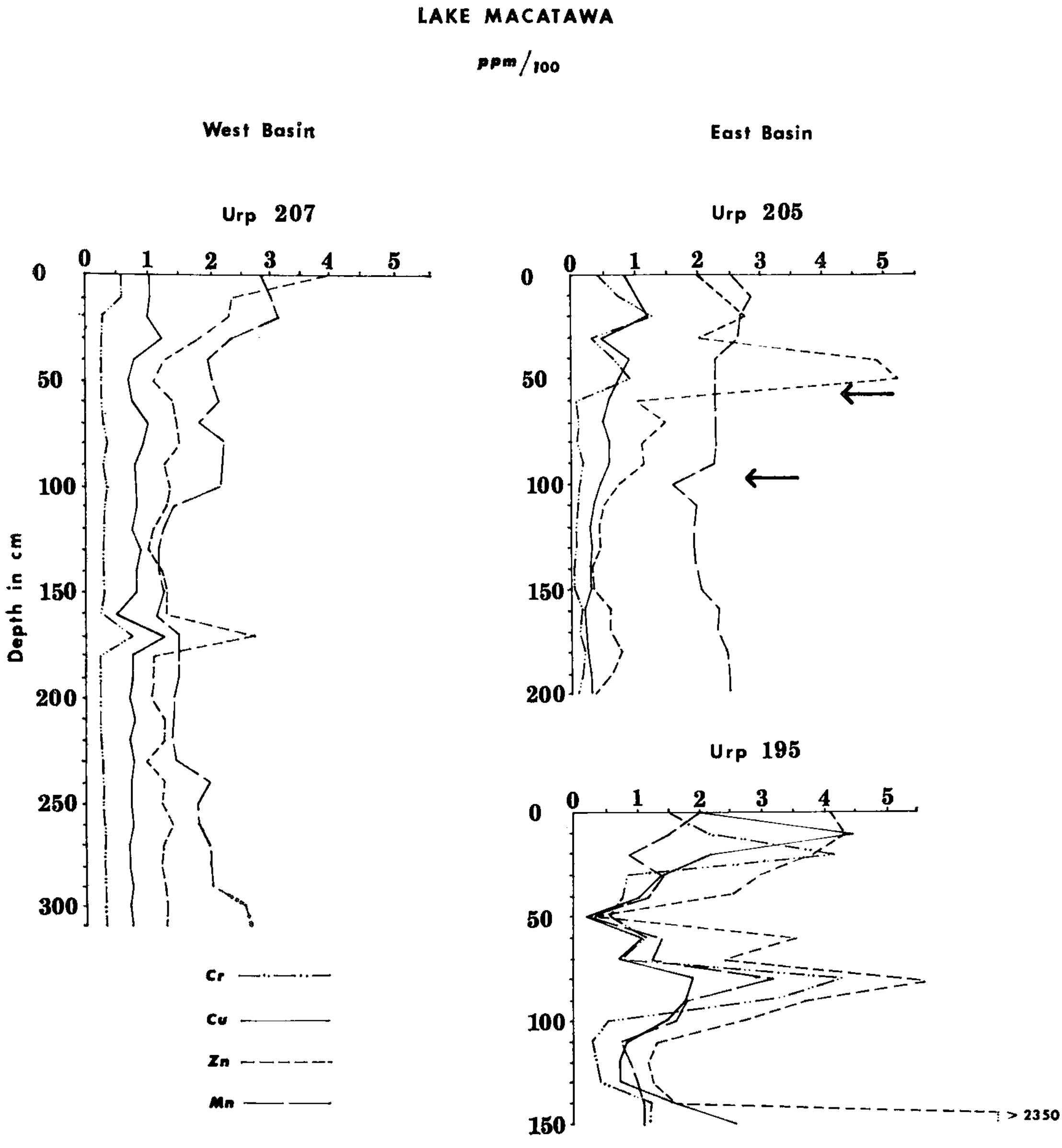

FIG. 7. Trace-element concentrations versus depth in core in cm. Arrows indicate agricultural and industrial horizons.

crease with distance from the source of contamination (Fig. 8). It is suspected that the cause of high sedimentation rates near the sewage outlet is electrochemical flocculation of suspended clays.

Sedimentation rates are generally lower in the western portion of the lake and average 1.5 cm/yr. Core Urp 207 for example, has an industrial horizon at 40 cm which yields a sedimentation rate of 1.0 cm/yr. The higher rates of the eastern portion of the lake, averaging 3.2 cm/yr, reflect proximity to the Black River which is the major source of sediment entering the lake. Reliable quantitative water-quality information is not available for the Black River.

The over-all sedimentation rate for Lake Macatawa is close to 3.0 cm/yr. This is high relative to the other three lakes. Both Muskegon

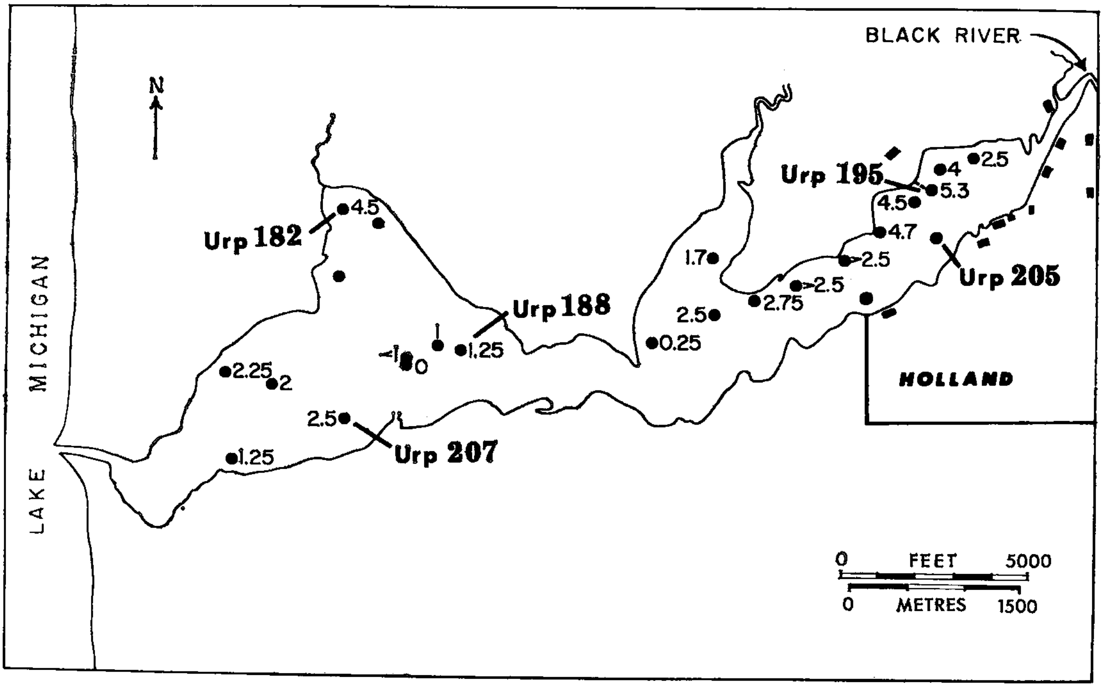

FIG. 8. Lake Macatawa; sedimentation rates in cm/yr (as determined from trace-element analysis of cores) and selected core locations.

Lake and White Lake have average sedimentation rates of 1.4 cm/yr. and Spring Lake has an average sedimentation rate of 1.1 cm/yr. Lake Macatawa's substantially higher rate of sedimentation is due first to the great amount of fine clastic material entering the lake as a result of agricultural activities in the Black River drainage basin, and less importantly, electrochemical flocculation of these fine terrigenous materials in the eastern part of the lake.

Conclusions

Trace-element geochemistry is an effective geochronologic tool for investigation of the effects of recent historical development in an area and for determination of sedimentation rates in a given locality. However, background levels of trace elements vary between lakes and even between core locations within a single lake. Aerosol and effluent concentrations will also vary depending upon the location of the lake and the sources of the pollutants. The energy regime of the depositional area will have an effect on quantities of trace elements deposited. Therefore, interpretation of trace-element concentration fluctuations down core is dependent on establishment of background levels for specific locations, determination of relative aerosol concentrations for the region, and sediment analysis of the cores.

Natural background levels were established in each lake and agricultural or industrial horizons were identified in the cores. Due to the predominantly sandy soils of the Spring, Muskegon Lake and White Lake drainage basins, agriculture is not significant in these areas. The fine-textured, highly organic soils of the Lake Macatawa basin are extensively farmed. An agricultural horizon is identifiable in Lake Macatawa sediment cores and predates the industrial horizon. Industrial horizons were identified in sediment cores from all four lakes and correlated with known industrial events or periods of industrialization. Average sedimentation rates as determined from trace element horizons are as follows:

Lake Macatawa	3.0 cm/yr	Muskegon Lake	1.4 cm/yr
Spring Lake	1.1 cm/yr	White Lake	1.4 cm/yr

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REFERENCES

DUNNING, C., SHEPLEY, S., WHEELER, R. & ANDERSON, J. B. (1975): Sedimentary, geochemical and fossil diatom analysis of sediment cores from Lake Macatawa: an assessment of man's impact. *Can. Mineral.* **13**, 307.

FOWKE, M. (1975): Pollen as a tool in the reconstruction of Lake Macatawa's more recent history. *Michigan Acad. Sci. Arts Letters Program 1975*, 32.

TESSE, J. L. & EVANS, E. D. (1972): Heavy metals in surface waters, sediments and fish in Michigan. *Michigan Water Resources Commission, Bur. Water Management, Dept. Nat. Res.*, 5-10.

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