

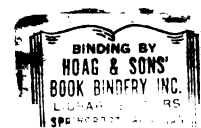
DISTRIBUTION OF SELECTED METALS
IN WATER AND SEDIMENT NEAR
THE WESTERN SHORE OF LAKE ERIE

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ABSTRACT

DISTRIBUTION OF SELECTED METALS IN WATER AND SEDIMENT NEAR THE WESTERN SHORE OF LAKE ERIE

The purpose of this research has been to define the behavior of selected trace elements (cobalt, iron, manganese, strontium, and zinc) in water and sediment along the western shore of Lake Erie. Spatial and seasonal variations during 1973 were observed in a small creek, Swan Creek, and in the lake adjacent to the mouth of the creek.

Major elements (calcium, chloride, sodium, and potassium) and all minor elements except zinc typically showed higher water concentrations in Swan Creek than in the lake, and minor and unsystematic variation among the lake stations. All major elements revealed statistically significant ($\alpha = .05$) seasonal variation, with calcium and strontium showing depressed levels during summer months, related to changes in primary productivity. Sodium, potassium, and chloride showed simultaneous, but otherwise irregular seasonal variation. Trace metals were characterized by high concentrations in April and June, then a sharp decline during summer months and gradually increasing levels in October and December. Factors controlling trace metal levels are uncertain.

Concentrations of all five trace elements in sediment were closely related to clay and organic content of sediments, with the log of metal concentrations proportional to the log of clay and organic content, and all correlations significant at the $\alpha = .01$ level.

Seasonal variations in the metal content of sediments were apparently lacking except for strontium, which was characterized by high summer concentrations and lower levels during autumn. Spatial variation reflected particle composition of sediments and the influence of the Detroit River, with relatively high metal levels at stations closest to the mouth of the Detroit River and lowest relative levels in Swan Creek which are unaffected by metal inputs from the Detroit River.

DISTRIBUTION OF SELECTED METALS IN WATER AND SEDIMENT
NEAR THE WESTERN SHORE OF LAKE ERIE

By

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INTRODUCTION

Continued improvements in power reactor technology, coupled with developing fossil-fuel shortages, suggest that nuclear power will play an increasing role in meeting rising electrical demands. Before nuclear power can play such a role however, public and scientific concerns about the safety of nuclear facilities must be answered. In addition to fears about core containment, one of the greatest areas of concern is the release of radioactive liquids to the aquatic system, primarily with cooling water. Current designs are intended to minimize radioactive waste discharges, but some low-level releases are unavoidable, due to leaks, activation of materials in cooling water and intentional releases of very dilute liquid waste. As nuclear facilities proliferate, it becomes increasingly important that we have a complete understanding of the fate of radioactive discharges within the aquatic system.

This study, sponsored by the Detroit Edison Company, is part of the preoperational study for the Fermi II nuclear generating station, now under construction by Detroit Edison on Western Lake Erie near Monroe, Michigan. The Fermi study is intended to predict the fate of individual isotopes which will be released when the facility begins operation, and to monitor releases during operation to determine whether the fate of these releases is similar to the predictive model.

One approach which has been developed for making a priori predictions of the fate of radioisotopes in an environment involves use

of the specific activity hypothesis (Nelson, et al., 1972; Kaye & Nelson, 1968). Specific activity refers to the ratio of radioisotope to total isotope. The specific activity hypothesis is based upon the presumption that biochemical and physiochemical processes do not discriminate between radioactive and stable isotopes of a given element; accordingly if stable and radioactive isotopes of an element are of a similar chemical form and are well mixed within a system we expect their dynamics and steady-state distribution within that system to be virtually identical. By determining the stable isotope distribution of an element within a system, we can predict the eventual fate of a radioisotope discharge of that element within the system. In other words, at equilibrium, the radioisotope/total isotope ratio for that element will be equal in all components of that system. This relationship is complicated by several factors, such as mass differences between stable and radioactive isotopes, physical decay of radioisotopes, biological uptake and elimination rates, and inconstant characteristics of the receiving system. The nature of the system which receives an effluent becomes critical in an open system such as Fermi, in which a relatively small plume will contain significant levels of radioactive materials; at the boundary of the observable plume materials will be diluted and dispersed by currents. No true equilibrium can ever be reached in such a system; motile organisms will be free to move into and out of the plume, and non-motile planktonic forms will be mixed with the plume by currents. Organisms should show radioisotope levels proportional to the amount of time spent in the plume area. Because of these several factors organisms will reach an equilibrium radioisotope burden below levels

predicted by specific activity; predicted levels will thus serve as an upper limit of possible concentrations attained by any component of the system.

The Fermi study is using the specific activity hypothesis as a means to predict the fate of radioisotopes which will be released to Lake Erie in effluents from Fermi II. Preoperational studies are intended to evaluate the distribution of several elements in various components of the lake system, in the vicinity of the plant and the cooling water discharge. These data eventually will be used to develop a predictive model for the fate of plant radioisotope releases. Elements currently under consideration (cobalt, iron, manganese, strontium, and zinc) represent those elements with the greatest potential for becoming a public health hazard around a nuclear generating facility, for several reasons: 1) these elements have radioisotopes produced by nuclear generating facilities; 2) these same radioisotopes have half-lives sufficiently long to make possible considerable accumulation within a system; and 3) these elements are either biologically required by organisms, or are chemically similar to required elements (Ca-Sr, K-Cs), resulting in a significant uptake of these elements and their radioisotopes by organisms.

This report focuses on the occurrence of these trace elements in water and sediment in the vicinity of Fermi II, evaluating the distribution of the elements in these two components of the lake system. Spatial variability in water was observed in order to assess homogeneity of the water mass, and also to evaluate the mixing zone where the plume of Swan Creek, a small stream, extends into the lake. Observation of this plume, it was hoped, could provide an indication

of the manner in which the plume from Fermi will behave; over how large an area a discrete plume will extend, and how readily the plume will mix with lake water due to wind and current action. Temporal variations were observed in the lake and in Swan Creek for comparison with seasonal changes in biota and sediments, to provide some indications of factors controlling trace element dynamics. Sediments, which become the eventual repository for the bulk of radioisotopes in aquatic systems, were analyzed for trace metal content and particle size distribution. It was originally planned to determine spatial and seasonal variability of trace elements in sediments, but early samples showed wide variability in concentrations of these elements, variability which appeared to be generally correlated with the particle size of the sediments. Due to particle size differences among stations, and of samples at the same station over time, it is impossible to determine true spatial or temporal changes in trace metal content unless a good correlation with sediment type can first be developed.

Trace metal dynamics in natural waters are not well understood; seasonal studies have often focused on hypolimnetic changes of iron and manganese related to oxygen depletion. Chawla (1971) has reported summer decreases of calcium levels in Lakes Erie and Ontario related to seasonal pH and alkalinity changes; it seems likely that these changes would similarly influence trace metal levels. The importance of biological uptake is uncertain, although Mills and Oglesby (1971) suggest that biological removal may be responsible for 5 to 10 fold reductions of dissolved zinc and cobalt concentrations in Cayuga Lake, New York during midsummer months. Both of these elements were originally present in very low quantities (≤ 1 ug/liter); however, so

that the actual quantity removed was small relative to the amounts present in enriched lakes such as Erie. Numerous authors have reported high suspended/dissolved ratios for various trace elements, particularly in streams. The importance of suspended material in lakes is less certain, due to the lower load of suspended matter which can be supported by less turbulent lake waters.

Finally, in areas such as Fermi, high inputs of sewage and industrial effluent into "upstream" waters (in this case the Detroit River) has a major, probably dominant effect on trace metal levels. Beeton (1971) and Hartley et al. (1966) indicate movement of a discrete, heavily polluted water mass along the American shore of the Detroit River and along the western shore of Lake Erie. The extent to which this mass extends into the Fermi II area very probably dictates trace metal concentrations in the survey area. Trace metal levels throughout the western basin of Lake Erie are several fold higher than levels in Lake Huron, at least partly reflecting the input of industrial effluents to the Detroit River. Once in the lake, a variety of processes act to modify these artificially high levels.

Trace metals become associated with sediments through a variety of processes: among the most important are the precipitation of oxides, hydroxides, and carbonates, especially of iron and manganese, a process which also involves scavenging of other polyvalent cations; binding with organic matter; and adsorption and absorption onto clay, silt, and larger inorganic particles. It has been widely observed, as might be expected, that trace metal concentrations of sediments vary inversely with mean particle diameter, that is, fine sediments (clay and silt) are characterized by high trace metal concentrations relative

to coarser sediments. Basic reasons for this are twofold; physical conditions conducive to settling of clay, silt, and organic debris are also conducive to settling of chemical precipitates, and for that portion of an element incorporated into sediments by various sorption processes, sorption is approximately proportional to surface area. Since area per unit weight is inversely proportional to particle size smaller particles have a greatly enhanced surface area per unit weight relative to larger particles, facilitating more extensive sorption. Clay particles often develop surface charges, yet further enhancing sorption.

Efforts in this study have been directed toward developing a general understanding of sediments within the survey area, of their nature (physical and chemical) and variability in terms of spatial and seasonal differences. To whatever extent possible, attempts will be made to determine relationships between trace element concentrations and particle size composition of individual sediment samples.

LITERATURE REVIEW

A Review of Factors Affecting Equilibrium of Trace Metals Between Water and Sediment, and Incorporation of Trace Metals into Sediments

A relatively good understanding has been developed of those factors which influence trace metal dynamics in natural waters, and the effects of individual factors. Generally lacking is an understanding of overall movements and equilibria of these elements; the relative importance of individual factors; possible interactions among factors; and the similarity of natural systems to laboratory systems and mathematical models. Major unanswered questions include: 1) In what forms do trace metals occur in natural systems, particularly with regard to organic complexing? 2) By what pathways and at what rates do these elements become associated with sediments? 3) Under what circumstances, and to what extent, are trace metals released from sediment back into the water column? Lee (1970) has compiled a literature review of various physical, biological, and chemical factors that can influence water-sediment equilibrium; although his discussion is oriented primarily toward phosphate exchange, the author includes a general discussion of individual factors and their probable effects. Jenne (1968) provides a thorough review of transition metal controls in water and resultant sedimentary forms of these elements.

The most basic, and ultimately most important factor controlling trace metal behavior in natural waters involves drainage basin geology

and the extent of a basin's human perturbation. Basin runoff will control the forms and amounts of any element entering a water system, as well as other characteristics such as buffer capacity, suspended solids, organic content and innumerable other factors which may directly or indirectly influence metal dynamics. Human influence can come in many forms, such as direct releases of sewage and industrial wastes, acid mine runoff, agricultural runoff of nutrients and suspended solids, and secondary effects of nutrient enrichment.

The alkaline earth elements (Mg, Ca, Sr, Ba) and the alkali metals (Na, K, Ru, Cs) have generally clearly defined behavior in water, with both groups typically existing as simple ions in solution (Childs, 1971). The alkali metals, in particular, are relatively soluble in water, although cesium, due to its ionic radius, is extensively and strongly bound to the lattice boundary of illite clays (Tamura and Jacobs, 1960). In systems with high suspended clay content, very extensive cesium sorption onto clay will result. Rubidium behavior is considerably different; Jenne and Wahlberg (1968) noted little loss of radioactive rubidium to sediments in White Oak Lake at Oak Ridge. That portion which was bound consisted of a hydrated rubidium-nitrate complex. Strontium, typical of the alkaline earths, shows very little association with suspended matter; Brungs (1967) and Parker (1963) show very little association of strontium with suspended solids, while Childs (1971) reports $\geq 93\%$ and $\geq 88\%$ of Mg, Ca, Sr, and Ba in model (without organic material) Lake Ontario water existing as the simple M^{++} ion at pH 8.0 and 9.0, respectively. At such pH levels, these elements begin to form sulfates and carbonates, which act to limit solubility.

Transition metal equilibrium in water is much more complex and much less fully understood compared to the first two groups. Although all of these elements normally occur in water at concentrations below 1 mg/liter, iron and manganese commonly occur in excess of their theoretical solubilities. One factor presumed responsible for maintaining at least a portion of the transition metal levels in water is the formation of organic complexes, although very little is actually known about the extent of natural complexation (Childs, 1971). Hodgson et al. (1966) indicate that for soil systems, 98-99% of copper, 84-99% of manganese, and up to 75% of zinc occurring in solution is in the form of organic complexes.

The physiochemical factors of pH and Eh control the solubility of the transition elements in water; in general, an increase in either parameter will decrease solubility (Lindsay, 1972). Both Lindsay (1972) and Jenne (1968) have provided inorganic phase equilibrium diagrams for iron and manganese showing the significance of pH-Eh changes. In addition to the self-regulation of these elements, their behavior greatly affects the other transition metals, through coprecipitation and sorption on to Fe and Mn oxide coatings on sediments (Jenne, 1968). Zinc and cobalt seldom reach or exceed their solubility limits in water, yet the bulk of these elements in water occurs in filterable forms (Nelson et al., 1971; Friend, 1963) a portion of which is incorporated with colloidal iron oxides.

Suspended solids play a highly significant, although variable role in controlling trace metal levels in water. Suspended solids is somewhat of a catch-all category which includes any filterable material, including some colloidal iron, organic macromolecules, particulates

of organic origin, or clay, silt and sand. As is the case with dissolved organics, little is known of the association of the transition metals with suspended solids. Precise determination of how and with which fraction of suspended material these metals are associated is a subject that requires further research.

Although there is considerable uncertainty with regard to the mechanisms that bind trace elements to sediment, it has been generally observed that the trace metal content of sediments increases with decreasing mean particle size. Most soil-metal binding processes are surface phenomena, and surface area per unit mass increases with decreasing particle size; thus such a relationship is not unexpected. Sayre et al. (1963) and Hubbell and Glenn (1973) have discussed the importance of sorption processes in binding of radioisotopes to sediments, noting that exchange capacity and resulting sorption is proportional to surface area. Kennedy (1965) has determined cation exchange capacities for suspended and bed sediments of rivers in the United States, observing sharp decreases in exchange capacities of larger particles. He further notes varieties in exchange capacity attributable to differences in mineralogy of various particle types, particularly for clays. Glenn (1973) has observed the relationship between sediment size, exchange capacity, and radioisotope concentration in the Colombia River downstream from the Hanford reactors, finding close correlations between mean particle size, cation exchange capacity, and radioisotope concentrations. He further noted the importance of increased organic content in enhancing radionuclide content of certain samples.

It has been well established that sorption on to clays, particularly illite, is the primary mechanism by which cesium is incorporated into

sediments (Reynolds, 1963; Tamura and Jacobs, 1960; Jenne and Wahlberg, 1968; Friend, 1963). Cesium uptake by suspended clay is very rapid, reaching equilibrium within a few minutes (Clanton, 1963); uptake is virtually unaffected by pH changes over the range found in natural waters but is considerably depressed by high concentrations of sodium or potassium (Reynolds, 1963). Once absorbed, cesium is generally non-exchangeable, that is it is not released back into solution.

Strontium behavior is considerably different from that of cesium; with strontium remaining almost entirely in a dissolved form as the simple Sr^{++} ion. At high pH conditions, strontium precipitates as a carbonate or sulfate, but these reactions are readily reversible with resolution of the precipitate as pH is lowered (Jenne and Wahlberg, 1968; Lomenick and Gardiner, 1965).

Several processes are thought to influence transition metal binding with sediments, although the relative importance of these processes remains a subject of considerable debate. Sorption processes particularly onto clay, have been proposed as the primary binding mechanism (Sayre et al., 1963; Lee, 1970; Friend, 1963).

Bachmann (1963) and Cushing and Watson (1968) suggest the importance of organic particulates, noting the very high uptake of ^{65}Zn by freshly killed algae, while Stevenson and Ardakani (1972) suggest a stable clay-metal-organic complex. Jenne (1968) indicates that simple sorption, precipitation, or organic binding reactions are inadequate to explain transition metal behavior, he proposes that sorption reactions with hydrous oxides (as coatings on sediments) of iron and manganese provide the principle control mechanism for the transition elements. Shimp et al. (1971) and Collinson and Shimp (1972)

dispute this hypothesis; using data from Southern Lake Michigan and Upper Peoria Lake, Illinois, they report better correlation of zinc and other metals with organic carbon levels than with the amounts of clay or iron-manganese oxides. Hodgson (1963) similarly found that transition metal concentrations in soil systems correlate more closely with organic content than with clay content.

In addition to the general mechanisms outlined above, individual elements have other characteristics which will affect their behavior in aqueous systems. Some of these characteristics, and a brief summary of the aqueous behavior of individual elements are provided in the following paragraphs.

Cobalt

Cobalt (AW=27, MW=58.94), an element of the first transition series, is normally found in natural waters at concentrations of 1 ug/liter or less. Naturally occurring in low concentrations in igneous rocks, cobalt is released to water by weathering of these materials. Two oxidation states exist (+2 and +3) but the trivalent ion is a strong oxidizing agent and hence unstable in water. Low input levels are partially responsible for the low cobalt concentrations normally found in nature; once in solution, however, cobalt is readily precipitated and strongly sorbed by oxidate or hydrolyzate sediments, particularly of iron and manganese. Dissolved/suspended ratios for cobalt in lakes are highly variable, although the suspended proportion normally increases in lakes characterized by high suspended solids. Ophel and Fraser (1973) report virtually all cobalt in waters of Perch Lake, Ontario, to be in dissolved form, with organic complexation enhancing the dissolved concentration. Conversely, Ophel and Fraser (1973),

note reported values of about 80% suspended cobalt in Lake Maggiore, Italy, while Nelson et al. (1971) found about 95% of the ^{60}Co released from the Big Rock Point nuclear station to be in suspended forms.

Biological requirements for cobalt are low, with primary importance of the element as a component of Vitamin B_{12} . Phytoplankton and macrophytes show considerable uptake of cobalt, but higher food chain organisms are characterized by decreasing cobalt concentrations (Ayers, 1971; Ophel and Fraser, 1973).

Three radioisotopes of cobalt ^{57}Co , ^{58}Co , and ^{60}Co have been regularly observed in association with nuclear generating station effluents; all three are neutron activation products. ^{60}Co is produced in low quantities relative to the lighter isotopes, but because of its much longer half-life ($t_{1/2}=272\text{d}$, 71d , 5.24y for ^{57}Co , ^{58}Co , ^{60}Co , respectively), it presents a potentially greater environmental hazard.

Iron

Iron (AW=26, MW=55.85) which comprises about 5% of the mass of the earth's crust, is the fourth most abundant element, and the most abundant of the transition elements. Because, however, of its low solubility under pH and redox conditions found in natural waters, iron is present only in $\mu\text{g/liter}$ to mg/liter quantities. As with cobalt, rock weathering is the major natural source of iron to water, with resolution of iron precipitates (iron oxides and hydroxides) providing an additional important source. Two oxidation states commonly are found in natural waters (+2 and +3); the ferrous state predominates at low redox potential ($<100\text{mV}$) or low pH, and ferric iron occurs in well oxygenated waters. Of these forms, the ferrous

ion is relatively more soluble, as manifested by high iron concentrations ($> 5\text{mg/liter}$) in hypolimnetic waters with low dissolved oxygen. Under such conditions, precipitation of ferrous sulfide normally limits iron solubility. Ferric iron, in contrast, is quite insoluble (solubility product for $\text{Fe}(\text{OH})_3 = 3 \times 10^{-38}$). Actual concentrations found in water range well above this level, due to formation of stable iron-organic complexes, sorption to suspended particles, and most especially abundant ferric hydroxide present as a colloid. The significance of non-dissolved iron is exemplified by Kopp and Kroner (1970), who report a suspended/dissolved iron ratio of 60:1 for 228 samples collected at municipal water intakes of U.S. cities.

In addition to regulating iron levels, the formation of colloidal iron is responsible for coprecipitation of most other transition elements, and it is thought also to catalyze manganese oxidation, with subsequent manganese dioxide precipitation. Jenne (1968) has further suggested that sorption onto hydrous iron and manganese oxides (as coatings on sediments) is a critical factor responsible for low levels of Zn, Co, Ni, Cu, and other elements in solution.

Iron is of great significance in biological organisms, functioning in a wide variety of enzymes in both plants and animals. Most noted among these is its role in oxygen and carbon dioxide transport by hemoglobin.

Two radioisotopes of iron have some potential significance ecologically, although neither of these is found in large quantities in typical nuclear effluents. Both of these isotopes ^{55}Fe ($t_{1/2}=2.4\text{y}$) and ^{59}Fe ($t_{1/2}=45\text{d}$) are activation products.

Manganese

Still another of the transition elements, manganese (AW=25, MW=54.94) greatly resembles iron in its occurrence and chemical behavior in water. Several oxidation states (+2, +3, +4) commonly exist, with Mn^{+4} forming highly insoluble MnO_2 . The divalent and trivalent forms are much more soluble in water (approximately 10^{-1} and 10^{-5} M for $Mn(OH)_2$ and $Mn(OH)_3$, respectively, compared to about 10^{-16} M for MnO_2 at pH8), although the solubility of these two forms falls sharply with increasing pH. Under conditions of low dissolved oxygen, up to several mg/liter manganese can redissolve from the sediment. As oxygen is depleted, manganese reduction occurs at a higher redox potential than iron, with iron sulfide precipitation further favoring manganese accumulation within the hypolimnion (Cowgill, 1968). As is the case with iron, manganese hydrous oxides are believed to play a significant role in control of other trace metals in water, through coprecipitation and sorption on to manganese oxide coatings or sediments (Jenne, 1968).

Manganese is an activator of numerous enzymes, and it plays a required, but as yet unspecified role in photosystem II. Manganese uptake by aquatic macrophytes appears to be proportional to dissolved manganese over a wide range of concentrations; conversely some fish species appear to regulate body manganese levels (Lentsch, et al., 1973). These authors further report decreasing manganese concentrations in higher food chain organisms; filamentous algae and macrophytes show the highest concentrations, while carnivorous and omnivorous fish had the lowest body concentrations. Only one radioisotope of manganese has any potential significance in aquatic systems; ^{54}Mn , an activation product with a half-life of 312 days.

Strontium

An alkaline earth element, strontium (AW=38, MW=87.63) has an aqueous behavior similar to calcium and barium. Strontium in nature normally occurs as sulfate or carbonate rock, usually in association with calcium and barium. Released to water by weathering of these rocks, strontium levels are controlled by input-output rates or by precipitation as a carbonate under conditions of high pH. Once in solution, strontium does not typically occur as a hydrated or chelated form, as is usually the case for the transition metals, but rather as the simple Sr^{++} ion. Strontium further shows little association with suspended matter, as evidenced by high dissolved/suspended ratios observed by Kopp and Kroner (1970) and Brungs (1967); in a controlled study using ^{85}Sr , Brungs (1967) found < 1% of strontium in the water column to be in suspended form.

Although strontium is not known to be a required element for either plants or animals, its chemical similarity to calcium results in considerable uptake by biota, with distributional patterns approximating those of calcium (Comar, 1965). Not surprisingly, highest strontium accumulations occur in bony portions of fish and other vertebrates, and in calcareous exoskeletons and shells of invertebrates.

Several radioisotopes of strontium have been reported in nuclear reactor effluents (^{89}Sr $t_{1/2}=50.6\text{d}$, ^{90}Sr $t_{1/2}=28.8\text{y}$, ^{91}Sr $t_{1/2}=9.7\text{hr}$, ^{92}Sr $t_{1/2}=2.7\text{hr}$) with all of these isotopes formed as fission products. Of these isotopes, ^{90}Sr is by far the most significant due to its long half-life. In addition to reactor effluents, considerable amounts of ^{90}Sr have been deposited by fallout as a consequence of atmospheric weapons testing, although fallout deposition has fallen sharply in the last decade.

Zinc

Another of the transition elements, zinc (AW=30, MW=65.38) is in most respects similar to these other elements in terms of its aqueous behavior. Present in nature primarily as an oxide or as a sulfide, zinc is released to waters by weathering of these materials. Zinc levels in water are usually in the 1-100 ug/liter range; at the pH range usually found in lakes and streams, zinc is maintained in solution as hydrated (ZnOH^+) or chelated forms, or is sorbed on either organic or inorganic suspended materials. Zinc is strongly sorbed on silts and clays, with some subsequent incorporation into clay lattices; Bachmann (1963) and Cushing (1970) have further reported very high uptake of zinc by both living and dead algae, with relatively higher accumulations on freshly killed algae. High sediment concentrations result from settling of materials with sorbed zinc, also from coprecipitation with colloidal iron oxides and sorption on iron and manganese oxide coatings on sediments.

Zinc has been widely demonstrated as a required micronutrient for both plants and animals; functioning as a specific or nonspecific activator in a variety of enzymes. Within aquatic systems, algae and macrophytes show the greatest degree in zinc uptake with lesser concentrations in higher food chain organisms.

One ecologically significant radioisotope of zinc exists, ^{65}Zn , an activation product with a 245 day half-life.

SITE DESCRIPTION

The study area is located along the western shore of the western basin of Lake Erie, adjacent to the site of Fermi II. Bordered on the east by Point Pelee and the Bass Islands, the western end of Lake Erie (Figure 1) is a shallow basin covering about 3100 km². The western basin strongly reflects the two major tributaries which feed it; the Detroit River, entering at the northwest corner of the basin, contributes about 95% of tributary flow into the basin. In addition to draining the upper Great Lakes, the Detroit River receives high quantities of sewage and industrial wastewater from the Detroit area. The second major river, the Maumee, enters in the southwest corner at Toledo. While the Maumee River contributes only about 3% of the tributary input to the basin it carries vast quantities of clay and silt (1.8×10^6 metric ton/year) into the lake, contributing to the high turbidity characteristic of the western basin (Langlois, 1954; Arnold, 1969). The Maumee River is also responsible for about 30% of the phosphorus and 20% of BOD introduced to the basin (FWPCA, 1968). In addition to these two rivers, numerous smaller streams flow into the western basin, mostly along the western and southern shores. Draining generally flat farmland, these streams enter the lake heavily laden with clay, silt and macromutrients.

Physically, the western basin is quite shallow, with a mean depth of only 8 meters and maximum depth of about 12 meters. Coupled with winds, this shallowness gives the basin two of its prominent

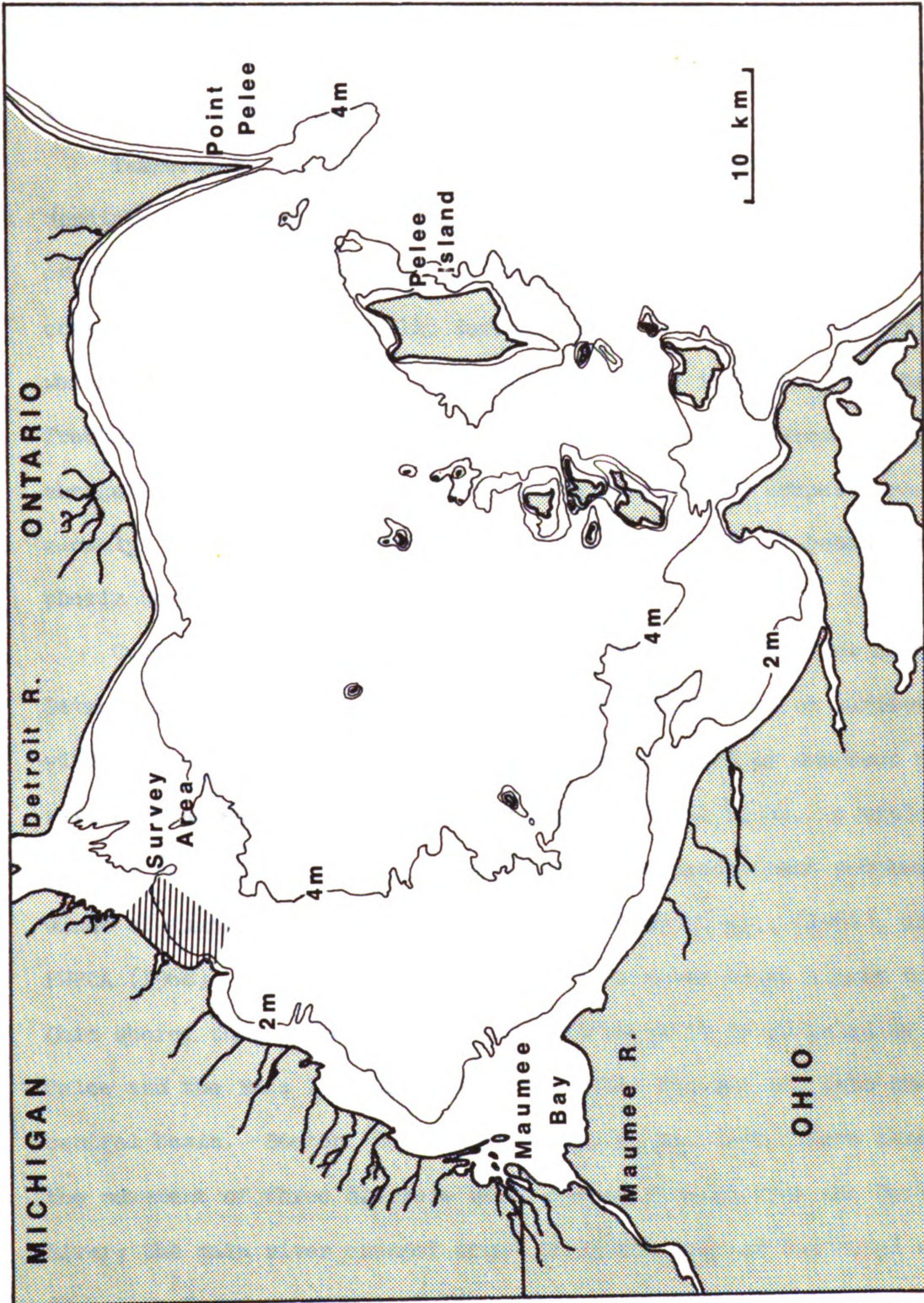


Figure 1. The western basin of Lake Erie, indicating the location of the survey area.

characteristics; the basin is seldom stratified, in terms of either temperature or dissolved oxygen; and wind-caused resuspension of sediments helps cause the characteristically high turbidity of the basin (clay and silt input from streams and high primary productivity are other contributing factors) (FWPCA, 1968).

Temperature regimes in the western basin, except for the isothermous conditions, are representative of lakes in the area. A summer maximum of 26 - 28° C is reached in August; temperatures then fall until ice cover begins to form, usually during December. Winter ice cover, which usually lasts until sometime in March, is irregular, as sheet ice fractures and forms floes, due to wind and seiche pressures. Temperature changes in small influent streams follow atmospheric temperatures closely, but lake temperature changes lag about 2 weeks behind atmospheric thermal patterns.

Current patterns in the basin strongly reflect the flow of the Detroit River, but the single most important influence on currents is winds. The divergence of current patterns reported by numerous authors reflect changes which occur with changes in local winds. A typical current pattern (Figure 2), controlled by the predominant southwest winds of summer, has been described by Hartley et al., (1966), and FWPCA (1968). Water from the Detroit River moves south almost to the Ohio shore, then spreads toward the east where it is funneled by Point Pelee and the Bass Islands through the Pelee Passage and into the central basin. Beeton (1971) and Hartley et al. (1966) have observed the movement of three discrete water masses flowing from the Detroit River; the main river channel consists essentially of unaltered water from Lake Huron, with a separate, enriched mass flowing along either

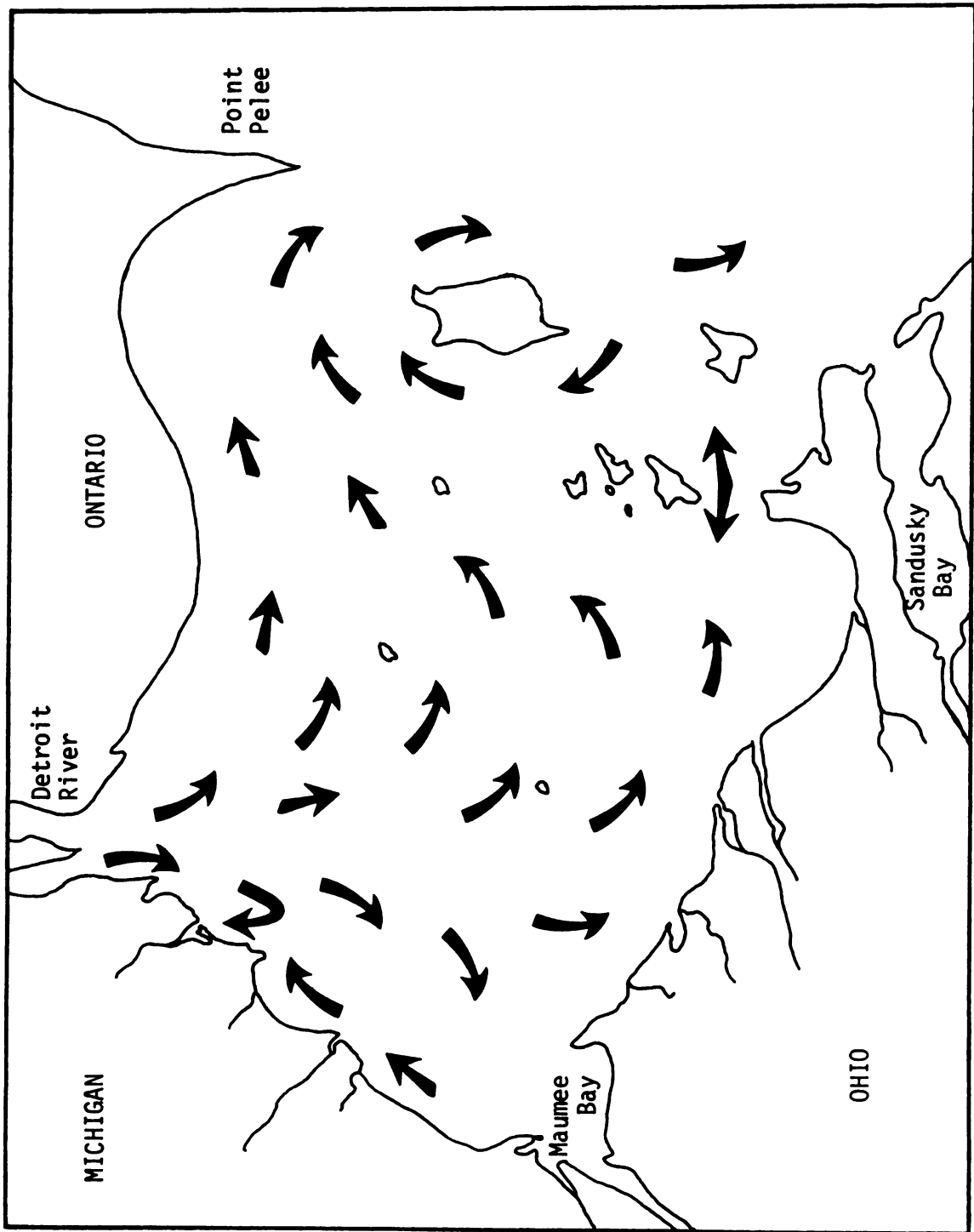


Figure 2. Typical summer current pattern in the western basin of Lake Erie.

shore. The Michigan shore mass, containing chloride, trace metal, and nutrient levels several times higher than water in the main channel, moves southward from the river mouth into the western basin along the Michigan shore, and was observed by Hartley et al. (1966) as far south as Monroe. The movement of water from the Maumee River, and nearshore currents along the Michigan shoreline are not as well defined.

The FWPCA (1968) suggests that flow from the Detroit River interrupts the eastward flow of water from the Maumee; winds then push this water northeasterly along the Michigan shore. The ILEWPB (1969) indicates a continuous northerly flow along the Michigan shore, but fails to indicate whether such currents are predominantly influenced by winds, eddy currents, or the flow of the Maumee. Subsurface currents generally follow surface flow patterns, except that the northerly flow along the Michigan shore is more pronounced. Subsurface flow in the Bass Island region is uncertain, but major flow to the central basin is again through the Pelee Passage (Hartley, 1968).

In addition to currents, seiches exert an intermittent, but highly significant influence on water movements in the western end of the lake. Sustained easterly winds push great amounts of water to the western end of the lake, raising water levels as much as six feet; conversely, sustained westerly-southwesterly winds result in easterly movement of water, and result in lowered water levels along the western shore. These movements interrupt normal flow patterns, and waves accompanying the northeast winds cause beach erosion and resuspension of sediments in shallow areas.

As a consequence of man's activities, the chemical characteristics of water in the western basin have undergone considerable change during

this century. Increased loadings of sewage and industrial wastes, along with agricultural runoff, all have contributed to increases in the concentrations of most major ions (Table 1) and nutrients (Table 2) during this century. Concentrations of all major ions except magnesium have increased to some extent, with chloride levels showing the sharpest increase. Nutrient increases have been more dramatic; phosphate levels have increased four to ten-fold since 1942, while ammonia, nitrate, and total nitrogen concentrations have increased 11, 3, and 4-fold, respectively (ILEWPB, 1969; Chawla, 1971). Verduin (1964) cites agricultural runoff as the most critical factor in nutrient increases, while the ILEWPB (1969) recognizes both agriculture and urban effluents as major factors in nutrient increases within the basin, implicating municipal waste as the primary contributor of phosphorus, while agricultural runoff is the major source of nitrate. Long term changes in trace element concentrations are unknown, as open lake data prior to the 1960's is lacking. For a comprehensive discussion of chemical, physical, and biological conditions and changes in Lake Erie, refer to ILEWPB (1969).

As previously mentioned the western basin is normally homothermous, with only infrequent stratification of temperature or dissolved oxygen. During periods when wind velocities are insufficient to maintain vertical mixing, stratification and oxygen depletion in the deeper waters occur rapidly (Carr et al., 1965). Dissolved oxygen levels remain near saturation throughout the year, with waters in the surface 2 to 3 meters often becoming supersaturated during the summer months, presumably as a result of high primary productivity (ILEWPB, 1969; Cole, 1972).

Table 1. Historical changes in the concentration of major ions in Lake Erie (all values reported in mg/liter).

	1906 ¹	1963-4 ²	1967 ³	1973 ⁴
Calcium	31.0	37.9	33.3	34.4
Magnesium	7.6	9.6	7.5	N.D.
Sodium	6.5	10.6	9.5	8.7
Potassium	N.D. ⁵	1.4	1.2	1.2
Sulfate	13.0	21.1	20.7	N.D.
Chloride	8.7	23.4	19.9	16.7
Total Alkalinity	114	95	103	92
Dissolved Solids	133	N.D.	165	N.D.

1. Dole (1909) average of monthly determinations at Buffalo, New York, water intake.
2. FWPCA (1968) average of lake data.
3. Weiler and Chawla (1968) average for 8 sample periods June-October 1967 for 3 stations in Western Basin.
4. Present study.
5. Not determined.

Table 2. Historical changes in nutrient concentrations in western Lake Erie (all values reported as ug/liter).

	1942 ¹	1963-4 ²	1970 ³	1973 ⁴
Soluble-P	3.9	30	70	26
Total-P	14.4	N.D. ⁵	100	75
NO ₃ -N	123	120	630	350
NH ₃ -N	36	160	390	140
Total N	265	710	1270	1070

1. Chandler and Weeks (1945) average of samples taken June-December, 1942, in Bass Island Region.
2. FWPCA (1968) average of data for western basin.
3. Cole (1972) average of samples taken May-November, 1970 along western shore of the western basin.
4. Present study.
5. Not determined.

As a consequence of nutrient enrichment in the western basin, the phytoplankton standing crop has increased greatly since 1927 (Davis, 1969). This increase has resulted in further chemical change in the lake, as a shift of bicarbonate-carbonate equilibrium resulting from CO_2 removal during photosynthesis. The pH values reported prior to 1950 reached a maximum of 8.7, with diurnal CO_2 changes equivalent to 32 μM /liter. By 1958 the pH maxima reached 9.2, and daily CO_2 changes amounted to 70 μM /liter (Verduin, 1964). pH changes such as this can be of considerable importance, because even small increases in pH can greatly decrease the solubility of polyvalent metal ions.

The specific region under consideration in this study centers around the mouth of Swan Creek, a small stream which empties into the western end of the lake adjacent to the Fermi site. The study region is shown in more detail in Figure 3, which also indicates the location of sampling stations. The broadening of the lower end of Swan Creek, typical of small streams of the western basin, is the result of flooding of the stream mouth by rising lake levels. This flooding is a result not only of current high lake levels, but also relatively faster geological uplift (approximately 15 cm/100 yrs.) at the eastern end of the Lake Erie basin (Gutenberg, 1941).

Station 1, located about one mile above the mouth of Swan Creek, is located in about 1.5 m of water. Conditions at this station reflect the drainage area of the creek, which is relatively flat agricultural land. Waters in the creek are turbid, due to the high load of organic debris, silt, and clay which it carries. Nutrient levels are high relative to lake concentrations, primarily as a result of agricultural runoff.

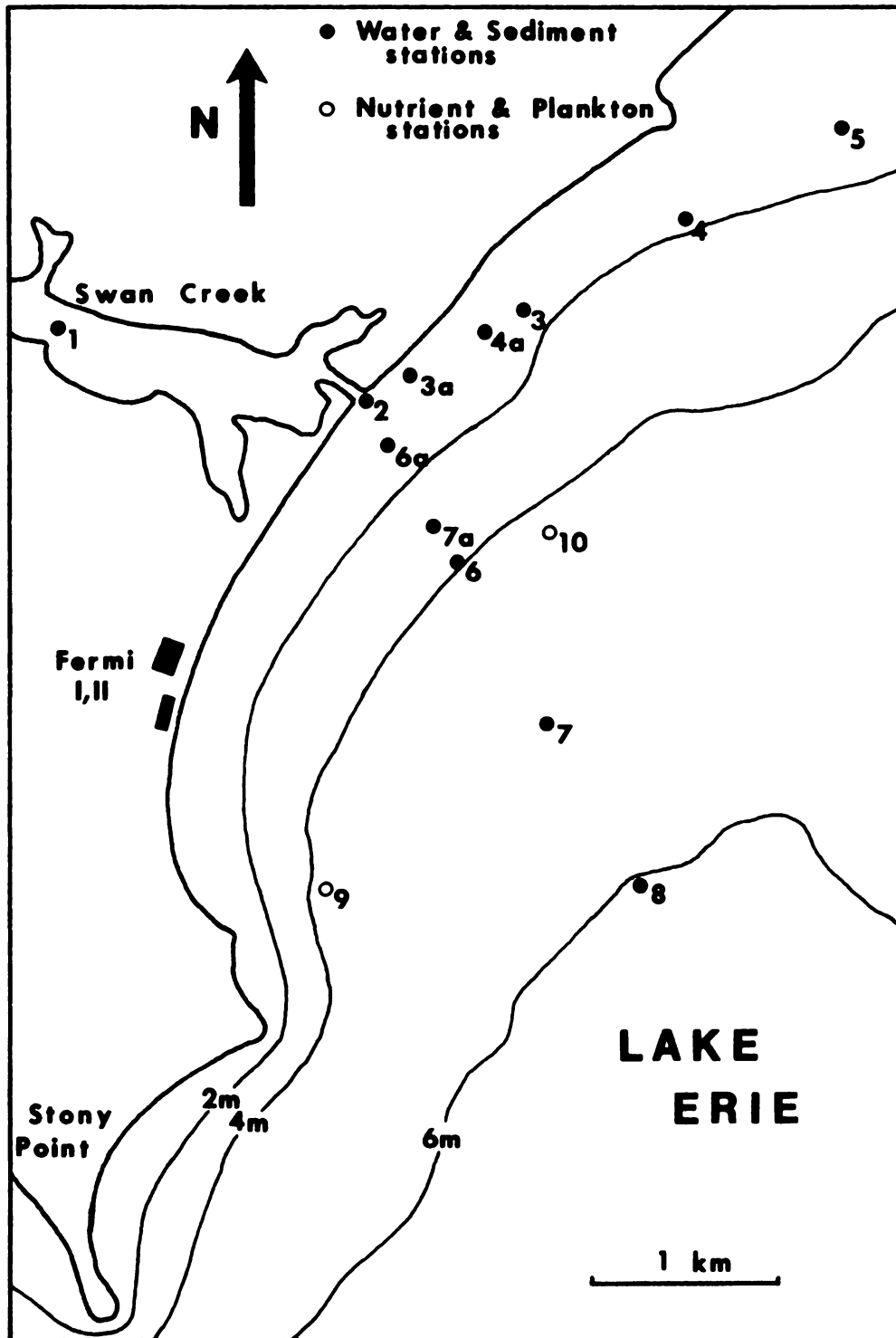


Figure 3. map of the survey area, indicating the location of sample stations.

Station 2, also in about 1.5 m of water is located about 25 m off-shore from the mouth of Swan Creek. Located in the mixing area of the creek plume with lake water, conditions at the station are intermediate between those of Swan Creek and the lake.

The six lake stations (3 through 8) are located along two transects emanating from the mouth of Swan Creek. The northern transect (compass bearing 60°) follows the "average" plume from Swan Creek, roughly paralleling the shore from the mouth of the creek. The southern transect, run perpendicular to the northern one, extends into the deepest part of the survey area almost directly off-shore from Fermi. Stations 3 through 6 are located in 1.5 - 2 m of water, while the depth at stations 7 and 8 is about 3 and 6 m, respectively. Station 3, 4, 6, and 7 were originally located farther from Swan Creek (designated as 3a, etc. on Figure 3) but were moved to their present locations midway through the study period in order to better observe the behavior of the plume from the creek as it entered the lake.

Two additional stations (9 and 10 in Figure 3) were established during 1973, located in the deeper waters of the survey area. Samples collected at these stations included quantitative phytoplankton and zooplankton samples, and water samples used for analysis of suspended solids and nutrients.

Preliminary grid surveys of various chemical parameters of the Fermi-Swan Creek area and a conductivity survey taken May 28, 1973, (Figure 4) suggest that lake water in the study area is comprised of an essentially homogeneous mass, with Swan Creek influencing a relatively small area. Chemical and physical data collected for the lake and Swan Creek during the study period have been summarized in Table 3.

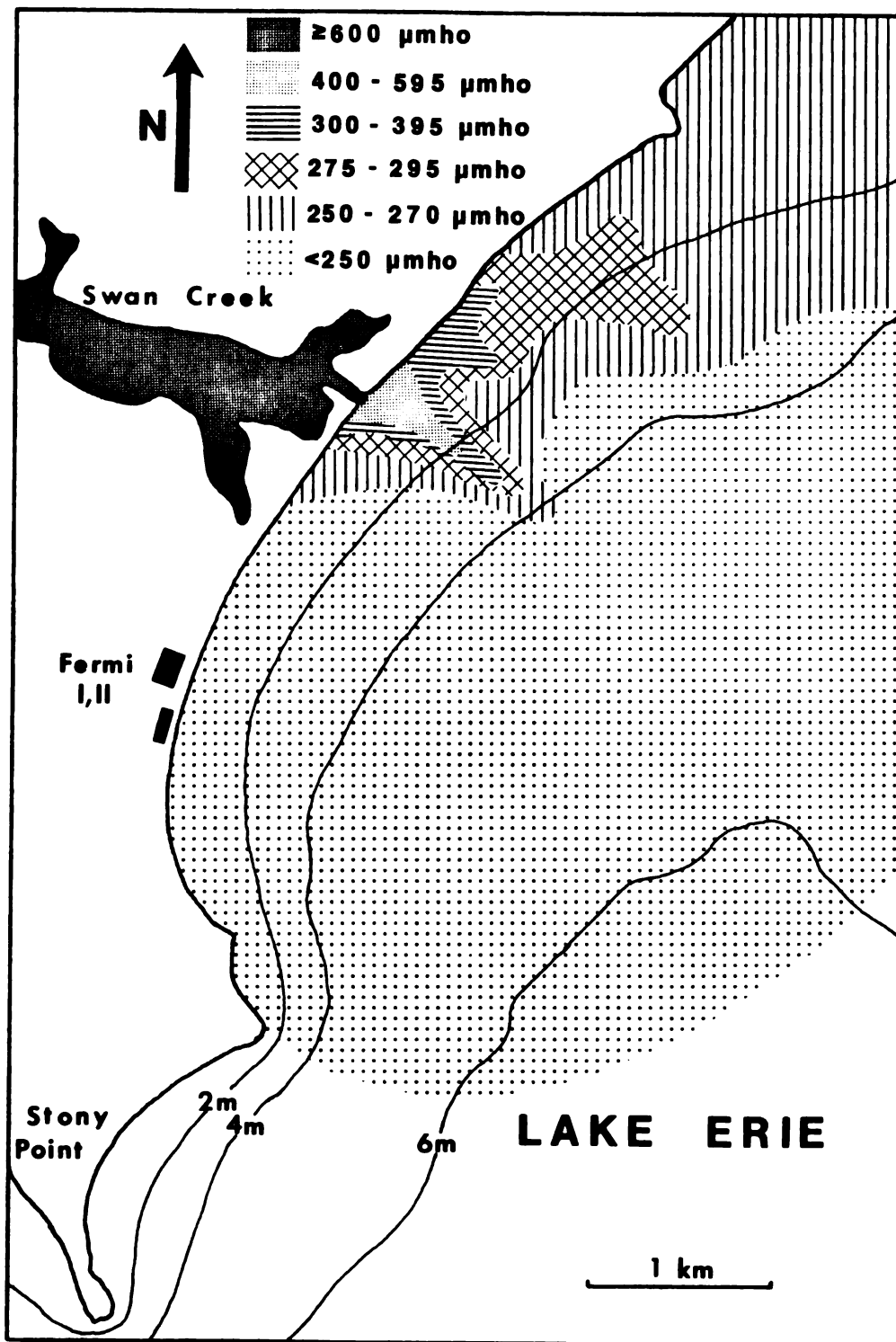


Figure 4. Conductivity in the survey area on 28 May 1973.

Table 3. Summary of general physiochemical and nutrient analyses in study area during 1972-1973.

PARAMETER	LOCATION	1972					1973					1973 MEAN
		9-11	10-27	4-2	6-6	7-19	9-12	10-15	12-8			
Temperature Degree Celcius	Swan Cr. Lake	-- --	9.5 9.4	9.2 7.1	18.6 15.9	27.0 26.4	22.0 21.9	16.1 17.5	3.3 5.0	ND		
Alkalinity (pHth/Total) mg CaCO3/liter	Swan Cr. Lake	9.7/105 0/89	0/91 3.7/77	-- --	7/174 5.2/89	7.1/108 4.3/83	7.7/93 2.0/83	0/101 2.1/90.5	0/117 0/112	ND		
Dissolved Oxygen mg/liter	Swan Cr. Lake	8.1 7.5	-- --	9.9 12.2	7.7 10.5	10.3 13.1	10.6 10.0	8.1 8.9	12.3 11.8	ND		
Dissolved Oxygen % Saturation	Swan Cr. Lake	-- --	-- --	88.0 103.0	84.0 108.1	131.5 165.8	123.5 116.3	83.8 94.8	94.9 94.2	ND		
Suspended Solids mg/liter	Swan Cr. Lake	21.0 16.3	48.7 31.9	93.3 33.8	48.3 12.4	34.3 8.6	36.3 14.1	45.7 19.1	23.7 18.3	46.9 17.7		
Soluble P mg/liter	Swan Cr. Lake	0.043 0.056	0.043 0.033	0.033 0.021	0.040 0.019	0.040 0.027	0.030 0.023	0.030 0.031	0.027 0.032	0.033 0.026		
Total P mg/liter	Swan Cr. Lake	0.15 0.09	0.12 0.10	0.14 0.10	0.12 0.06	0.12 0.07	0.10 0.06	0.11 0.07	0.08 0.10	0.11 0.08		
NO3-N mg/liter	Swan Cr. Lake	0.10 0.28	1.40 0.96	2.20 0.61	1.38 0.41	0.07 0.19	0.13 0.17	0.23 0.26	1.23 0.46	0.87 0.35		

Table 3 (Cont'd):

PARAMETER	LOCATION	1972					1973				
		9-11	10-27	4-2	6-6	7-19	9-12	10-15	12-8	1973 MEAN	
NH ₃ -N mg/liter	Swan Cr. Lake	0.03 0.17	0.04 0.07	0.10 0.16	0.10 0.01	0.04 0.10	0.06 0.10	0.14 0.14	0.20 0.34	0.11 0.14	
ORG-N mg/liter	Swan Cr. Lake	1.22 0.47	1.33 0.81	1.16 0.49	1.72 0.82	0.93 0.49	0.85 0.50	0.81 0.59	0.56 0.59	1.01 0.58	
Total N mg/liter	Swan Cr. Lake	1.35 0.92	2.78 1.77	3.46 1.26	3.20 1.24	1.04 0.78	1.04 0.78	1.18 0.99	1.99 1.39	1.99 1.07	
Organic C mg/liter	Swan Cr. Lake	6.7 3.5	9.0 4.9	11.3 3.6	11.3 5.5	6.0 3.8	8.0 4.5	6.0 4.4	3.7 4.9	7.7 4.5	
Total C mg/liter	Swan Cr. Lake	24.3 --	27.7 21.3	39.7 20.1	44.7 21.7	30.0 22.6	27.0 21.8	26.3 21.8	31.7 27.0	33.2 22.5	

1. Swan Creek includes only station 1.

Lake station value represents mean of stations 3 through 8 for all 1972 data, and for 1973 data for temperature, alkalinity, and dissolved oxygen. 1973 data for suspended solids and nutrients represents mean of data for stations 9 and 10.

Sediments in the study area (Figure 5) have been characterized as part of a grid survey taken during the summer of 1972. Sample station locations have been marked on Figure 5 to indicate general characteristics of sediments for each station. Near shore areas are generally underlain by fine to medium sands, except at the mouth of Swan Creek, where currents have washed smaller particles from the area, leaving a gravel-pebble bottom. Deepwater sediments in the northern portion of the area consist of hard clay; as one moves farther south this bottom has been covered by progressively thicker deposits of silt and organic matter. Sediments in Swan Creek consist of an unconsolidated mixture of clay, silt, and organic debris. Although some annual variation in sediment distribution might be expected as a result of seasonal variations in wind and currents, general sediment characteristics appear to have remained essentially constant during the survey period.

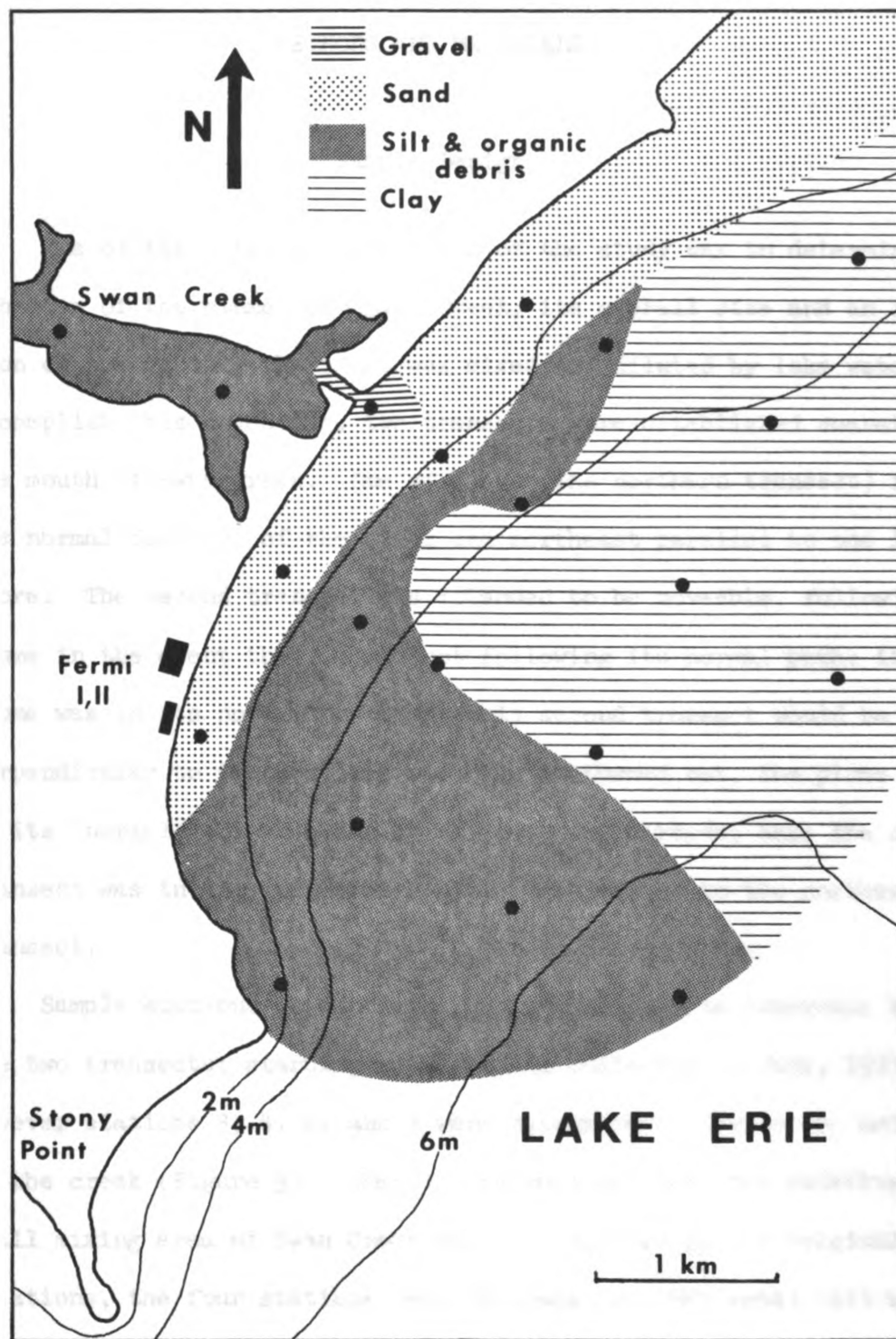


Figure 5. sediments in the survey area.

METHODS AND MATERIALS

Sample Design

One of the original intentions of the study was to determine the behavior of the plume from Swan Creek, its overall size and an indication of how rapidly the plume was mixed and diluted by lake water. To accomplish this objective, two transects were established emanating from the mouth of Swan Creek. One of these (the northern transect) follows the normal flow out of the creek and northeast parallel to the lake shore. The second transect was intended to be moveable, following the plume in the event that it was not following its normal path; if the plume was in its normal position, this second transect would be run perpendicular to the northern one. As it turned out, the plume was in its "normal" position during all sampling periods; thus the southern transect was in all instances run at right angles to the northern transect.

Sample stations were originally located at 1 km intervals along the two transects; starting with samples collected in June, 1973, however stations 3, 4, 6, and 7 were relocated closer to the mouth of the creek (Figure 3). When it was realized that the relatively small mixing area of Swan Creek was not observed by the original sample locations, the four stations were relocated so they would fall within the mixing zone.

Field Collections

Water samples were taken in triplicate from each station at a depth of 0.5 m, using a Van Dorn water sampler, and stored in polyethylene bottles. Samples used for trace metal analysis were preserved using 2 ml HCl (added to bottle prior to sample), and samples used for nutrient analysis were preserved using HgCl_2 . Chloride samples were unpreserved. Field measurements included temperature, alkalinity, and dissolved oxygen; temperature was determined using either a mercury thermometer or YSI temp./D.O. probe, alkalinity by H_2SO_4 titration, and dissolved oxygen by azide-modified Winkler determinations. Sediment samples were collected in triplicate, using either Ponar or Ekman dredges, and stored in glass jars until analysis.

Laboratory Procedures

Water samples were filtered using 0.45u Millipore filters, with a 25-30 ml subsample of the filtrate then taken for direct analysis of calcium, sodium, and potassium. To facilitate analysis of the remaining elements, cobalt, iron, manganese, strontium, and zinc, a concentration procedure involving freeze-drying was used; 400-500 ml of the filtered sample were reduced to dryness, with the residue redissolved in 20-25 ml HCl for analysis by atomic absorption or flame emission. Table 4 outlines the stepwise procedure used for the preparation of water samples.

Prior to trace metal analysis, sediment samples were mixed and a subsample taken for particle size analysis. Using a wet sorting method (Cummins, 1962), silt and clay were separated from larger particles. A 10 to 25 gram aliquot of the sediment was shaken

Table 4. The preparation of water samples for the analysis of trace elements.

-
1. Using 1 liter sample preserved with HCl, pass 100 ml through 0.45 μ millipore filter; discard the filtrate. (This first aliquot is used as a precautionary step to rinse the filter and flask).
 2. Pass the remainder of the sample through the filter; after filtration, store the sample in an acid-washed polyethylene bottle.
 3. Take a 25-30 ml subsample of the filtrate, analyze directly for calcium, sodium, and potassium.
 4. Weigh 500 g¹ subsample into a freeze-dryer flask, and dry the sample.
 5. Add 25 ml of 2N HCl² to the flask; swirl acid in the flask until all residue is in solution.
 6. Take a 5 ml subsample of the acid solution from step 5, add 0.5 ml of 12.5% W/V lanthanum chloride and analyze for strontium.
 7. Analyze the remainder of the acid solution from step 5 for manganese, zinc, cobalt, and iron.
-
1. A smaller subsample may be used here; however, a proportionally smaller volume of acid should be used to redissolve the residue.
 2. July, 1973 and subsequent samples were prepared using 1N HCl.

vigorously in 60-75 ml water then allowed to settle 15 seconds; clay and silt remain in suspension, and are later separated on the basis of differential settling times. Coarse sediments are dried and separated using a series of standard sieves. Organic content was determined using a tared, oven dried subsample which was heated to 600°C for 24 hours, with organic content determined from weight loss. The particle size determination procedure has been outlined in Table 5.

For chemical analysis of sediments, the sample was oven-dried at 70-80°C, then mixed and a representative subsample taken for analysis. The sample was heated with 6N HCl for 24 hours to leach the elements from the insoluble portion, with the acid solution then filtered, diluted, and analysed by flame emission/atomic absorption. Table 6 describes this procedure in detail.

Flame emission and atomic absorption analyses were carried out using a Jarrell-Ash #82-800 spectrophotometer; Table 7 lists operating conditions for the analysis of individual elements. Standards were prepared for each element, using 1N or 2N HCl for trace elements, and weak HCl matrix (pH=2) for Ca, Na, K. Standards were run at frequent intervals during analysis of each set of samples, and a standard curve developed for determination of sample concentration.

In order to test the reliability of the freeze-drying procedure and the accuracy of atomic absorption/flame emission analysis, a series of test samples were prepared and analyzed. Using a major ion matrix comparable to Lake Erie water, samples were prepared with trace metal concentrations covering the range found in lake samples. These samples were freeze-dried, the residue redissolved and analyzed by AA/FE. Results are shown graphically in Figure 6.

Table 5. Determination of particle size composition of sediments.

-
1. To a 100 or 125 ml bottle, add 20-25 ml of fresh sediment (equivalent to 10-30 g dry weight).
 2. Add 60-70 ml distilled water to bottle and agitate vigorously.
 3. Allow sample to stand 15 seconds, then decant supernatant into a second container.
 4. Repeat steps 2 and 3 as necessary, until supernatant is clear following the 15 second settling period.
 5. Reagitate combined supernatant from steps 3 and 4, and allow mixture to stand 15 minutes.
 6. Siphon or decant supernatant into an additional container; dry and weigh the settled portion (silt).
 7. Allow supernatant from step 6 to settle 24 hours; dry and weigh settled portion (clay).
 8. Dry coarse material from step 4, separate into the following size categories using U.S. standard sieves: 297u (fine sand); 595u (medium sand); 1.0mm (coarse sand); 4.0mm (gravel); 40.0mm (pebbles). Weigh individual size fractions.
-

Table 6. Preparation of sediment for the analysis of trace elements.

-
1. Oven-dry the sample at 70°C.
 2. Weigh a 10 gram subsample into a 500 ml boiling flask - a larger subsample may be used if the sample consists of sand or coarse material.
 3. Add 5 ml of Dow Anti-Foaming Agent to the flask to prevent excessive foaming.
 4. Add 83 ml of 6N HCl to the flask and allow the reaction to proceed at room temperature.
 5. Apply heat to the flask such that the mixture boils gently. Continue to apply the heat for 20-24 hours.
 6. Allow the mixture to cool, then filter through ashless paper (Whatman 41, 42, or equivalent). Rinse the flask and filter with distilled water.
 7. Using distilled water, adjust the final volume of the solution to 100 ml.
 8. Dilute a 10 ml subsample of this solution to 25 ml with distilled water; analyze for zinc and cobalt.
 9. Take a 5 ml subsample from the solution of step 8 and add 0.5 ml of 12.5% W/V lanthanum chloride and analyze for strontium.
 10. Using 2N HCl¹, dilute 1 ml of the original acid solution (step 7) to a volume of 50 ml and analyze for iron and manganese.
-

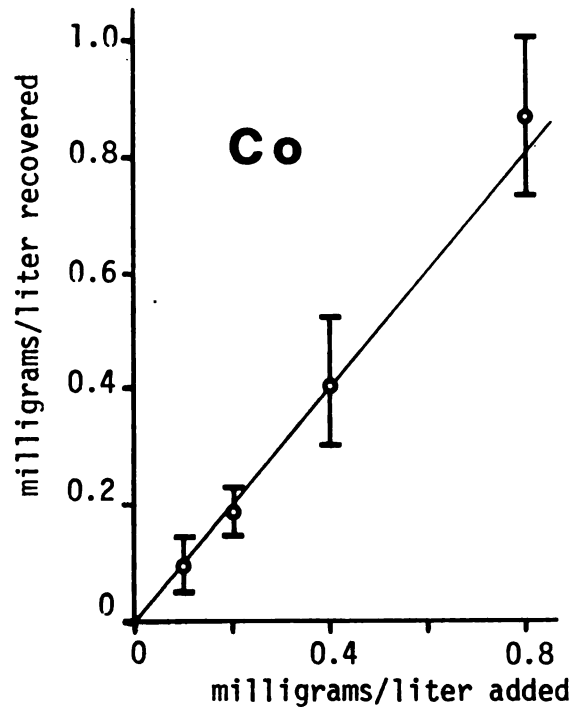
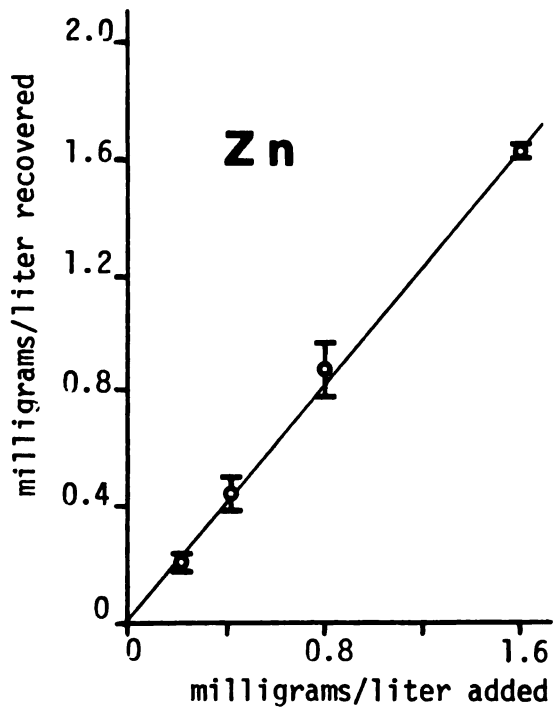
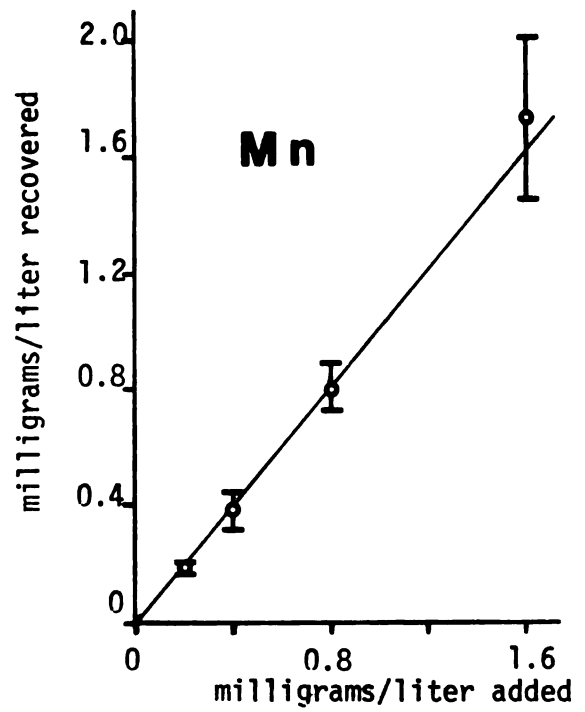
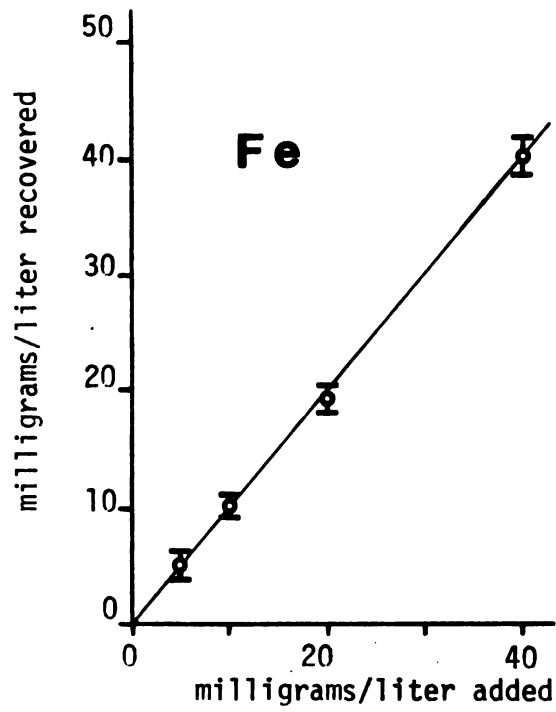
1. July, 1973 and subsequent samples were prepared using 1N HCl.

Table 7. Operating conditions for analysis of selected elements by atomic absorption and flame emission.¹

Element	Resonance Line A°	Sensitivity ug/ml	Absorption or Emission	Remarks
Ca	4227	0.08	Absorption	Add 1% W/V lanthanum chloride to prevent PO ₄ interference. Add K to suppress ionization.
Cs	8521	0.03	Emission	Add K to suppress ionization.
Co	2407	0.2	Absorption	
Fe	2483	0.1	Absorption	
Mn	2795	0.06	Absorption	
K	7665	0.03	Emission	
Na	5890	0.08	Emission	Add K to suppress ionization.
Sr	4607	0.15	Emission	Add 1% W/V lanthanum chloride to prevent PO ₄ , Al, Si interference.
Zn	2139	0.03	Absorption	

1. Table based on Elwell and Gidley (1967), and data supplied by Jarrell-Ash Division, Fischer Scientific Company.

Figure 6. Recovery and analysis of known samples, prepared by freeze drying and resolution of residue. (Mean $\pm$ 95% confidence limits, $n=4$ for all means, values shown on figure represent concentrated residue as analysed by AA/FE).



Data Analysis

Variance among stations for the concentration of each element in water was analysed for each sampling date. Differences among stations were determined using Tukey's multiple range comparisons of least significant differences. Temporal variations were determined using pooled data for the six lake stations; lake means for each date were tested for differences, again using Tukey's test.

Log-log plots were drawn comparing concentrations of each trace element to clay, organic carbon, and combined clay-organic carbon composition for individual sediment samples. Correlation coefficients were determined for each element on each date to further define trace element-sediment relationships.

RESULTS

Water

Mean concentrations of each element have been tabulated for each station and sampling date, multiple range comparisons of these elements for each sampling date (Tables A1-9, Appendix A) indicate generally homogeneous conditions among the lake stations. Major elements (Ca, Cl, Na, K) show frequent, but unsystematic differences among the lake station on several dates. Low levels were observed at stations 7 in April, 1973 and 8 in December, 1973; significantly high concentrations occurred at station 5 in July and 4 in December, when levels of all major ions exceeded levels found in Swan Creek. The strongest differentiation among lake stations occurred in October, 1972, when a strong north-south gradient was observed, with highest concentrations in the southern portion of the survey area.

Excepting the high concentrations found at station 4 in December, Swan Creek characteristically had levels of the four major ions significantly higher than lake levels, with concentrations often twice as high as those for the lake. Levels of these elements at station 2 varied greatly; ranging from levels no higher than the lake stations to values only slightly below those found in Swan Creek. Relatively high levels occurred during periods of high discharge from Swan Creek, when creek waters were less subject to dilution before reaching station 2. Conversely when creek discharge is low in summer and

autumn months, considerable dilution is observed, due to the presence of creek water in the lower end of the creek (lake water used for cooling at Fermi is released to the creek, and winds and seiches push additional lake water into the creek).

Temporal changes in the distribution of major ions (Table A-10, Figures 7-10) show two modes of behavior; one for calcium, and another for the three monovalent ions, chloride, sodium, and potassium. Calcium, the predominant cation in solution, is characterized by high levels during late fall to spring, with concentrations dropping to low levels during the warmer months (June-October). Concurrent with low calcium levels are high phenolphthalein alkalinity, reduced total alkalinity, and supersaturation of dissolved oxygen.

The monovalent ions, especially sodium and chloride, show similar distribution patterns; considerable, but unsystematic changes. Sodium and chloride concentrations fluctuate freely, but over a relatively small range of concentrations, with no apparent seasonal trends. Potassium, on the other hand, shows wide fluctuation but a definite trend toward higher winter concentrations, as levels rise sharply during autumn months, falling sharply in the spring.

Trace element distribution in the Fermi area differs considerably from major ion behavior, with differences in both spatial and temporal aspects of their distribution. Variation among these elements was also observed; these differences are discussed in subsequent paragraphs.

Because of its chemical similarity to calcium, strontium would be expected to show similar behavior in its distribution patterns; such a similarity does exist to a large extent, but with certain temporal differences. Spatial distribution for strontium (Table A-5) is generally

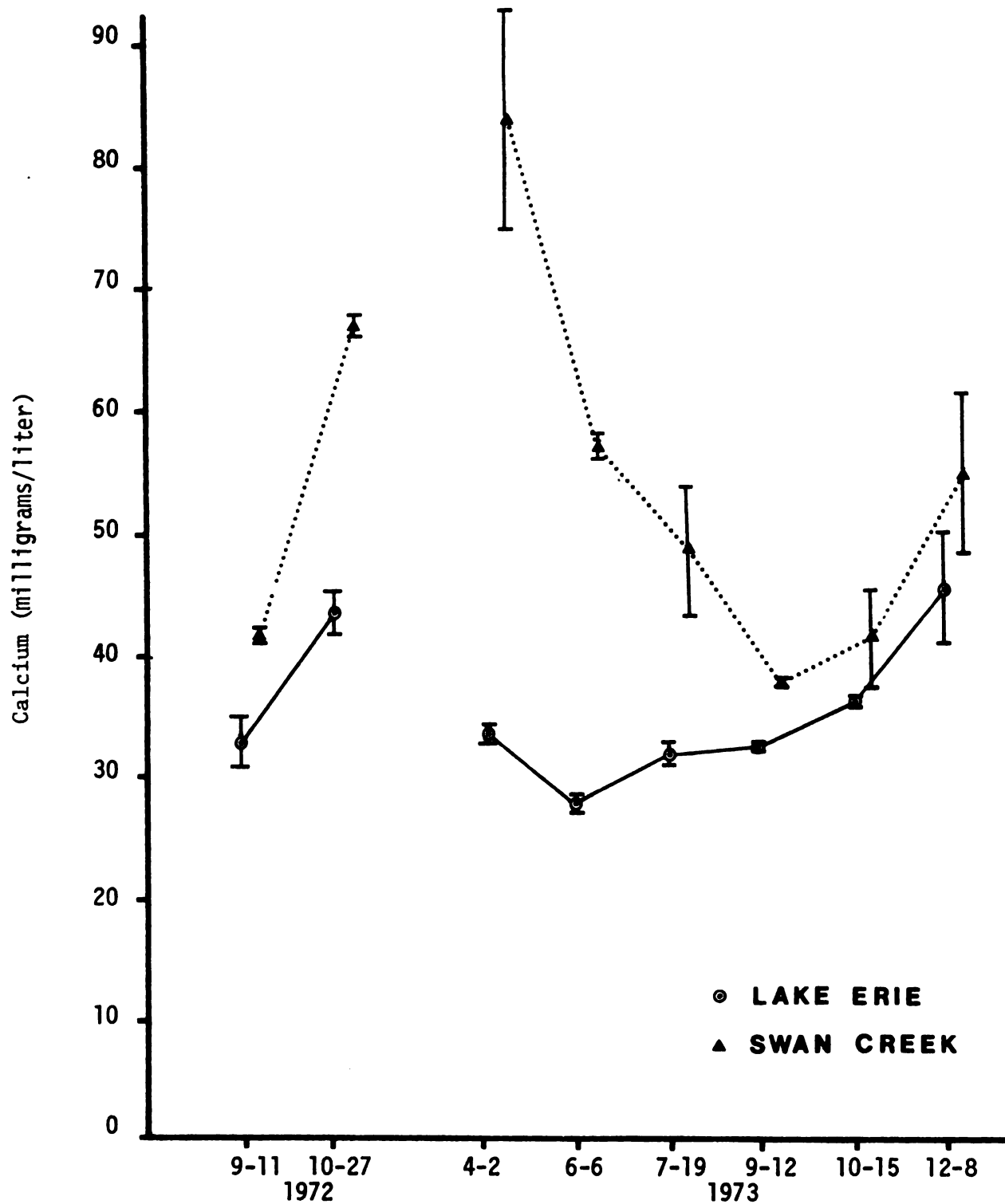


FIG. 7. Temporal variation of calcium in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

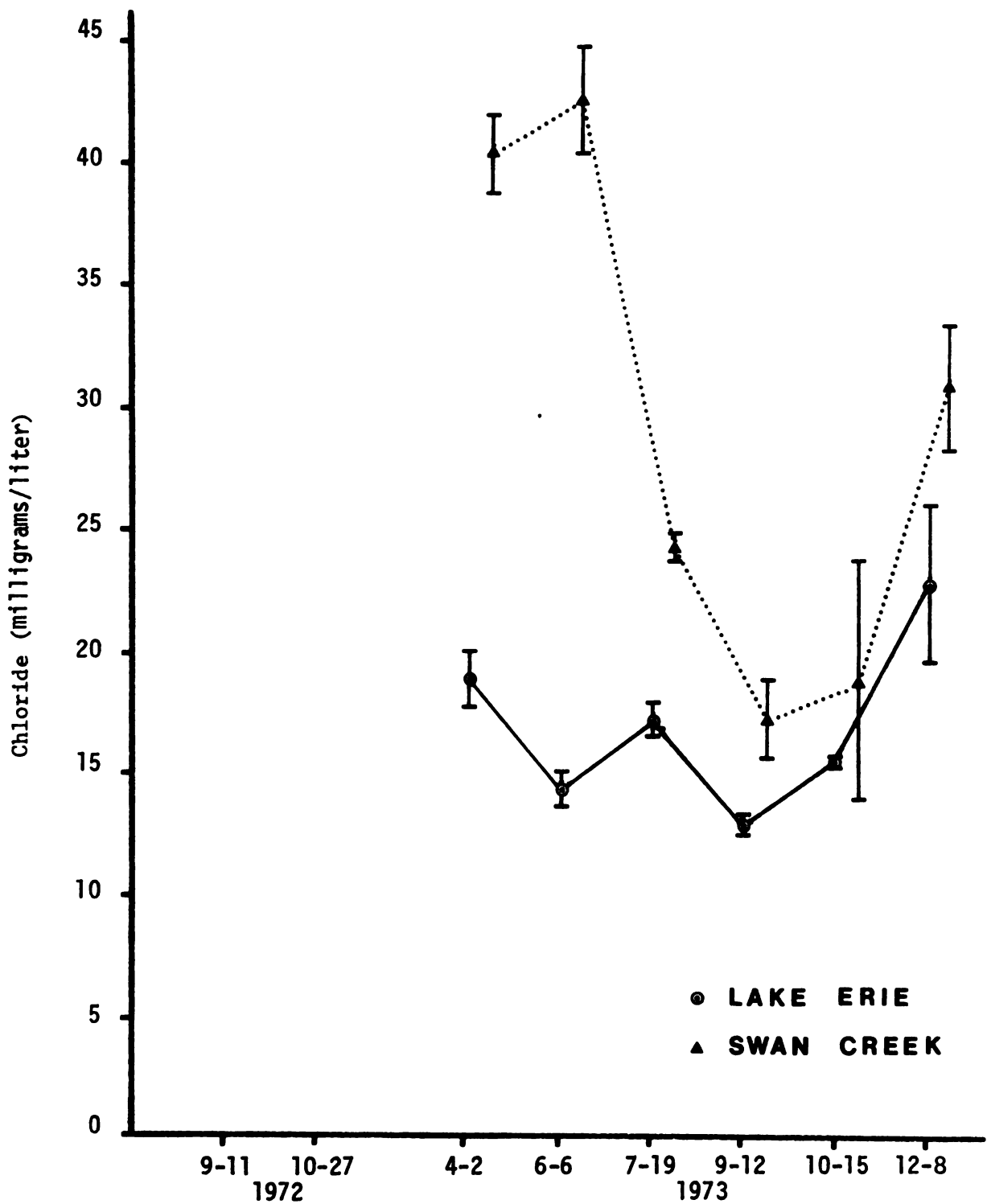


FIG. 8. Temporal variation of chloride in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

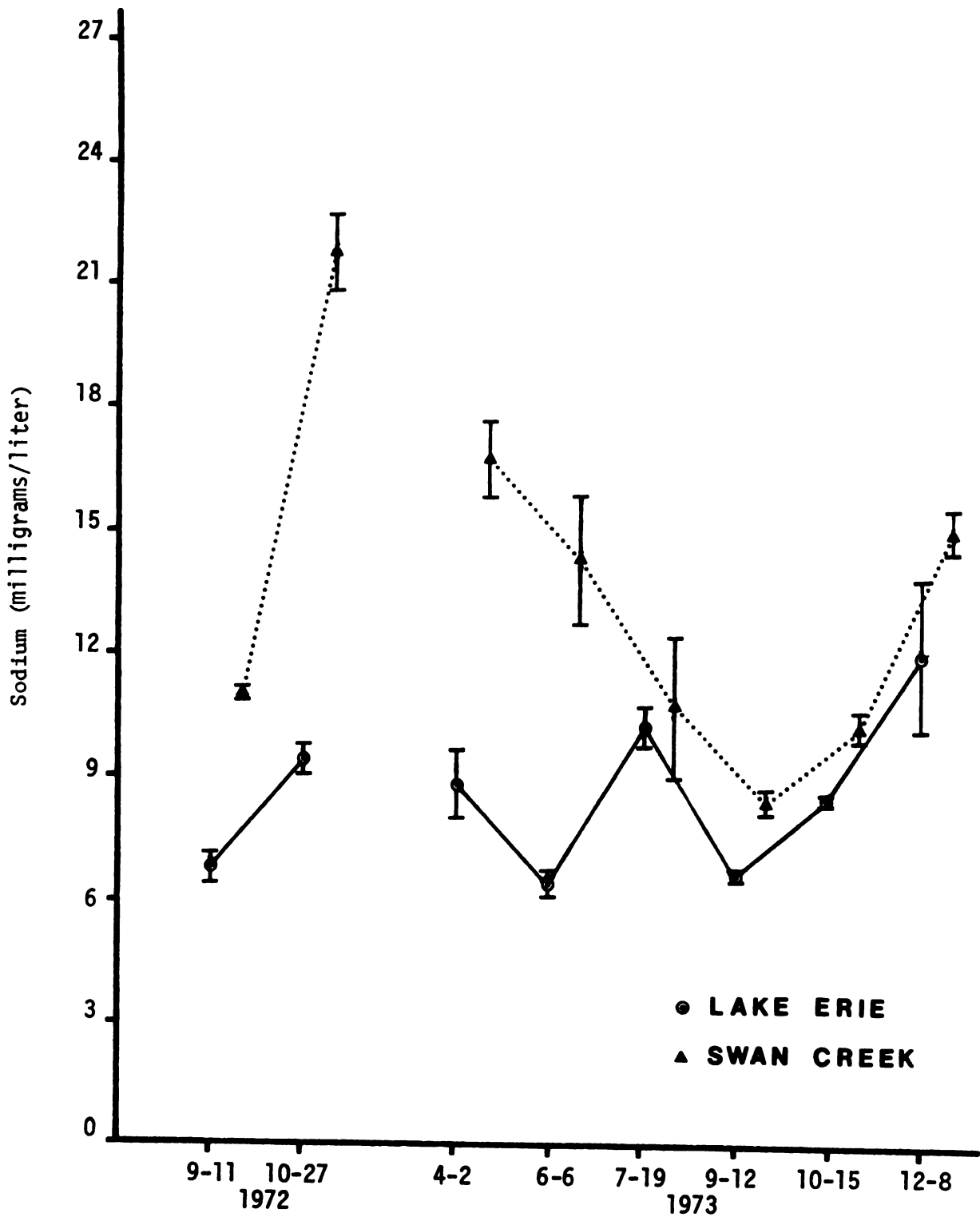


FIG. 9. Temporal variation of sodium in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

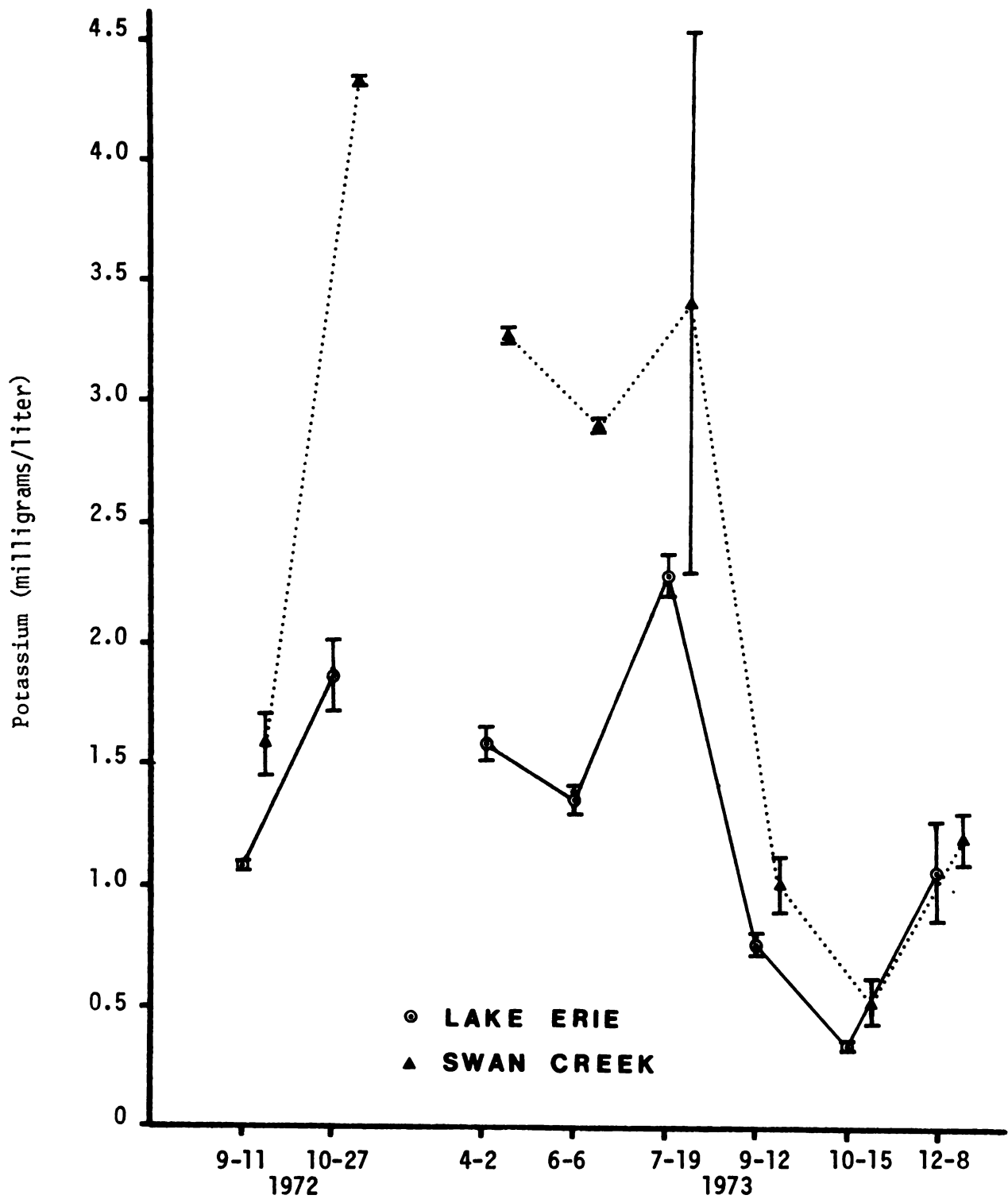


FIG. 10. Temporal variation of potassium in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

similar to the major ions, with high levels occurring in Swan Creek, intermediate and variable concentrations at station 2, and relatively low levels at the lake stations. Variability among the lake stations was unsystematic, with individual differences similar to those described for major elements.

Seasonal changes in strontium concentration (Figure 11) are generally similar to those of calcium, except for an unexpectedly low value for April, 1973. With this one exception, strontium is characterized by high values during the colder months, with low levels in summer and early autumn.

The remaining four elements; cobalt, iron, manganese, and zinc; all members of the first transition series, show considerable differences from the major elements as well as from each other (Tables A-6-9). While concentrations of all elements except zinc are often significantly high in Swan Creek compared to lake stations, this elevation is intermittent, lacking the consistency of high concentrations of major elements found in the creek. Zinc concentrations rarely are high in the creek compared to the lake stations; to the contrary, the mean concentration of zinc during 1973 was lower in Swan Creek than in the lake. Iron and zinc show, on several occasions, enhanced levels at stations 4 and 5 relative to the remaining lake stations. Increases in the concentrations of these two elements at these stations do not always occur simultaneously, but the frequency of these events indicates a real and semi-regular influx of zinc and iron laden waters, rather than just statistical artifact.

Temporal variation (Table A-10, Figures 12-15) in the distribution of these four elements is difficult to characterize; no clear seasonal

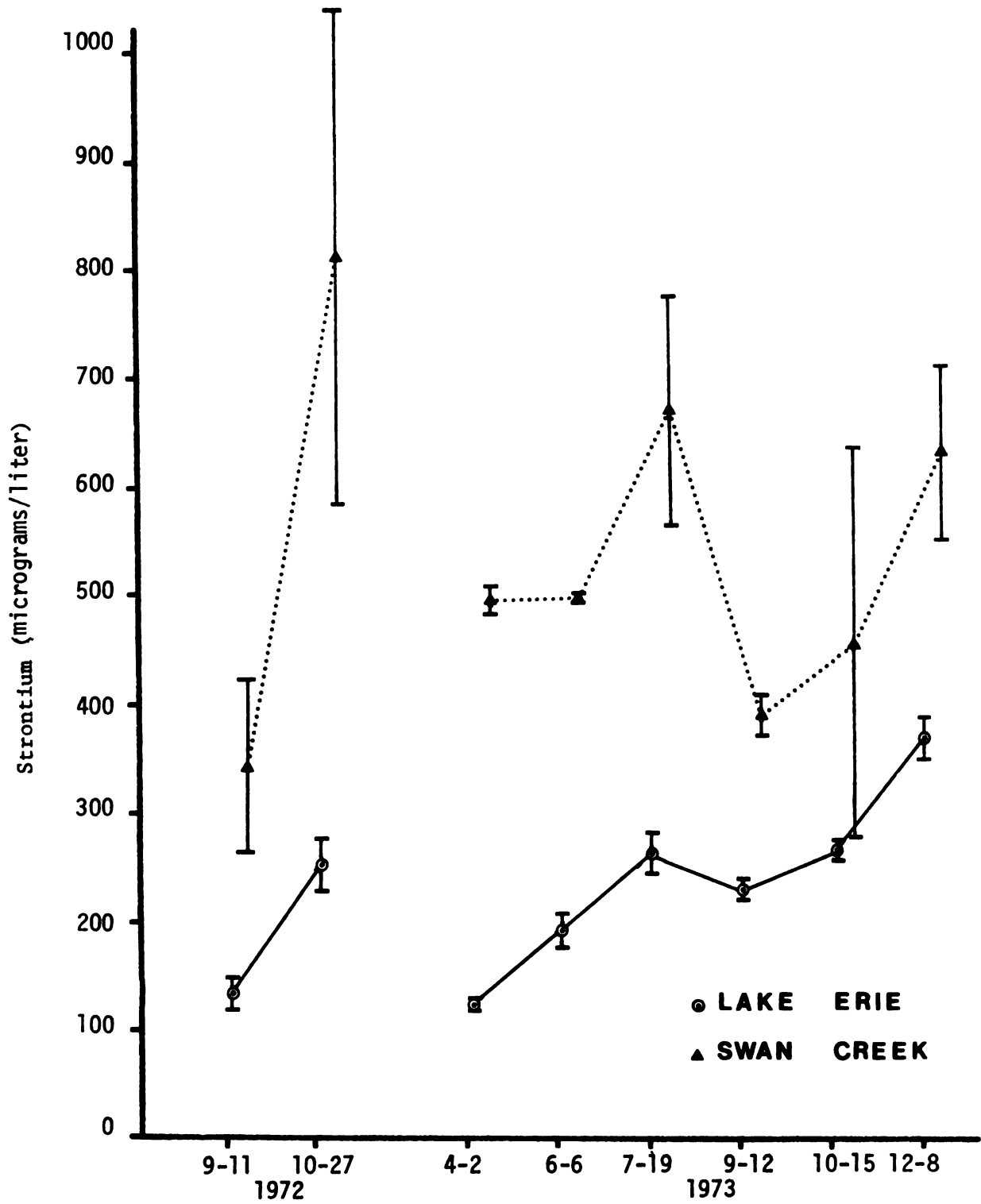


FIG. 11. Temporal variation of strontium in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

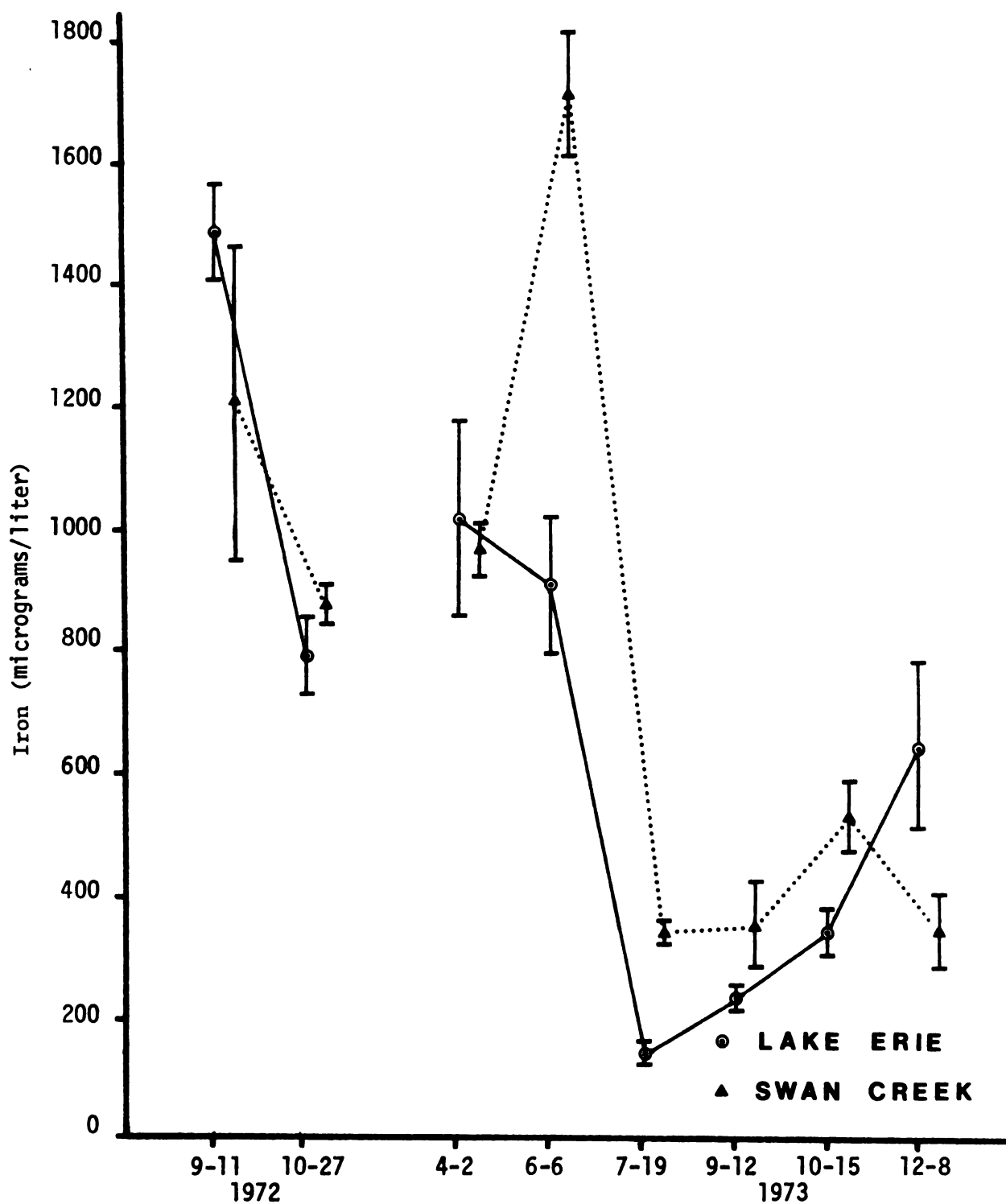


FIG. 12. Temporal variation of iron in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

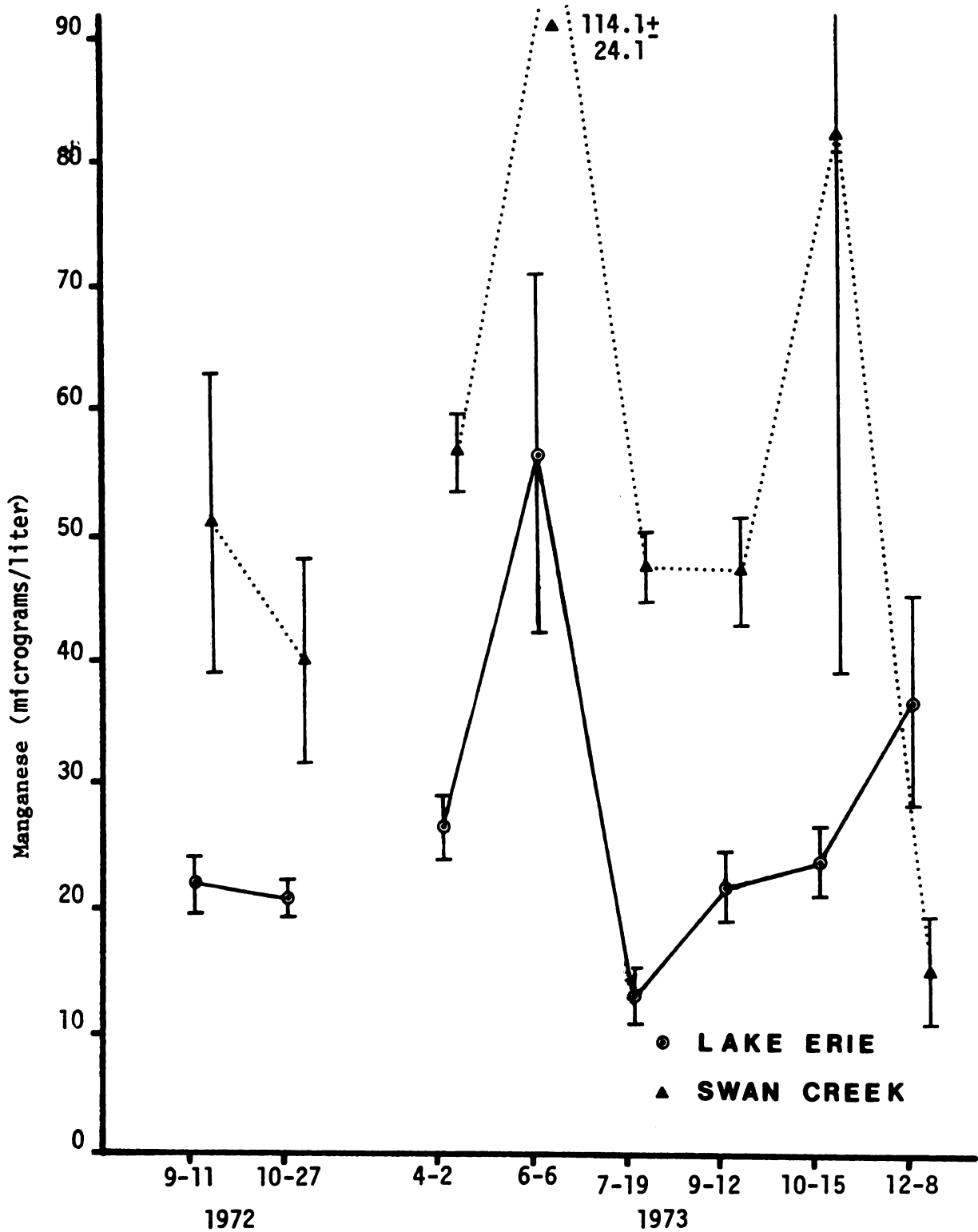


FIG. 13. Temporal variation of manganese in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

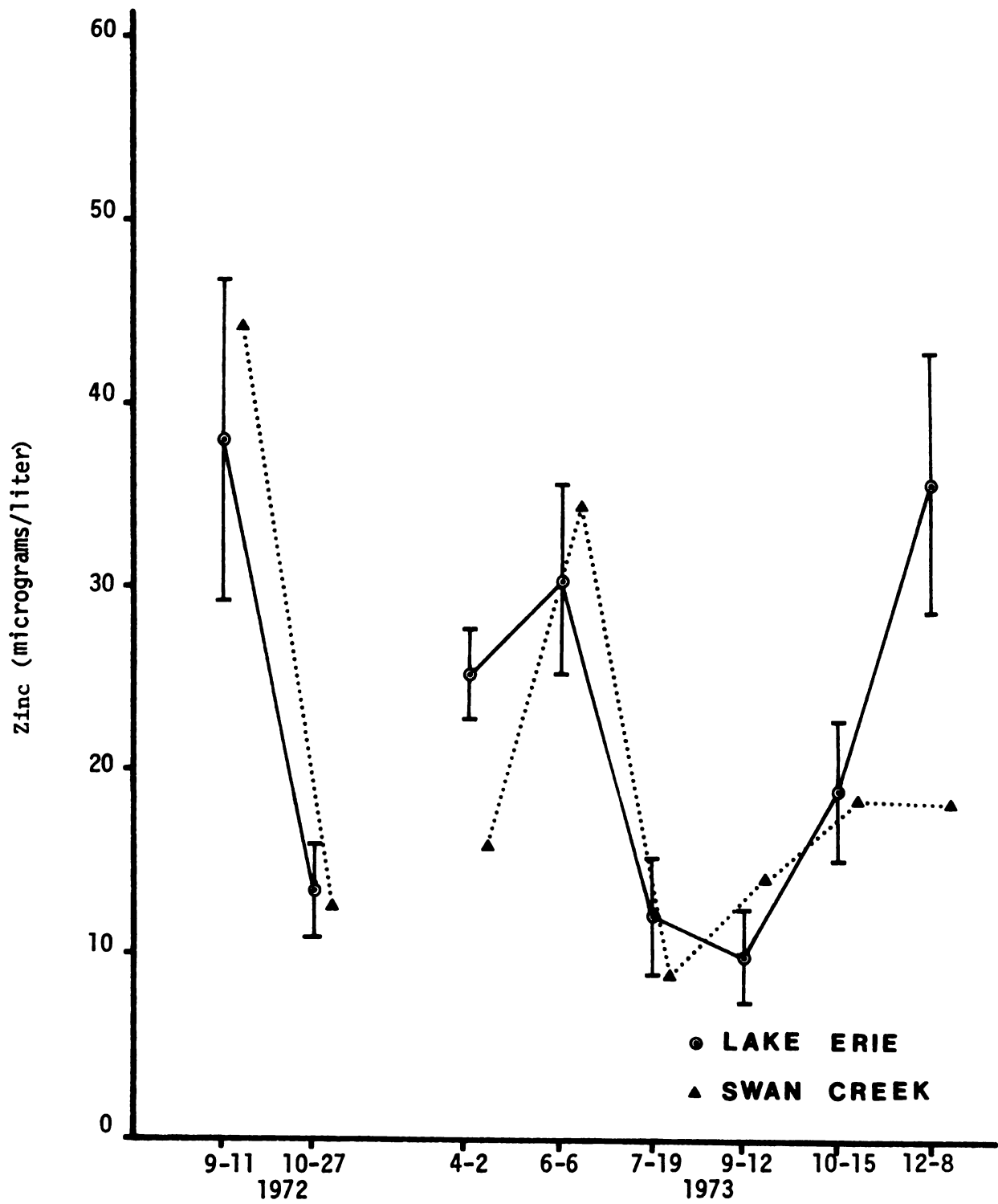


FIG. 14. Temporal variation of zinc in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

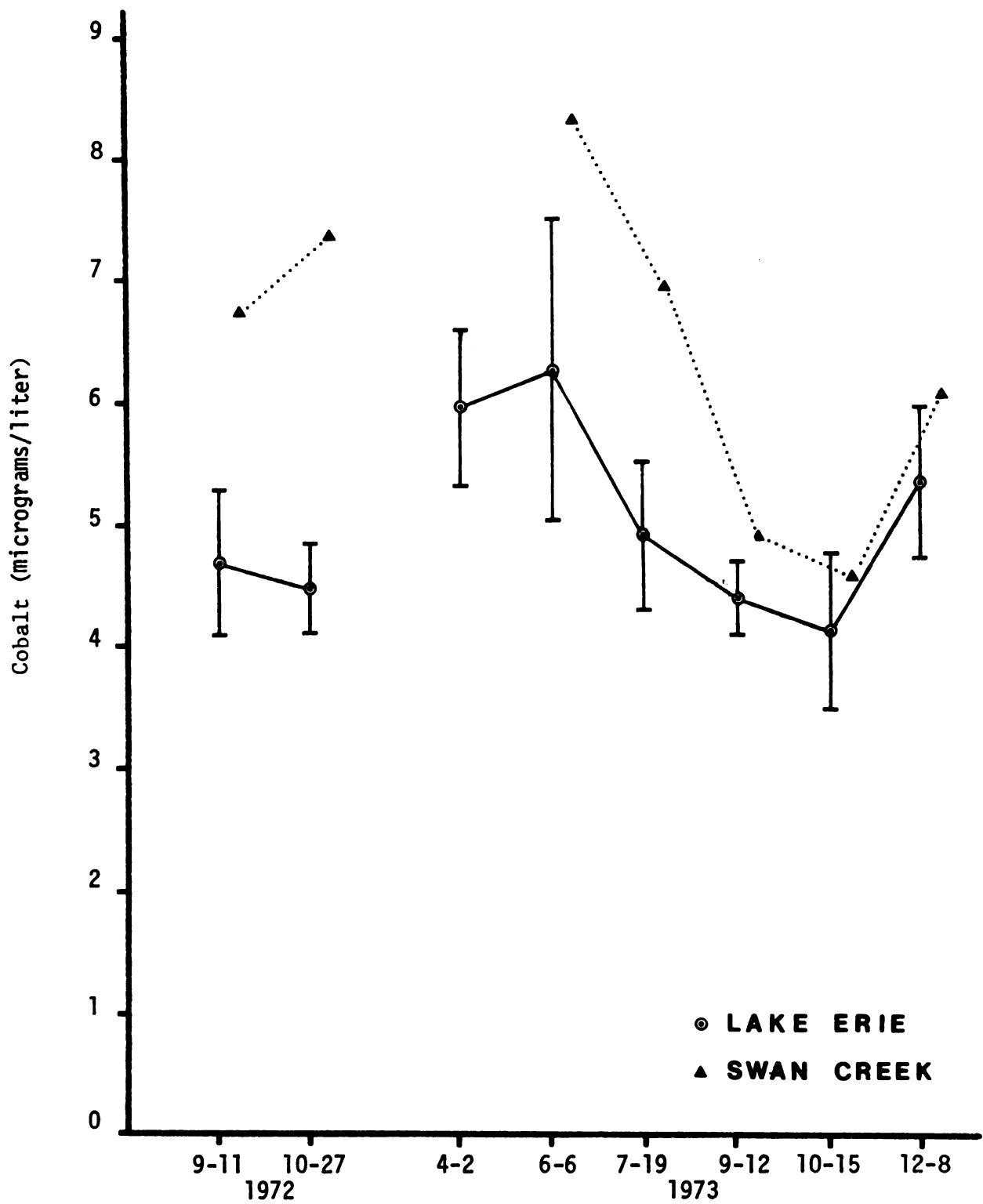


FIG. 15. Temporal variation of cobalt in water in Lake Erie and Swan Creek (Mean $\pm$ 95% confidence interval).

trends are obvious. A pattern approximating that of calcium seems to occur for all elements, with the notable exception that all four metals show high levels in June, 1973. These high levels occur as calcium reaches a seasonal low, indicating that different regulatory mechanisms affect calcium and the trace metals. The high June levels do not correspond with any changes in monovalent major ions, pH, alkalinity, or suspended solids. Organic carbon and nitrogen levels showed seasonal highs in June, suggesting a relationship between the transition metals and organic materials, but graphical plots of these parameters (Figure A-1) indicate only a weak association.

A final parameter was examined to determine a possible relationship with temporal changes in metal concentrations; precipitation data for a period of 14 days preceeding each sampling date (NOAA, 1972; 1973) were compared to trace element variations, but no interrelationship was observed.

Mean levels of major and minor elements have been calculated for 1973 for Swan Creek and the lake stations, with values shown in Table 8.

Sediment

Mean concentrations of the five trace elements in sediment have been tabulated for each sample station and date (Appendix A, Table A-11-17). Data for some stations are missing for several sampling dates due to a variety of problems, including rough lake conditions and equipment problems. For discussion purposes, only the final four sampling dates will be considered; size fraction analysis was carried out for these dates only, and except for one instance (Station 8 in September) complete sample sets were collected on these dates. High concentrations of all elements typically occurred at one of three

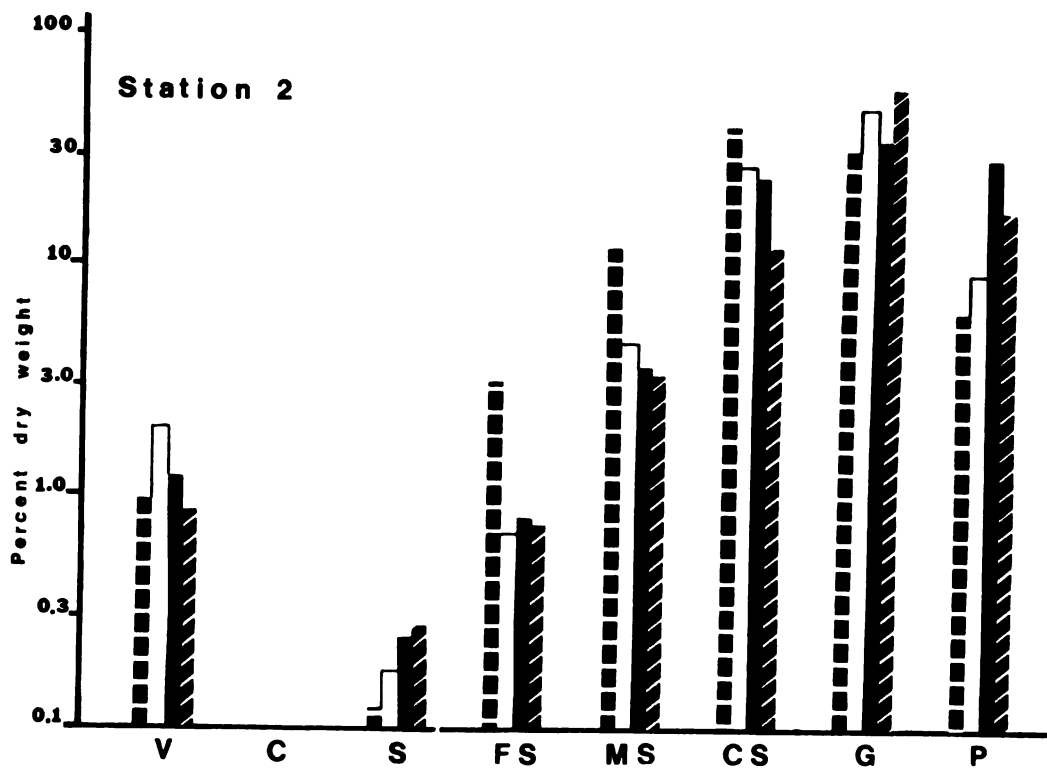
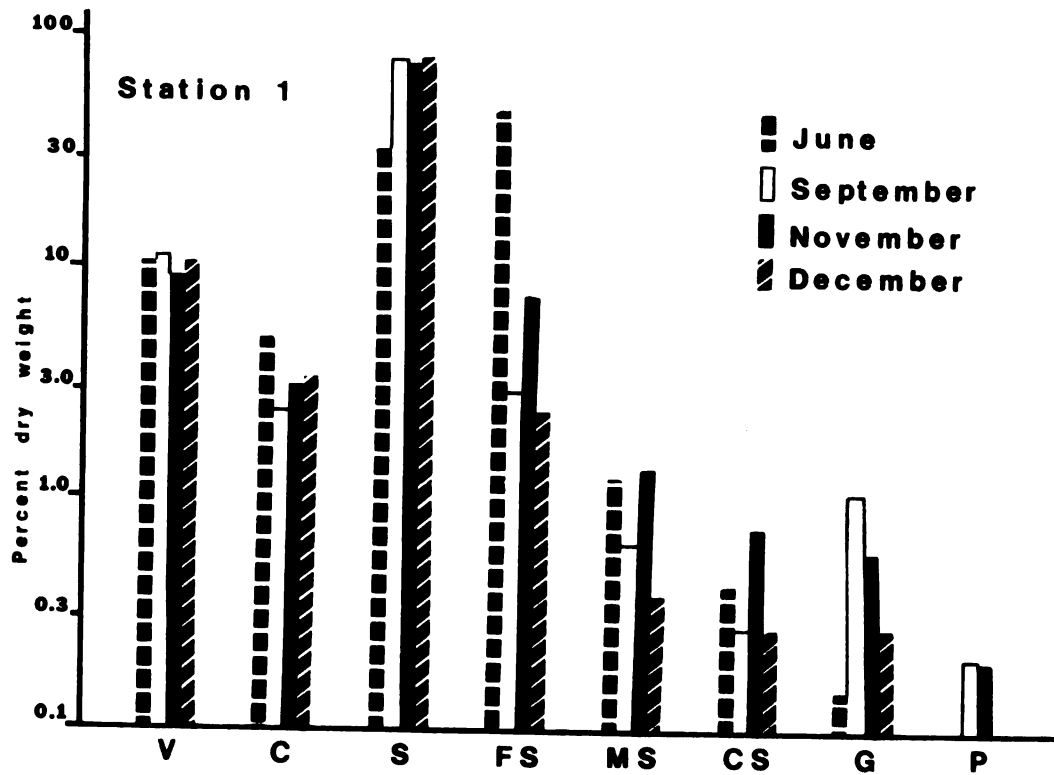
Table 8. Mean concentration of major and minor elements in survey area during 1973.

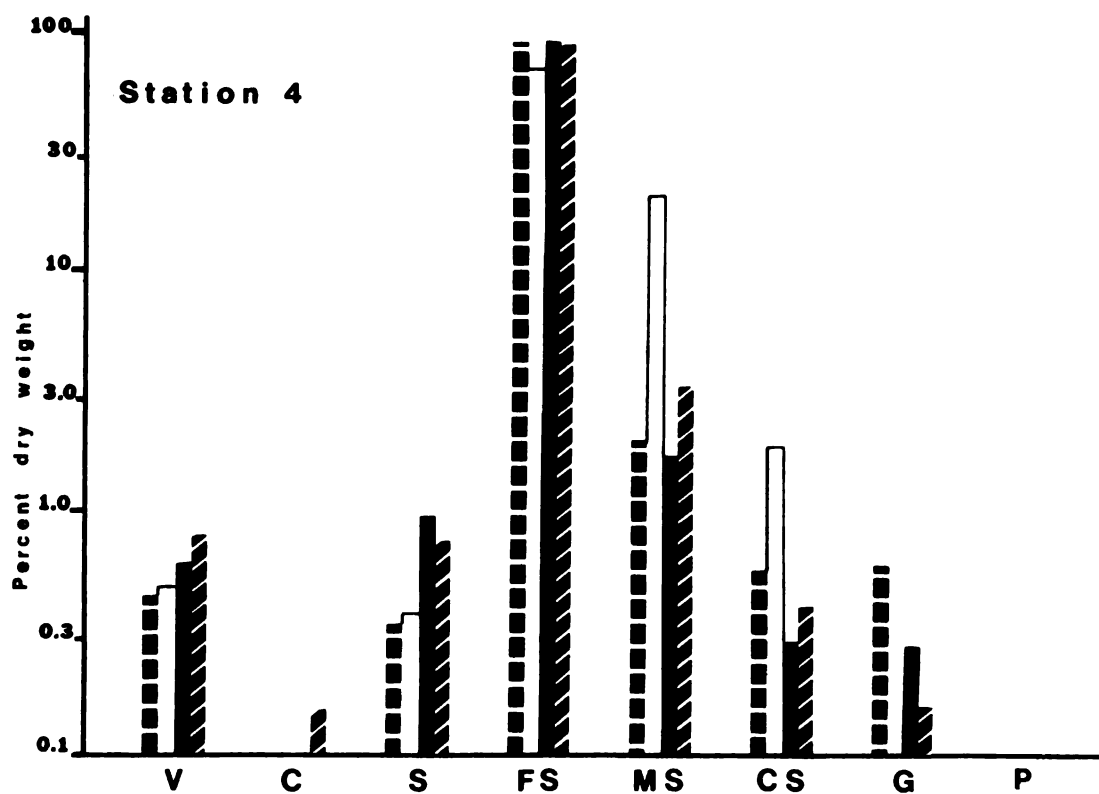
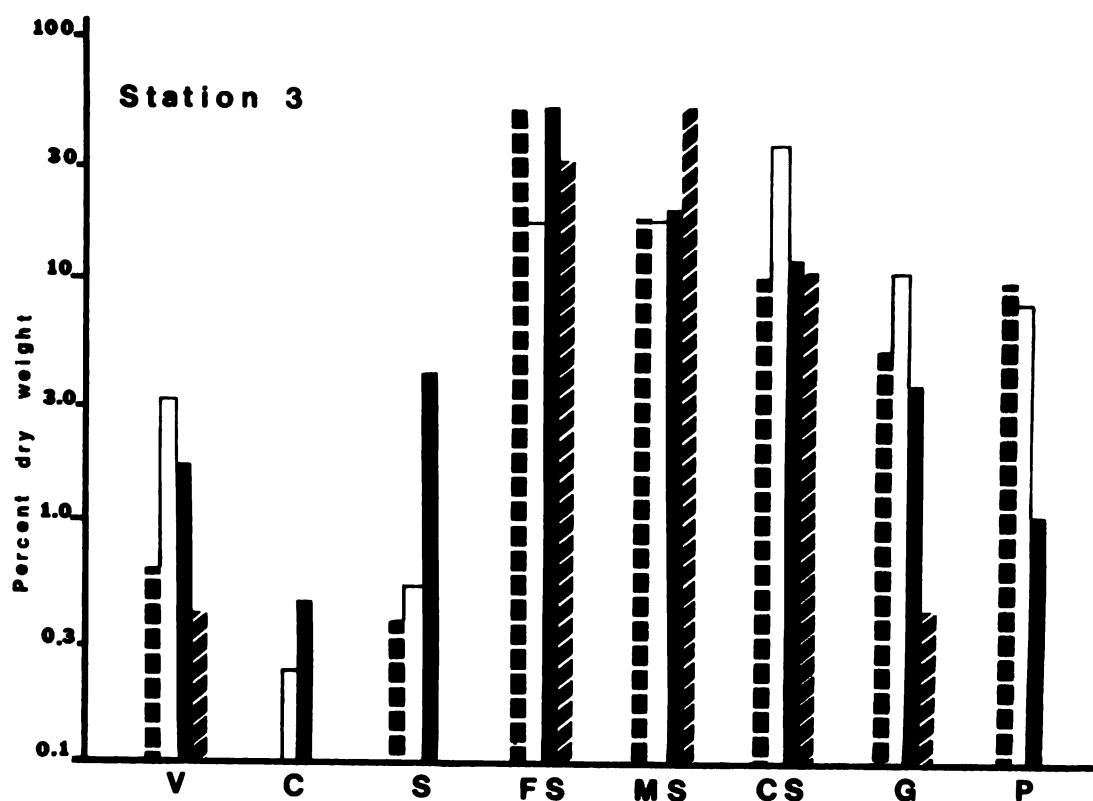
Element	Swan Creek		Lake		Creek/Lake Ratio
	Mean	Range	Mean	Range	
Ca mg/liter	54.0	37.7 87.9	34.4	25.7 65.0	1.57
Cl mg/liter	29.1	16.5 44.7	16.7	11.0 36.8	1.74
Na mg/liter	12.6	8.3 17.2	8.7	4.8 20.9	1.45
K mg/liter	2.06	0.51 3.76	1.22	0.21 2.56	1.69
Sr ug/liter	528.	372. 723.	239.	97. 407.	2.21
Fe ug/liter	703.	319. 1755.	542.	98. 1580.	1.30
Mn ug/liter	60.3	13.7 116.3	29.5	4.8 129.0	2.04
Zn ug/liter	18.5	7.5 55.6	22.3	4.3 61.0	0.83
Co ug/liter	6.2	4.0 8.9	5.2	2.3 14.0	1.19

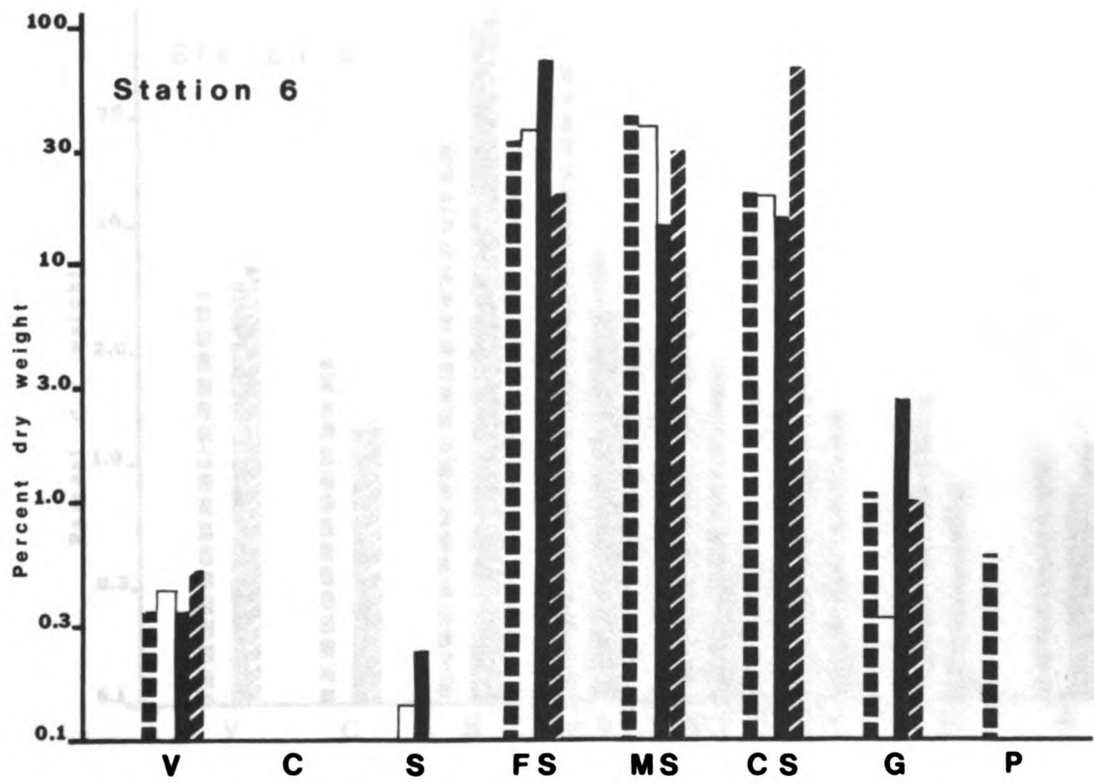
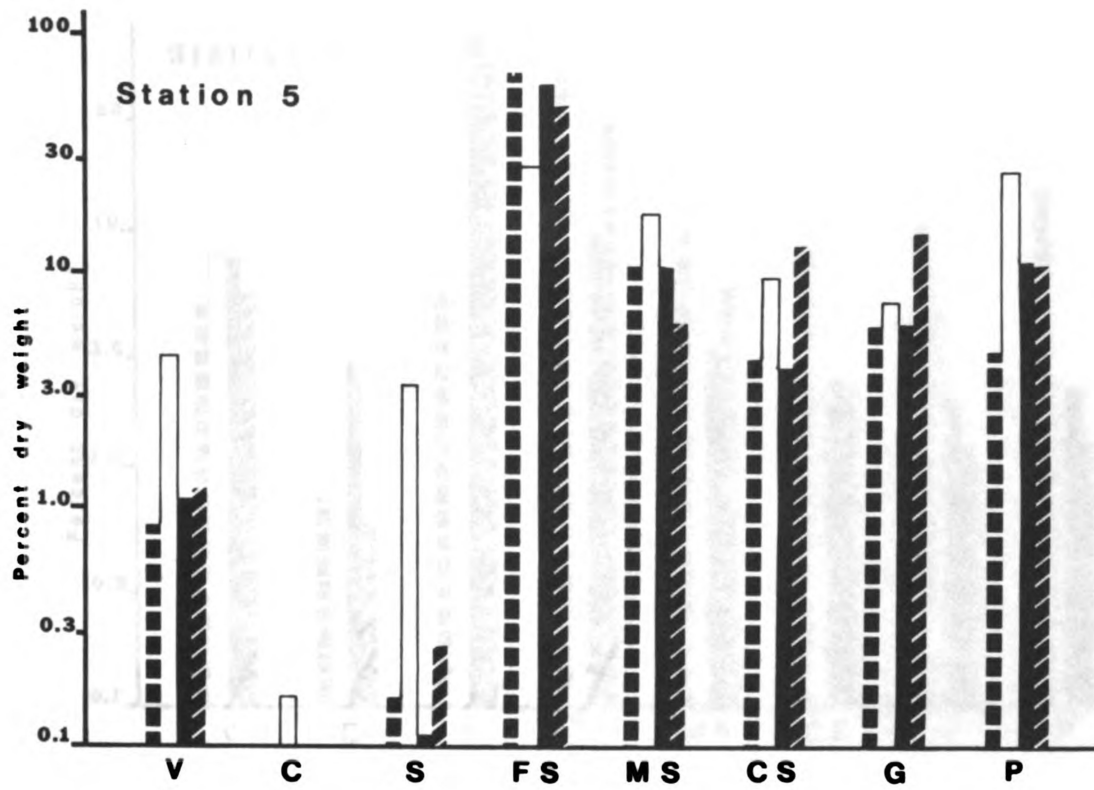
stations - 1, 7, or 8, where the finest sediments were also found. The lowest concentrations occurred at stations typified by sand and other coarse materials with low organic and clay content (2, 3, 4, and 6). Strontium in all instances occurred at highest concentrations at station 1; cobalt similarly was often found at higher concentrations in creek sediments compared to stations 7 and 8. Zinc, on the other hand was found at higher concentrations at stations 7 and 8 on all dates, and iron and manganese at equal or higher levels at the two lake stations compared to Swan Creek sediments.

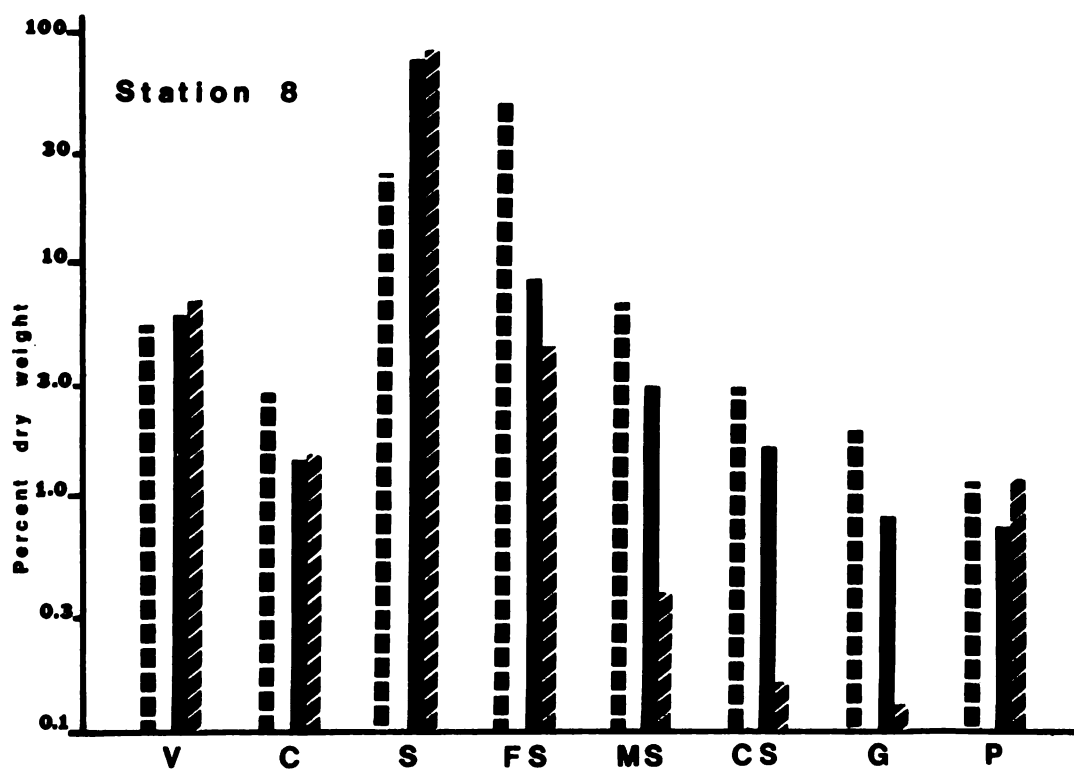
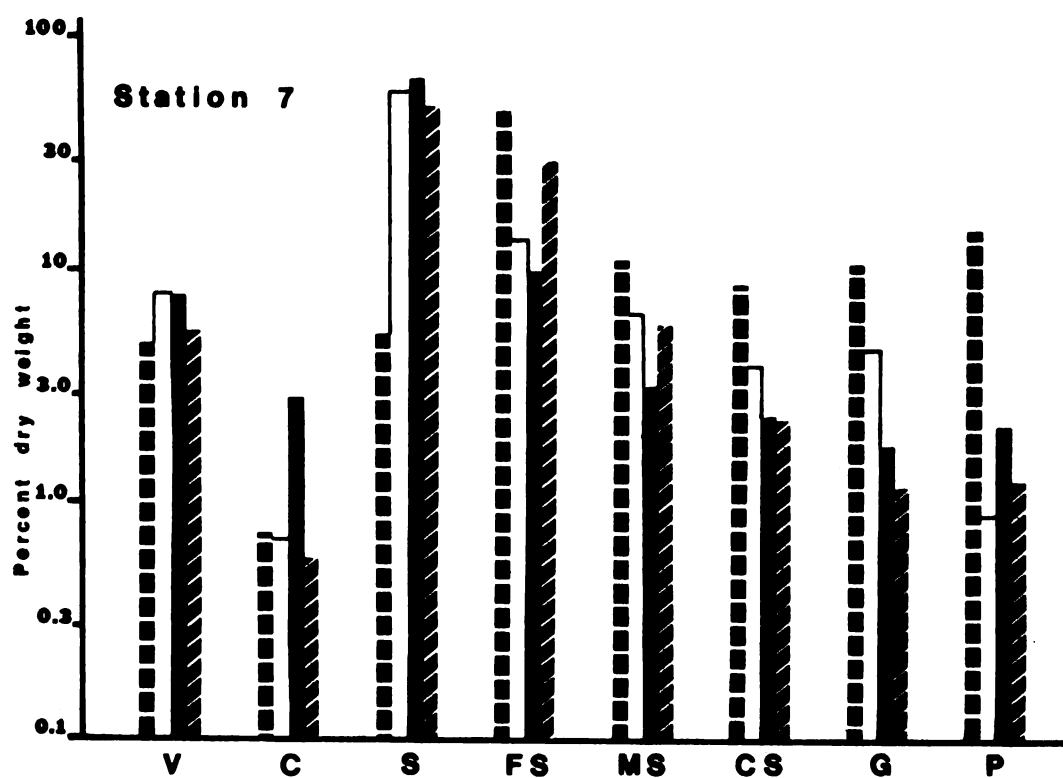
Size fractions of sediments have been determined for 1973, with means for each station and date shown graphically in Figure 16. Size composition of sediments at the various stations showed in most cases relatively little variation over time. Station 1 and 8 typically consisted primarily of silt, with moderate amounts of organic matter, clay and fine sand, and only very small percentages of coarser materials. Station 2, in the outwash area at the mouth of Swan Creek, had the coarsest sediments found in the survey area; a mixture of coarse sand, gravel, and pebbles, with very low amounts of smaller particles. Moving away from Swan Creek, sediment composition at stations 3 and 4 suggests settling of progressively finer particles as the plume flows along the northeast shore. Station 3 is composed of mixed sand and gravel, while fine sand predominates at station 4. At station 5, the bottom is well-mixed with about 50% fine sand and the remainder a mixture of larger particles including considerable pebble and shell fragments. South of Swan Creek, at station 6, a variable mixture of fine to coarse sand occurred, marked by very low percentages of either larger or smaller particles. Station 7 showed probably the most even

Figure 16. Particle size distribution of Fermi sediments during 1973.
(V-volatile material, C-clay, S-silt, FS-fine sand, MS-medium sand, CS-coarse sand, G-gravel, P-pebbles).









distribution of all particle sizes; clay and organic content were relatively high, with high silt content and gradually decreasing fractions of larger particles.

No attempt has been made to determine spatial or seasonal changes in trace element content of sediments; it is assumed that physical size differences (particularly of the clay and organic fraction) are the primary factor responsible for variation among samples, obscuring actual temporal or spatial changes which may occur. Assuming that volatile materials consists primarily of organic matter, and using an approximation that 40% of organic material is carbon, it can be estimated that 40% of volatile material is organic carbon. Using this approximation, along with clay content, concentration of each element has been plotted against clay, organic carbon, and clay plus organic carbon. Means for each station for June-December 1973 and individual samples for December have been plotted, with results shown in Figures A-2 to A-11, Appendix A.

These figures, along with correlation coefficients (Table 9) indicate the good correlation of most elements with both clay and organic carbon, with all correlations significant at the 99% level. No clear trends are evident, however, whether metal-clay or metal-organic carbon correlations are better. It is somewhat difficult to accurately interpret these data, however, as we have no way of knowing whether the poorer relationships are indicative of imperfect sample analysis or of great variability among samples. We also have no way of determining cause and effect relationships between physical and chemical characteristics of the sediments.

Table 9. Correlation coefficients of selected trace elements with clay and organic carbon for Fermi sediments during 1973 (R values listed).

Element	Sampling Date	Clay	Organic Carbon	Clay plus Organic Carbon
Strontium	6-6-73	0.8288	0.8755	0.8611
	9-12-73	0.9448	0.8692	0.8940
	11-7-73	0.6038	0.8948	0.8388
	12-8-73	0.9118	0.9201	0.9118
Iron	6-6-73	0.8504	0.8969	0.8831
	9-12-73	0.9232	0.8417	0.8557
	11-7-73	0.8377	0.8814	0.8943
	12-8-73	0.9352	0.9559	0.9563
Manganese	6-6-73	0.7207	0.7930	0.7884
	9-12-73	0.9195	0.7406	0.7758
	11-7-73	0.7080	0.8129	0.8052
	12-8-73	0.8357	0.7820	0.8005
Zinc	6-6-73	0.9046	0.8683	0.8726
	9-12-73	0.9151	0.7283	0.7623
	11-7-73	0.8778	0.8595	0.8794
	12-8-73	0.8554	0.9495	0.9457
Cobalt	6-6-73	0.7465	0.8282	0.7743
	9-12-73	0.8617	0.8943	0.9056
	11-7-73	0.6858	0.8743	0.8393
	12-8-73	0.8947	0.9176	0.9156

In terms of spatial or temporal differences of sediments, two stations suggest some sort of spatial variation. Station 1, in Swan Creek, shows unexpectedly low concentrations for all elements except strontium. Conversely, at station 5, the northernmost lake station, all elements except zinc show higher trace element concentrations than would be expected, based upon particle composition. Temporal variation is essentially absent, except for strontium, which was characterized by high sediment levels in June and September, and relatively low levels in November and December (Figure A-2).

DISCUSSION

Water

Variation in the distribution of major elements in the Fermi area probably reflects the importance of two major factors which regulate concentrations of these elements. One regulatory mechanism, of importance to calcium and other polyvalent cations, involves sorption and precipitation processes resulting from seasonal pH and alkalinity changes. pH increases during periods of high primary productivity, causing precipitation of hydrous oxides and carbonates. The second, and probably most significant factor however, is variation in inputs of these elements into the survey area. The three monovalent major ions (sodium, potassium, chloride) are not significantly affected by pH and alkalinity changes such as occur in the Fermi area, yet these ions show significant seasonal variations. In the case of the polyvalent ions, both of these factors hold some influence, although their relative importance is usually difficult to determine. In one sense, variable inputs could be regarded as the sole regulatory factor for water, as there is a constant movement of water from Swan Creek and the Detroit River through the survey area. pH and alkalinity changes are not restricted to the survey area, therefore changes of these parameters before water reaches the study area will influence the level of the polyvalent ions determined within the survey area.

A third factor appears to influence calcium and to some extent strontium levels, particularly in Swan Creek. Bedrock surrounding and underlying the western basin of Lake Erie is comprised of limestones and dolomites; (ILEWPB, 1969) solution of this material is evidenced by the high levels of both calcium and strontium recorded in Swan Creek, particularly during periods of high discharge.

As elements whose concentrations have been relatively unaffected by man's activities, calcium and strontium variations probably best represent a seasonal distribution controlled by pH and alkalinity changes. These two elements, along with bicarbonate, are characterized by high winter and early spring values, with levels falling and remaining significantly lower during summer and autumn months, and rising again by late fall. Chawla (1971) observed similar calcium distribution patterns in both Lakes Erie and Ontario, changes he similarly attributed to pH and alkalinity changes brought on by high summer primary productivity.

Sodium, potassium, and chloride concentrations are largely unaffected by pH changes, and biological activity has little effect on concentrations of these ions; thus seasonal changes of these elements can be attributed largely to changes in the levels of these ions moving into the Fermi area. Concentrations of these three ions are increased greatly as waters pass from Lake Huron through the Detroit River (about 4 fold for Na^+ and Cl^- , 2 fold for K^+) (Beeton, 1971), with most added materials flowing along the Michigan shore downriver and along the western shore of the lake. Weiler and Chawla (1969) noted no significant temporal changes in the levels of these ions in the open waters of Lakes Erie and Ontario; this study shows significant, but irregular variation for all three of these ions. In all probability variations

in source inputs to the Detroit River, or else variation in the mixing of Detroit River waters in the lake account for the observed variability in the levels of these three ions.

The four transition metals reflect complex overlapping regulatory mechanisms, with pH and alkalinity changes, organic matter, and input variation all playing a role. Of these three factors, input variation would appear to ultimately be the most significant. Data compiled by the Canada Centre for Inland Waters (Weiler and Chawla, 1968; 1969) indicate considerable enrichment of minor elements as waters pass through the Detroit River. Such enrichment not only surpasses "natural" levels of these elements that would be expected for the lakes, but also exceeds the solubility of some elements, notably iron and manganese. Bahr (1972) has estimated the extent of heavy metals enrichment from three types of sources in southeastern Michigan; industrial effluents, municipal sewage effluents, and transfer of airborne metals to surface waters. Assuming that all these inputs are thoroughly mixed into the Detroit River and that input rates are constant through the year, metal levels in the river would be enriched by levels as shown in Table 10.

The high trace element levels observed at Fermi suggest even greater enrichment than that estimated in Table 10; more likely, however, these inputs are being contained within the water mass along the American shore of the Detroit River. This water mass subsequently moves into the Fermi area, resulting in the very high trace metal levels observed in this study. Entering the lake at high, and apparently highly variable concentrations, levels of these elements are subsequently reduced by precipitation, coprecipitation with iron and

Table 10. Estimated enrichment of Detroit River waters from man-made sources in southeastern Michigan (all concentrations in ug/liter final concentration). (From Bahr, 1972).

Element	Source			Total
	Industrial Effluents	Municipal Sewage Effluents	Airborne Fallout	
Co	< 0.01	< 0.01	< 0.01	< 0.01
Fe	19.01	46.86	6.66	72.61
Mn	1.05	0.24	0.21	1.50
Zn	1.87	3.54	0.51	5.92

manganese oxides, and settling of suspended forms. The high zinc and iron levels observed at stations 4 and 5 reinforce the concept that the Detroit River is the source of trace metals entering the Fermi area.

It is difficult to determine the relative importance of other factors which affect transition metal levels in water. All four elements show low levels during summer months, suggesting the influence of sorption-precipitation reactions induced by summer pH increases. High June concentrations do not conform to such a mechanism, but do coincide with a sharp increase in organic materials, as evidenced by organic nitrogen and organic carbon (Table 3) levels in June. The overall correlation between the trace metals and organic material (Figure 16) is weak, suggestive of perhaps an intermittent influence. Overall, it is suggested that inputs provide an unmaintainably high level of transition metals into the lake system, at which point various regulatory mechanisms act to either maintain or depress concentration. Complex formation, particularly organic chelation, can greatly enhance solubility relative to the simple ions, helping to maintain high metal concentrations. Sorption on suspended particulates, either organic or inorganic, prolongs the residence time of the metals in water, but sorbed ions will gradually be carried to the sediment. Precipitation and coprecipitation depress metal levels, with the influence of these processes increasing with pH. At Fermi high suspended solids and high organics contribute to high metal levels in April and June, respectively. By July, declining levels of these two parameters, coupled with an increase in pH, result in sharply lowered levels of the metals; levels which remain low until December when pH has declined.

One feature of the survey area which should be noted is the almost negligible impact of Swan Creek upon the lake, even during periods of relatively high creek discharge. The general homogeneity of the lake, demonstrated by multiple range comparisons for individual elements and by the conductivity survey of 28 May, 1973, indicate almost complete mixing and dilution of the creek plume with lake water within about 0.25 km from the mouth of the creek. Even taking into account the high discharge from Fermi compared to Swan Creek, if we extend this pattern and predict comparable mixing of effluents released from Fermi II, it is apparent that in only a small area will significant radioisotope contamination be identifiable. Nelson et al. (1971) report 10 to 20 fold reduction of radioisotope levels within 1 km from the discharge point at Big Rock Point. With the high turbidity and extensive wind driven mixing characteristics of waters around Fermi, a comparable or even sharper dilution gradient is likely to occur for Fermi effluents.

Sediment

Although trace element-sediment relationships show wide variation, there is clearly a general pattern of increasing trace element content with increasing clay and organic content. While observed relationships are probably not strictly correlated with clay and organic content, increases of these two parameters correspond to a general shift from coarse particles toward finer particle sizes; the result being that increasing clay or organic content represents decreased mean particle size and increased surface area per unit weight. Sorption processes are intimately related to surface area of sediments, while deposition

of precipitates and coprecipitates occurs simultaneously with deposition of clay and organic particulates. The end result of all these processes is simultaneous occurrence of fine sediments and high trace metal concentrations.

One of the more interesting aspects of sediment data were the good correlations of strontium with clay and especially with organic carbon. The larger size fractions of sediments included a considerable amount of shell debris, and it was thought that strontium contained in such debris might have raised the strontium content of coarser sediments. Additionally, strontium provided the only indication of temporal variation of sediments, with high concentrations occurring in June and September and low sediment levels in November and December. Such a distribution pattern is not unexpected, due to chemical precipitation of strontium during periods of high primary productivity, with some subsequent resolution of precipitates as pH falls and carbonate alkalinity is reduced to zero.

Iron consistently shows the best correlation of any of the elements considered, showing very high R values with both clay and organic carbon. Because of the similar behavior of iron and manganese in water under oxidizing conditions, one would anticipate comparable distribution in sediment for these two elements; to the contrary, however, manganese shows the poorest correlation for any of the elements considered. Zinc and cobalt levels showed good correlations with both clay and organic carbon levels, with no indication that either element occurred preferentially with one sediment type or the other. For all of these elements, we have little indication of which sediment fraction binds the metal; however, until such time

as one can separate the various clay and organic fractions, such binding processes must remain speculative.

As previously mentioned, strontium provides what appears to be the only evidence of temporal variation of sediments. Two stations, 1 and 5, suggest at least some degree of spatial variability within the survey area. High levels of four elements at station 5 apparently confirm observations for water of high inputs from the Detroit River, with settling and sorption enriching sediments. The low levels at station 1 suggest that input from the Detroit River is in fact enriching sediments throughout the lake portion of the survey area, although the effects are most pronounced at station 5.

General Discussion and Conclusions

Overall data for water and sediments suggest the inputs and dynamics of major and minor elements within the survey area. As previously indicated calcium and strontium inputs are primarily of natural origin, coming from solution of limestone-dolomite bedrock. Inputs are primarily in a dissolved form, with high inputs in the spring corresponding to high runoff. Seasonal levels of these two elements are controlled by primary productivity, resulting in high winter and spring concentrations in water, and low levels within sediments. In summer and early autumn, high pH caused by primary productivity results in precipitation of carbonates and sulfates, with correspondingly low calcium and strontium levels in water and enhanced levels within sediments.

The three monovalent ions (Na, K, Cl) are controlled by input levels, with relatively little influence from other factors. Lake

levels are controlled almost entirely by Detroit River flow, while Swan Creek is typified by high spring levels of all three elements, resulting from high runoff generally, and possibly from road salt in particular.

Like the monovalent ions, the transition metals show independent behavior in the creek and lake, with lake levels ultimately controlled by inputs from the Detroit River. High levels of suspended solids and organic materials help maintain trace metal levels, while reduced flow rates in the lake cause eventual settling of colloids and particulates, reducing levels in water while enriching sediments. The high concentrations of several elements at the northern end of the survey area, occurring in both water and sediment, clearly mark the Detroit River as the primary input source, with data further suggesting that settling of material from this source is enriching sediments throughout the lake portion of the survey area. Despite the lack of industrial effluents to Swan Creek, levels of all transition metals except zinc are characteristically higher in the creek than at lake stations. These high creek levels most likely are a result of sorption onto and chelation by the high dissolved and suspended organics and clay characteristic of the creek.

Of those elements considered in this study, radioisotopes of strontium probably present the lowest potential for significant accumulation and consequent hazard to man. Because strontium normally remains in solution for long periods of time, its radioisotopes will be diluted by lake water and dispersed over virtually the entire western basin of Lake Erie.

The fate of transition metals around Fermi are much less certain than for strontium, with local currents being a critical factor in

determining their eventual distribution. Most literature indicates that metal radioisotopes will be in a dissolved form for a relatively short time, with most ions being sorbed to suspended particulates, both organic and inorganic. (In fact, activation products may quite likely be suspended at the time of their activation). Data from this study indicates rapid mixing of Swan Creek with lake water, so it appears likely that Fermi discharge will similarly mix rapidly. We have little indication, however, of the settling rate of suspended particles in waters of the survey area; we further have little information concerning currents in the Fermi discharge area. Current data provided by Hartley et al. (1966) and ILEWPB (1969) and sediment texture off Fermi suggest that the bay area off Fermi is characterized by eddy currents and the deposition of sediments south of Swan Creek. If this is the case, transition metal radioisotopes will settle within a confined area within the bay area off Fermi. In order to make reasonable predictions of the eventual fate of Fermi discharges, it seems imperative that a full understanding be developed of current behavior and settling of suspended materials adjacent to the discharge area. Such studies should be conducted, and if they confirm that contaminated sediments will be deposited within such a small area, consideration should be given to relocating the Fermi discharge to a point from which effluents would be diluted and dispersed.

In terms of more general questions raised by this research, two primary areas might merit further attention: 1) What factors are regulating trace metal levels within the Fermi area, with particular regard to the role of dissolved and suspended organics, and pH-alkalinity changes induced by primary production? 2) How are transition metals

becoming associated with sediments (i.e., which sediment fraction(s) and by what physical or chemical bonding mechanisms), and to what extent are water-sediment reactions reversible?

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APPENDIX A

DATA TABLES

Table A-1. Spatial variation of calcium (mg/liter), arranged by increasing concentration at the sample stations.

11 September 1972								
Station	4	8	3	5	6	2	7	1
Mean	30.3	30.7	31.4	31.5	34.3	35.8	38.6	41.6
Multiple Range								
27 October 1973								
Station	4	5	2	3	8	7	6	1
Mean	38.5	39.1	40.0	43.5	45.3	46.7	47.4	66.8
Multiple Range								
2 April 1973								
Station	4	7	5	3	6	8	2	1
Mean	31.5	32.2	33.1	33.3	54.5	36.1	56.2	84.0
Multiple Range								
6 June 1973								
Station	7	5	6	8	3	4	2	1
Mean	26.0	26.1	26.4	28.9	29.2	29.3	31.5	57.1
Multiple Range								
19 July 1973								
Station	8	3	7	4	2	6	5	1
Mean	29.9	30.2	30.3	31.1	32.8	33.9	35.1	48.6
Multiple Range								

Table A-1 (cont'd):

12 September 1973								
Station	7	8	6	5	2	3	4	1
Mean	31.3	32.0	32.0	32.2	33.1	33.2	33.5	38.0
Multiple Range								
15 October 1973								
Station	2	4	7	8	6	5	3	1
Mean	35.3	35.5	35.9	36.0	36.0	36.0	36.2	41.6
Multiple Range								
8 December 1973								
Station	8	7	5	6	2	3	1	4
Mean	34.3	40.4	42.0	43.0	46.3	49.5	54.8	64.0
Multiple Range								

Table A-2. Spatial variation of chloride (mg/liter), arranged by increasing concentration at the sample stations.

2 April 1973								
Station	7	4	5	6	8	3	2	1
Mean	14.6	18.0	18.5	18.9	20.5	21.5	32.3	40.5
Multiple Range	_____		_____		_____			
6 June 1973								
Station	5	6	7	4	8	3	2	1
Mean	12.1	13.0	13.1	14.7	15.3	16.0	16.3	42.7
Multiple Range	_____		_____		_____			
19 July 1973								
Station	8	3	4	2	7	6	5	1
Mean	15.9	15.9	16.2	16.3	16.6	17.0	20.6	24.3
Multiple Range	_____		_____					
12 September 1973								
Station	7	6	2	3	8	5	4	1
Mean	11.4	12.0	12.4	12.6	13.0	13.2	13.6	17.2
Multiple Range	_____		_____					
12 October 1973								
Station	4	6	5	3	8	2	7	1
Mean	15.0	15.3	15.3	15.3	15.4	15.4	15.6	18.8
Multiple Range	_____							

Table A-2 (cont'd):

 8 December 1973

Station	8	7	6	2	3	5	1	4
Mean	17.1	18.7	18.8	19.6	21.5	23.7	30.9	35.5
Multiple Range								

Table A-3. Spatial variation of sodium (mg/liter), arranged by increasing concentration at the sample stations.

Station	4	8	7	5	3	6	1	2
Mean	5.68	5.92	6.17	7.31	7.52	7.79	11.06	12.77
Multiple Range	_____		_____			_____		

27 October 1972

Station	5	4	2	3	8	7	6	1
Mean	8.21	8.42	8.88	9.43	10.00	10.02	10.27	21.77
Multiple Range								

2 April 1973

Station	7	4	8	5	3	6	2	1
Mean	5.30	8.33	9.30	9.53	9.93	10.20	16.37	16.73
Multiple Range								

6 June 1973

Station	5	7	6	8	4	2	3	1
Mean	5.72	5.83	6.08	6.65	6.66	6.95	7.35	14.37
Multiple Range								

19 July 1973

Station	4	2	3	8	6	7	1	5
Mean	8.44	9.78	9.93	10.14	10.28	10.55	10.71	12.11
Multiple Range								

Station	7	6	5	2	8	3	4	1
Mean	5.85	6.21	6.29	6.46	6.64	6.99	7.11	8.39
Multiple Range	_____		_____			_____		_____

Station	7	4	2	5	3	8	6	1
Mean	8.34	8.38	8.50	8.56	8.56	8.60	8.63	10.22
Multiple Range								

Station	8	6	2	7	3	5	1	4
Mean	8.78	9.25	9.30	9.40	10.83	14.44	14.98	18.70
Multiple Range								

Table A-4. Spatial variation of potassium (mg/liter), arranged by increasing concentration at the sample stations.

11 September 1972								
Station	8	7	4	3	5	6	2	1
Mean	1.02	1.03	1.05	1.10	1.10	1.15	1.36	1.58
Multiple Range								
27 October 1972								
Station	5	4	2	3	8	6	7	1
Mean	1.50	1.51	1.59	1.85	2.02	2.13	2.14	4.34
Multiple Range								
2 April 1973								
Station	7	3	4	8	6	5	2	1
Mean	1.26	1.55	1.56	1.64	1.68	1.74	2.28	3.28
Multiple Range								
6 June 1973								
Station	5	6	7	4	8	3	2	1
Mean	1.22	1.26	1.27	1.42	1.45	1.50	1.64	2.91
Multiple Range								
19 July 1973								
Station	2	6	8	4	3	5	7	1
Mean	2.20	2.20	2.50	2.26	2.28	2.34	2.35	3.42
Multiple Range								

Table A-4 (cont'd):

12 September 1973

Station	7	2	5	6	8	3	4	1
Mean	.61	.66	.70	.70	.73	.83	.89	1.02
Multiple Range								

15 October 1973

Station	2	4	3	5	6	7	8	1
Mean	.17	.22	.23	.26	.32	.33	.50	.54
Multiple Range								

8 December 1973

Station	8	2	7	6	5	3	1	4
Mean	.49	.90	.94	.99	.99	1.06	1.20	1.84
Multiple Range								

Table A-5. Spatial variation of strontium (ug/liter), arranged by increasing concentration at the sample stations.

11 September 1972

Station	4	3	5	8	6	7	2	1
Mean	108.0	119.2	129.3	131.8	151.7	152.7	191.0	345.2
Multiple Range								

27 October 1972

Station	5	4	2	3	8	6	7	1
Mean	108.2	206.3	236.0	246.0	268.5	293.7	309.2	817.8
Multiple Range								

2 April 1973

Station	7	5	6	3	8	4	2	1
Mean	100.3	116.3	121.7	124.7	126.7	127.7	278.7	501.7
Multiple Range								

6 June 1973

Station	5	7	8	6	4	3	2	1
Mean	152.7	166.3	191.5	198.8	205.2	223.3	245.2	502.2
Multiple Range								

19 July 1973

Station	8	5	6	4	7	3	2	1
Mean	225.8	245.5	251.0	268.8	275.7	336.2	369.0	675.8
Multiple Range								

Table A-5 (cont'd):

 12 September 1973

Station	7	6	5	8	2	4	3	1
Mean	202.7	212.7	225.8	230.3	251.5	254.2	258.2	393.0
Multiple Range								

15 October 1973

Station	4	3	2	5	6	8	7	1
Mean	240.3	250.2	250.8	267.5	274.7	277.0	277.0	457.5
Multiple Range								

8 December 1973

Station	5	8	7	6	2	4	3	1
Mean	315.3	326.7	379.0	381.2	383.0	402.7	404.7	636.7
Multiple Range								

Table A-6. Spatial variation of iron (ug/liter), arranged by increasing concentration at the sample stations.

11 September 1972								
Station	1	4	2	8	3	6	5	7
Mean	1207.0	1214.0	1410.0	1454.0	1465.0	1546.0	1559.0	1570.0
Multiple Range	_____		_____					
27 October 1972								
Station	6	8	7	2	5	3	1	4
Mean	679.7	680.7	711.8	814.9	840.5	840.7	877.4	963.1
Multiple Range	_____		_____		_____			_____
2 April 1973								
Station	5	3	4	6	1	2	7	8
Mean	705.7	745.0	859.3	933.3	960.0	1016.7	1315.0	1540.0
Multiple Range	_____		_____					
6 June 1973								
Station	8	4	3	6	7	2	5	1
Mean	675.0	748.3	845.0	1010.0	1041.7	1065.0	1085.0	1713.3
Multiple Range	_____		_____			_____		
19 July 1973								
Station	4	7	3	8	2	6	5	1
Mean	99.2	116.8	118.8	129.5	142.2	153.2	219.5	334.5
Multiple Range	_____		_____			_____		

Table A-6 (cont'd):

 12 September 1973

Station	8	4	6	7	2	3	5	1
Mean	170.5	200.7	213.0	236.0	236.3	254.3	276.3	350.3
Multiple Range								

15 October 1973

Station	6	2	3	7	8	4	5	1
Mean	250.3	275.3	282.7	297.3	313.0	396.3	463.0	526.7
Multiple Range								

8 December 1973

Station	8	1	7	4	6	2	5	3
Mean	189.7	333.3	384.3	652.3	764.0	863.3	896.0	918.3
Multiple Range								

Table A-7. Spatial variation of manganese (ug/liter), arranged by increasing concentration at the sample stations.

11 September 1972

Station	8	4	6	3	7	5	2	1
Mean	16.0	20.2	21.0	23.0	24.2	26.2	27.2	51.0
Multiple Range	_____		_____			_____		

27 October 1972

Station	8	6	2	5	7	3	4	1
Mean	15.4	20.4	21.4	21.5	21.5	22.5	23.2	39.9
Multiple Range								

2 April 1973

Station	5	6	3	8	4	7	2	1
Mean	22.9	23.8	24.1	25.5	26.6	35.0	37.5	56.5
Multiple Range								

6 June 1973

Station	8	3	5	7	6	4	1	2
Mean	19.8	38.8	56.8	57.8	64.3	100.8	114.1	159.7
Multiple Range	_____		_____			_____		

19 July 1973

Station	8	7	6	4	5	3	2	1
Mean	6.6	8.5	13.5	13.9	16.0	17.7	21.8	47.2
Multiple Range	_____			_____		_____		

Table A-7 (cont'd):

12 September 1973

Station	2	4	5	8	3	6	7	1
Mean	16.4	18.7	19.6	21.5	22.6	22.9	25.4	47.0
Multiple Range								

15 October 1973

Station	7	6	3	8	4	5	2	1
Mean	17.6	22.4	23.2	24.7	24.9	27.5	44.8	82.1
Multiple Range								

8 December 1973

Station	8	1	7	6	2	5	3	4
Mean	10.1	14.8	17.6	38.6	45.4	46.5	48.5	55.3
Multiple Range								

Table A-8. Spatial variation of zinc (ug/liter), arranged by increasing concentration at the sample stations.

11 September 1972								
Station	8	3	4	5	1	6	2	7
Mean	15.8	31.6	37.3	38.8	44.0	47.8	56.8	56.9
Multiple Range								
27 October 1972								
Station	6	2	3	8	1	7	5	4
Mean	9.1	10.0	11.2	11.2	12.7	13.6	17.1	19.2
Multiple Range								
2 April 1973								
Station	1	7	2	6	3	8	5	4
Mean	16.4	19.5	22.7	24.4	26.4	27.2	27.6	28.1
Multiple Range								
6 June 1973								
Station	8	2	6	7	5	3	1	4
Mean	24.9	25.9	27.2	27.5	30.9	33.5	34.7	39.8
Multiple Range								
19 July 1973								
Station	4	3	1	6	5	2	8	7
Mean	6.8	8.4	9.3	10.3	10.9	14.8	17.6	20.5
Multiple Range								

Table A-8 (cont'd):

12 September 1973								
Station	4	2	3	6	5	1	8	7
Mean	5.8	6.6	7.4	7.6	8.7	14.3	14.3	17.2
Multiple Range								
15 October 1973								
Station	6	7	2	3	1	8	4	5
Mean	11.6	11.7	12.4	16.0	18.4	22.6	25.1	28.7
Multiple Range								
8 December 1973								
Station	1	7	8	6	2	3	4	5
Mean	18.1	20.9	28.7	34.6	38.4	39.5	42.5	49.5
Multiple Range								

Table A-9. Spatial variation of cobalt (ug/liter), arranged by increasing concentration at the sample stations.

11 September 1972								
Station	5	4	2	7	8	6	3	1
Mean	4.02	4.42	4.72	4.89	5.00	5.36	5.76	6.74
Multiple Range								
27 October 1972								
Station	5	4	2	7	8	6	3	1
Mean	4.00	4.38	4.45	4.50	4.66	4.86	4.87	7.41
Multiple Range								
2 April 1973								
Station		4	5	8	7	6		
Mean		4.80	5.62	6.35	6.37	6.83		
Multiple Range								
6 June 1973								
Station	4	2	6	3	8	7	1	5
Mean	3.68	3.80	5.95	6.07	6.13	6.38	8.36	9.50
Multiple Range								
19 July 1973								
Station	4	7	3	8	2	6	5	1
Mean	3.70	3.82	4.42	5.13	5.42	5.88	6.57	6.97
Multiple Range								

Table A-9 (cont'd):

12 September 1973

Station	7	5	8	6	4	2	3	1
Mean	3.88	4.23	4.25	4.42	4.53	4.93	5.23	6.42
Multiple Range								

15 October 1973

Station	6	4	8	7	1	5	3	2
Mean	2.88	3.63	3.70	3.92	4.57	4.58	6.15	6.57
Multiple Range								

8 December 1973

Station	7	8	6	5	1	4	3	2
Mean	3.73	4.92	5.30	5.38	6.10	6.37	6.43	7.15
Multiple Range								

Table A-10. Temporal variation of major and minor elements in lake portion of the survey area.

Calcium (mg/liter)								
Date	6-6-73	7-19-73	9-12-73	9-11-73	4-2-73	10-15-73	10-26-72	12-8-73
Mean	27.64	31.73	32.35	32.84	33.44	35.94	43.40	45.53
Multiple Range								
Chloride (mg/liter)								
Date	9-12-73	6-6-73	10-15-73	7-19-73	4-2-73	12-8-73		
Mean	12.62	14.05	15.32	17.02	18.67	22.55		
Multiple Range								
Sodium (mg/liter)								
Date	6-6-73	9-12-73	9-11-73	10-15-73	4-2-73	10-26-73	7-19-73	12-8-73
Mean	6.38	6.61	6.73	8.51	8.77	9.39	10.24	11.90
Multiple Range								

Table A-10 (cont'd):

Potassium (ug/liter)									
Date	10-15-73	9-12-73	12-8-73	9-11-72	6-6-73	4-2-73	10-26-72	7-19-73	
Mean	0.31	0.74	1.05	1.07	1.35	1.57	1.86	2.28	
Multiple Range									
Strontium (ug/liter)									
Date	4-2-73	9-11-72	6-6-73	9-12-73	10-26-72	7-19-73	10-15-73	12-8-73	
Mean	119.6	133.5	189.6	230.6	250.6	260.5	264.4	368.3	
Multiple Range									
Iron (ug/liter)									
Date	7-19-73	9-12-73	10-15-73	12-8-73	10-26-72	6-6-73	4-2-73	9-11-72	
Mean	139.5	225.1	333.8	634.1	786.1	900.8	1016.4	1482.9	
Multiple Range									

Table A-10 (cont'd):

Manganese (ug/liter)							
Date	7-19-73	10-26-72	9-12-73	9-11-72	10-15-73	4-2-73	12-8-73 6-6-73
Mean	12.7	20.8	21.8	21.8	23.4	26.3	36.1 56.5
Multiple Range							
Zinc (ug/liter)							
Date	9-12-73	7-19-73	10-26-72	10-15-73	4-2-73	6-6-73	12-8-73 9-11-72
Mean	10.06	12.41	13.57	19.30	25.54	30.63	35.97 38.05
Multiple Range							
Cobalt (ug/liter)							
Date	10-15-73	9-12-73	10-26-72	9-11-72	7-19-73	12-8-73	4-2-73 6-6-73
Mean	4.14	4.43	4.51	4.70	4.92	5.36	5.97 6.29
Multiple Range							

Table A-11. Mean concentration of trace elements in sediments in the survey area on 11 September 1972 (Mean $\pm$ 1 S.E., all concentrations in ug/g).

Element	Station				
	1	2	3	4	5
Strontium		37.6 ⁺ 0.9 ⁻	143.1 ⁺ 10.9 ⁻	103.2 ⁺ 4.2 ⁻	46.7 ⁺ 4.3 ⁻
Iron		10740 ⁺ 53 ⁻	30680 ⁺ 1580 ⁻	25370 ⁺ 970 ⁻	12500 ⁺ 1430 ⁻
Manganese		218.6 ⁺ 7.4 ⁻	625.0 ⁺ 18.8 ⁻	580.8 ⁺ 30.6 ⁻	341.4 ⁺ 33.4 ⁻
Zinc		20.4 ⁺ 1.0 ⁻	224.4 ⁺ 26.0 ⁻	66.1 ⁺ 2.9 ⁻	48.3 ⁺ 1.1 ⁻
Cobalt		5.16 ⁺ 0.10 ⁻	16.37 ⁺ 0.32 ⁻	19.67 ⁺ 1.16 ⁻	6.48 ⁺ 0.56 ⁻

Table A-12. Mean concentration of trace elements in the survey area on 26 October 1972 (Mean $\pm$ 1 S.E., all concentrations in ug/g).

Element	Station				
	1	2	3	4	5
Strontium	143.4 $\pm$ —				
Iron	29830 $\pm$ 330 $\pm$		26020 $\pm$ 620 $\pm$	22180 $\pm$ 650 $\pm$	33400 $\pm$ 860 $\pm$
Manganese	352.3 $\pm$ 4.5 $\pm$		450.0 $\pm$ 10.9 $\pm$	445.2 $\pm$ 15.5 $\pm$	542.5 $\pm$ 36.6 $\pm$
Zinc	140.0 $\pm$ 3.3 $\pm$		273.8 $\pm$ 9.7 $\pm$	200.9 $\pm$ 7.3 $\pm$	304.2 $\pm$ 12.7 $\pm$
Cobalt	15.13 $\pm$ 0.79 $\pm$		17.73 $\pm$ 0.27 $\pm$	16.29 $\pm$ 0.72 $\pm$	19.03 $\pm$ 0.41 $\pm$

Table A-13. Mean concentration of trace elements in the survey area
on 2 April 1973 (Mean $\pm$ 1 S.E., all concentrations in ug/g).

Element	Station				
	1	2	3	4	5
Strontium		28.3 ⁺ 0.9 ⁻	72.2 ⁺ 8.3 ⁻	47.4 ⁺ 10.7 ⁻	73.9 ⁺ 4.1 ⁻
Iron		8060 ⁺ 130 ⁻	23670 ⁺ 850 ⁻	13990 ⁺ 3700 ⁻	20642 ⁺ ₋
Manganese		199.8 ⁺ 8.4 ⁻	375.0 ⁺ 97.9 ⁻	326.4 ⁺ 63.9 ⁻	361.1 ⁺ 9.4 ⁻
Zinc			82.8 ⁺ 16.3 ⁻	39.5 ⁺ 6.0 ⁻	187.0 ⁺ 3.9 ⁻
Cobalt		6.14 ⁺ 0.18 ⁻	17.39 ⁺ 1.47 ⁻	6.72 ⁺ 1.22 ⁻	10.53 ⁺ 0.17 ⁻

Table A-14. Mean concentration of trace elements in the survey area on 6 June 1973 (Mean $\pm$ 1 S.E., all concentrations in $\mu\text{g/g}$).

Element	Station							
	1	2	3	4	5	6	7	8
Strontium	152.6 $\pm$ 12.2 $\pm$	59.5 $\pm$ 6.1 $\pm$	52.6 $\pm$ 12.0 $\pm$	35.6 $\pm$ 2.8 $\pm$	54.6 $\pm$ 9.1 $\pm$	46.1 $\pm$ 8.8 $\pm$	97.2 $\pm$ 18.3 $\pm$	83.3 $\pm$ 1.5 $\pm$
Iron	24780 $\pm$ 520 $\pm$	11700 $\pm$ 180 $\pm$	11250 $\pm$ 1290 $\pm$	10980 $\pm$ 1090 $\pm$	21700 $\pm$ 3790 $\pm$	10490 $\pm$ 690 $\pm$	22340 $\pm$ 2260 $\pm$	24790 $\pm$ 1860 $\pm$
Manganese	471.7 $\pm$ 19.7 $\pm$	290.8 $\pm$ 6.8 $\pm$	349.0 $\pm$ 70.1 $\pm$	311.7 $\pm$ 27.1 $\pm$	521.2 $\pm$ 73.1 $\pm$	237.3 $\pm$ 5.5 $\pm$	448.3 $\pm$ 14.5 $\pm$	488.3 $\pm$ 72.2 $\pm$
Zinc	159.8 $\pm$ 1.5 $\pm$	33.3 $\pm$ 0.5 $\pm$	34.7 $\pm$ 3.3 $\pm$	58.3 $\pm$ 12.0 $\pm$	56.5 $\pm$ 3.3 $\pm$	37.9 $\pm$ 7.0 $\pm$	121.1 $\pm$ 21.8 $\pm$	209.1 $\pm$ 28.8 $\pm$
Cobalt	24.10 $\pm$ 2.30 $\pm$	12.81 $\pm$ 2.78 $\pm$	12.45 $\pm$ 2.22 $\pm$	8.26 $\pm$ 1.67 $\pm$	11.59 $\pm$ 0.88 $\pm$	7.08 $\pm$ 0.30 $\pm$	13.76 $\pm$ 0.60 $\pm$	17.55 $\pm$ 0.65 $\pm$

Table A-15. Mean concentration of trace elements in the survey area on 27 September 1973 (Mean $\pm$ 1 S.E., all concentrations in ug/g).

Element	Station							
	1	2	3	4	5	6	7	8
Strontium	147.4+ 3.6-	60.4+ 3.2-	70.2+ 5.2-	60.5+ 0.7-	73.6+ 3.3-	53.6+ 0.8-	98.3+ 1.8-	---
Iron	23300+ 800-	12360+ 560-	14790+ 1360-	13560+ 240-	18540+ 1320-	10360+ 510-	28080+ 630-	---
Manganese	400.0+ 25.2-	222.4+ 3.4-	293.6+ 21.2-	268.9+ 3.0-	388.0+ 59.9-	226.7+ 20.7-	426.8+ 17.3-	---
Zinc	139.6+ 0.9-	26.0+ 0.6-	61.4+ 18.5-	44.7+ 0.4-	43.1+ .53-	45.3+ 3.2-	188.3+ 10.0-	---
Cobalt	33.65+ .30-	15.96+ .26-	17.57+ .46-	12.06+ 1.06-	19.25+ 1.08-	13.52+ .21-	27.10+ .73-	---

Table A-16. Mean concentration of trace elements in the survey area on 7 November 1973 (Mean $\pm$ 1 S.E., all concentrations in $\mu\text{g/g}$).

Element	1	2	3	Station 4	5	6	7	8
Strontium	91.5+ 0.5-	38.6+ 1.8-	22.5+ 0.4-	21.5+ 0.2-	43.3+ 2.7-	17.1+ 1.0-	55.8+ 4.3-	54.0+ 0.9-
Iron	28770+ 170-	12680+ 110-	12730+ 530-	12480+ 260-	18980+ 1820-	12600+ 170-	32130+ 1560-	35920+ 1900-
Manganese	324.9+ 3.6-	262.9+ 12.9-	197.5+ 13.9-	218.4+ 5.3-	390.8+ 31.0-	247.5+ 8.8-	470.0+ 13.0-	523.8+ 22.4-
Zinc	143.8+ 1.4-	22.5+ 0.8-	30.4+ 1.1-	36.0+ 0.2-	44.9+ 0.7-	32.3+ 0.8-	404.2+ 27.1-	445.8+ 30.1-
Cobalt	21.20+ .22-	10.21+ 17-	6.63+ .12-	6.98+ .14-	11.57+ .69-	6.45+ .17-	16.94+ 1.27	20.52+ 42

Table A-17. Mean concentration of trace elements in the survey area on 8 December 1973 (Mean $\pm$ 1 S.E., all concentrations in ug/g).

Element	Station							
	1	2	3	4	5	6	7	8
Strontium	95.3 $\pm$ 5.4	32.2 $\pm$ 5.2	17.2 $\pm$ 1.2	25.8 $\pm$ 0.9	68.8 $\pm$ 4.3	25.2 $\pm$ 0.6	57.0 $\pm$ 3.4	55.4 $\pm$ 0.8
Iron	25830 $\pm$ 270	12250 $\pm$ 220	7900 $\pm$ 470	13100 $\pm$ 560	19030 $\pm$ 1710	10880 $\pm$ 1810	32170 $\pm$ 2680	37580 $\pm$ 80
Manganese	429.2 $\pm$ 6.7	318.3 $\pm$ 25.3	251.7 $\pm$ 13.6	340.0 $\pm$ 15.3	427.9 $\pm$ 7.9	172.9 $\pm$ 25.1	412.8 $\pm$ 16.6	495.8 $\pm$ 0.8
Zinc	121.0 $\pm$ 1.0	21.7 $\pm$ 1.3	30.4 $\pm$ 0.4	42.3 $\pm$ 5.5	45.3 $\pm$ 3.7	31.2 $\pm$ 0.7	346.4 $\pm$ 55.4	447.5 $\pm$ 2.5
Cobalt	21.58 $\pm$.40	10.37 $\pm$.51	3.44 $\pm$.19	6.70 $\pm$.12	19.99 $\pm$.50	5.92 $\pm$.42	18.03 $\pm$ 1.48	20.30 $\pm$.15

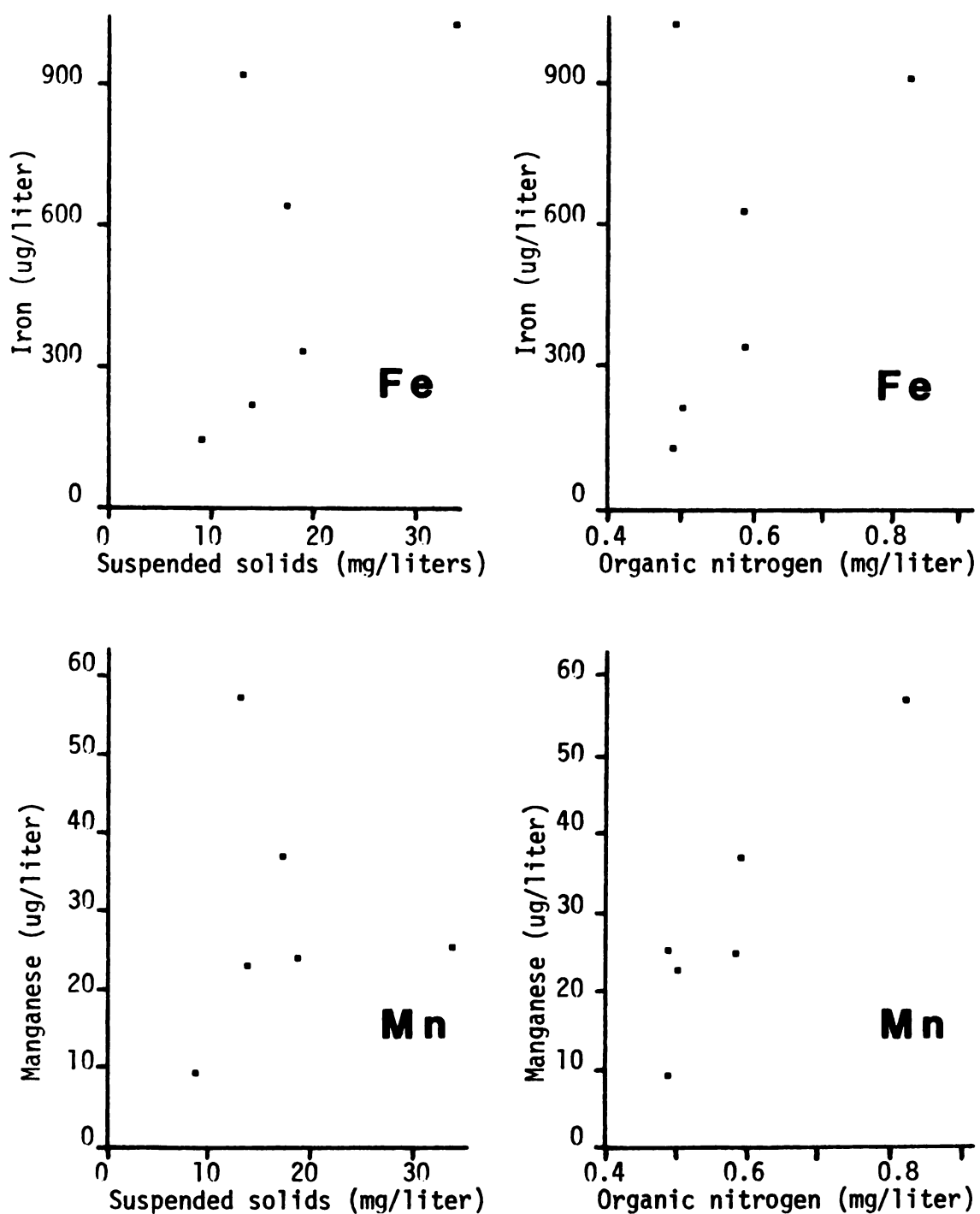


Figure A-1. Correlation of transition metal levels in water with suspended solids and organic nitrogen.

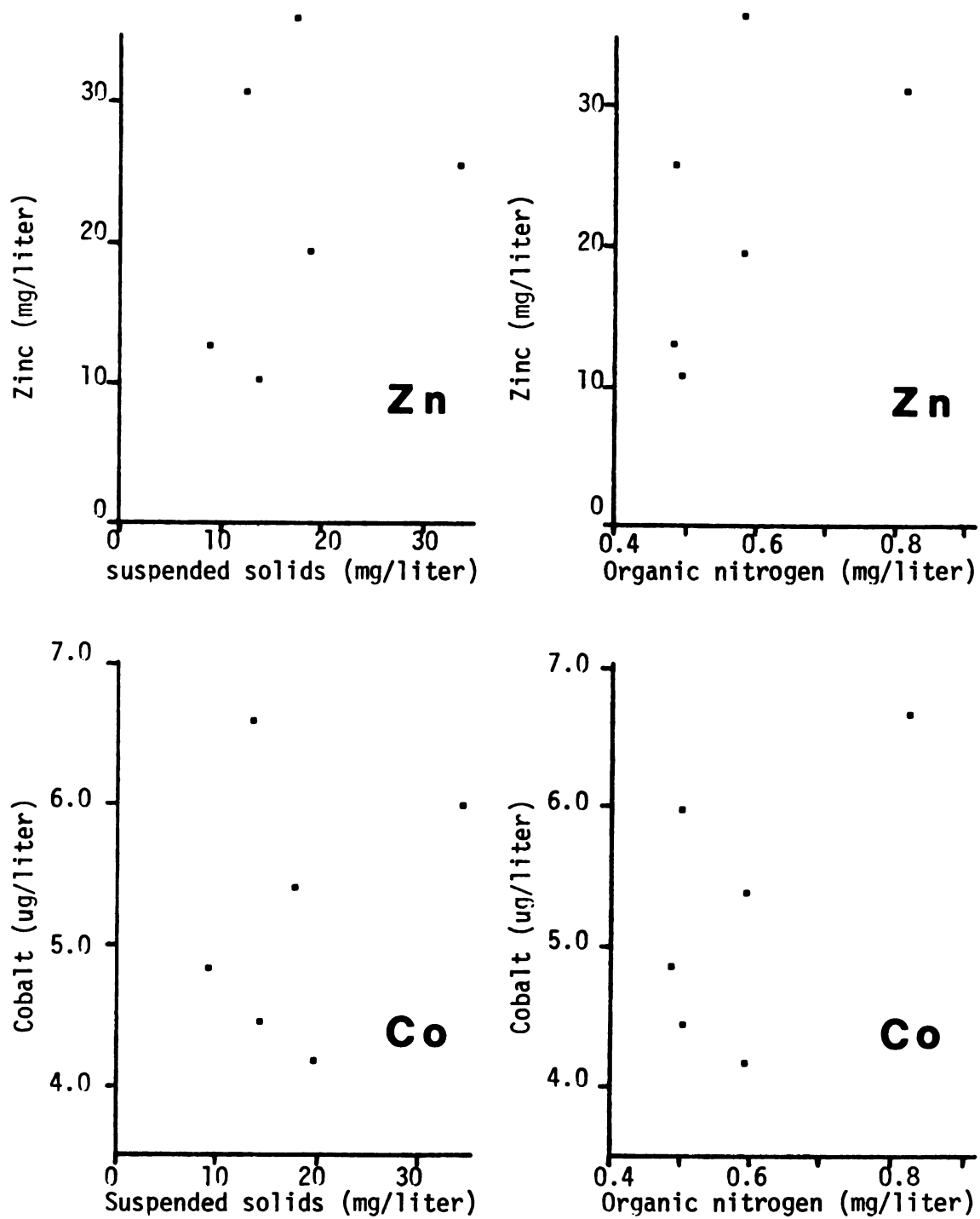


Figure A-1. continued.

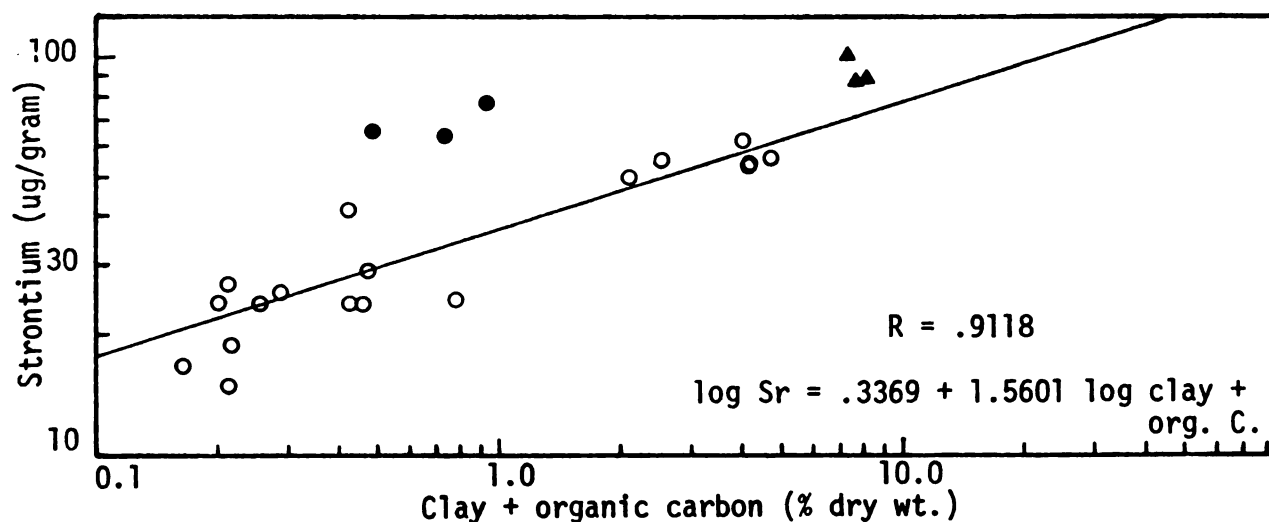
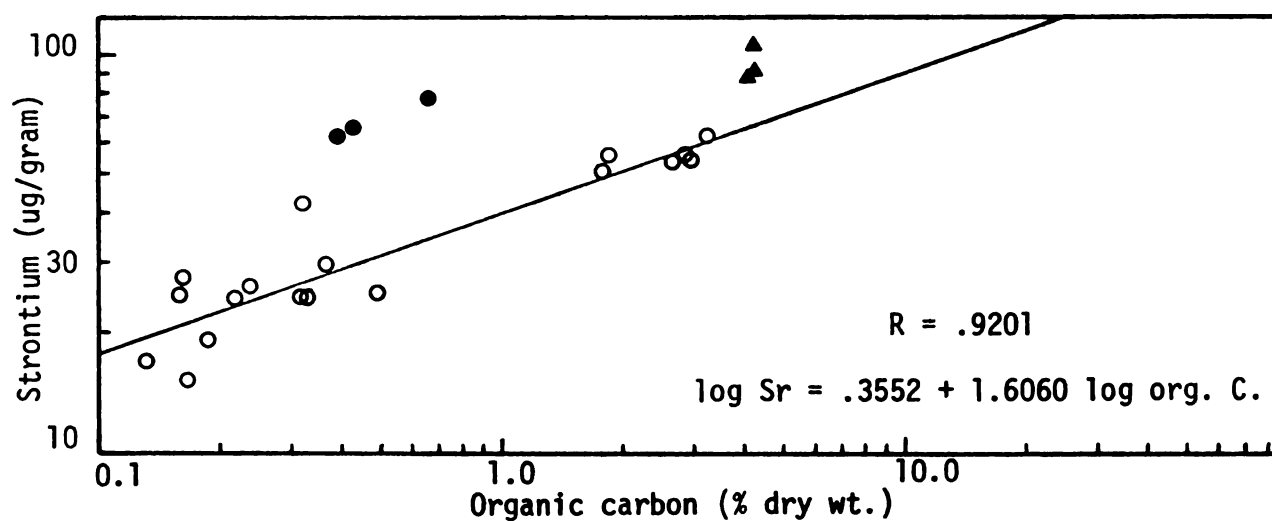
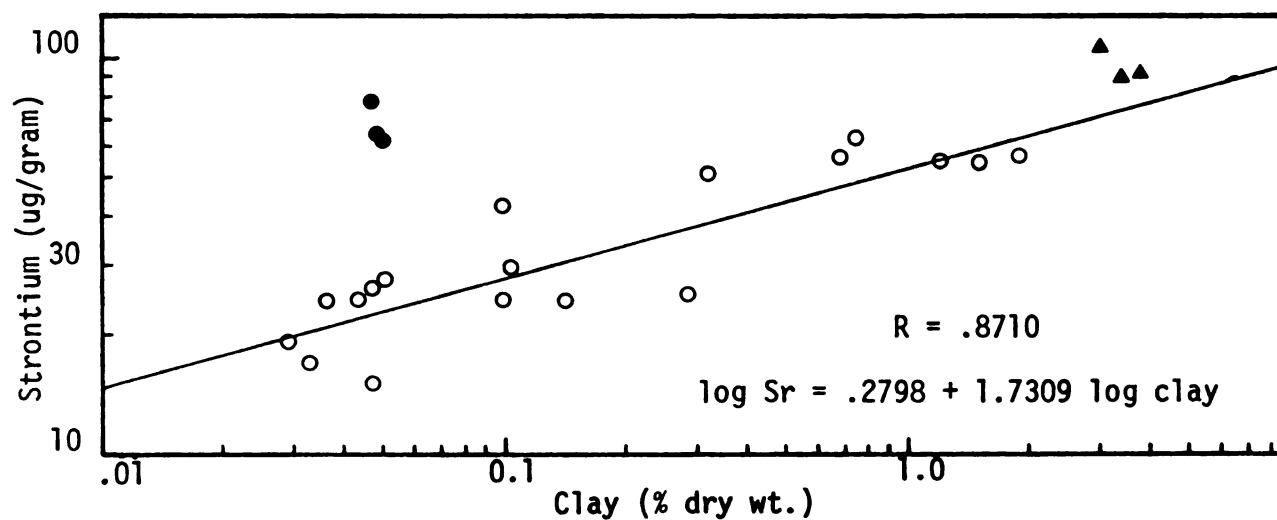


Figure A-2. Strontium-sediment relationships for December, 1973.
(▲-Station 1, ●-Station 5, ○-other stations.)

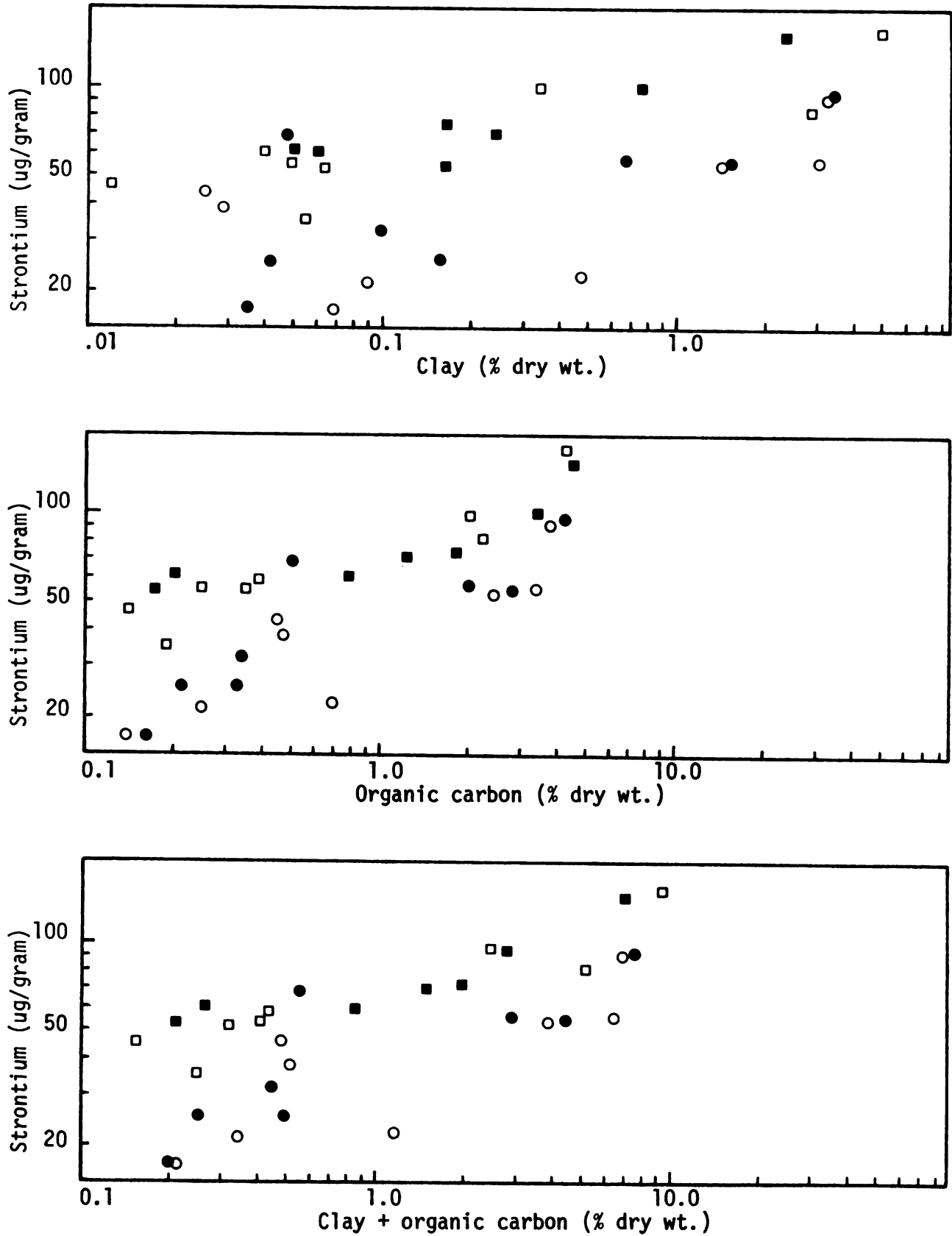


Figure A-3. Strontium-sediment relationships for June-December 1973.
($\square$ - June, $\blacksquare$ - Sept., $\circ$ - Nov., $\bullet$ - Dec.)

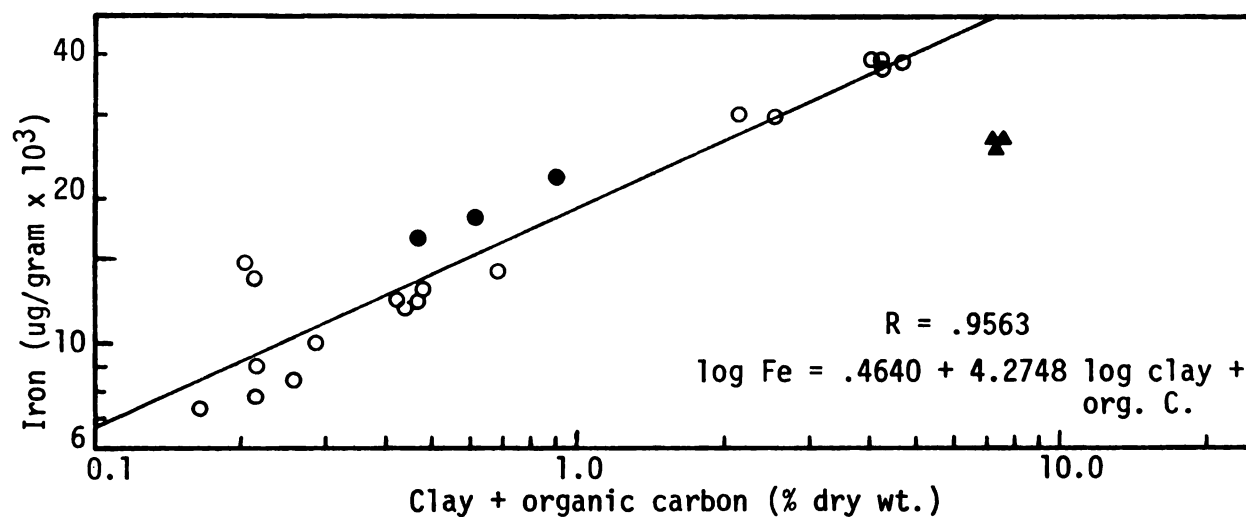
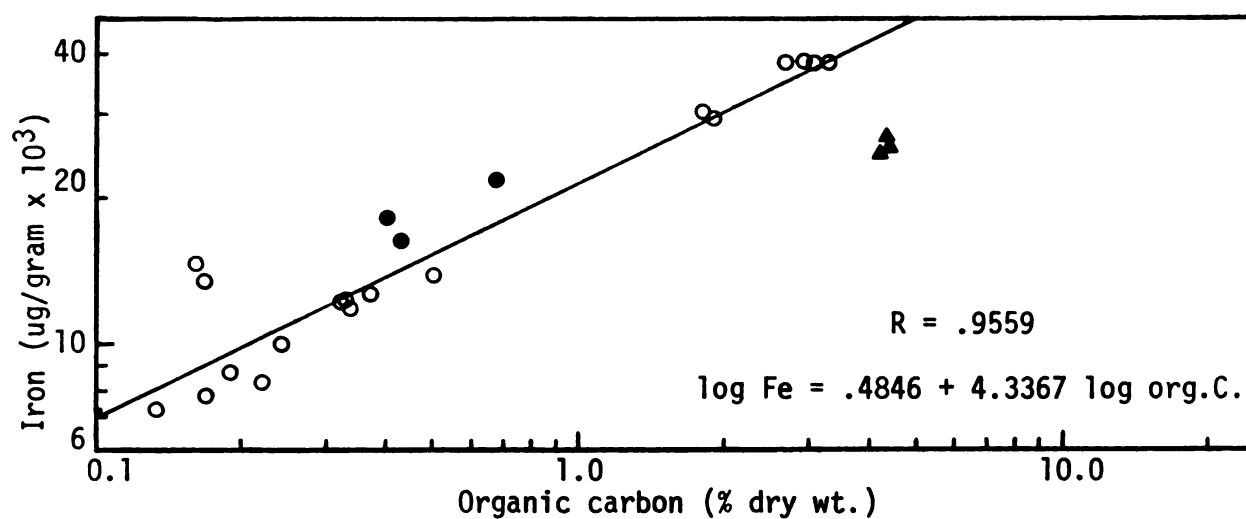
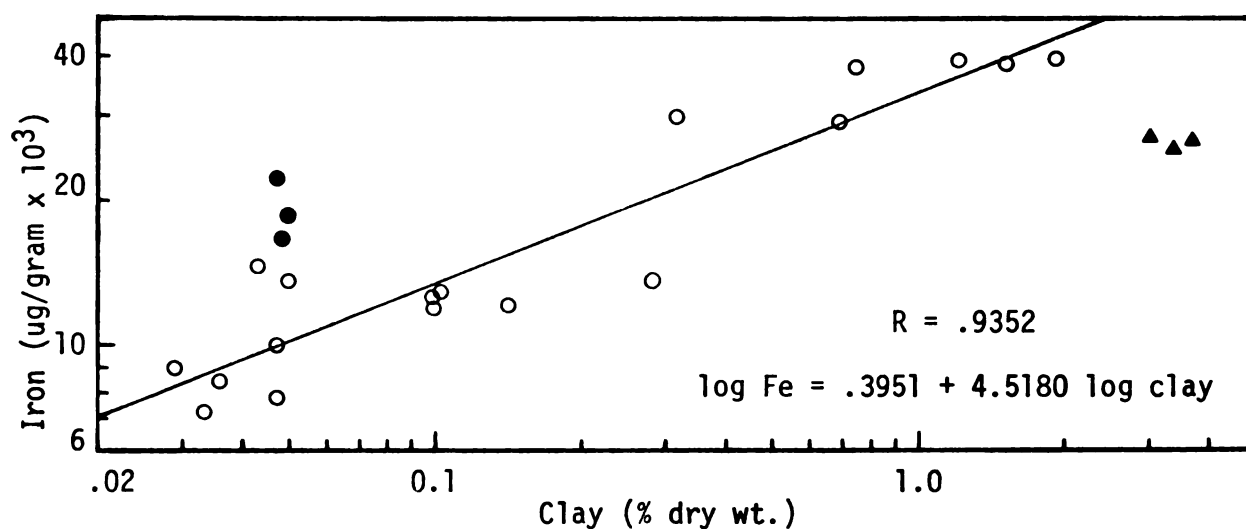


Figure A-4. Iron-sediment relationships for december 1973.
(▲-Station 1, ●-Station 5, ○-other stations.)

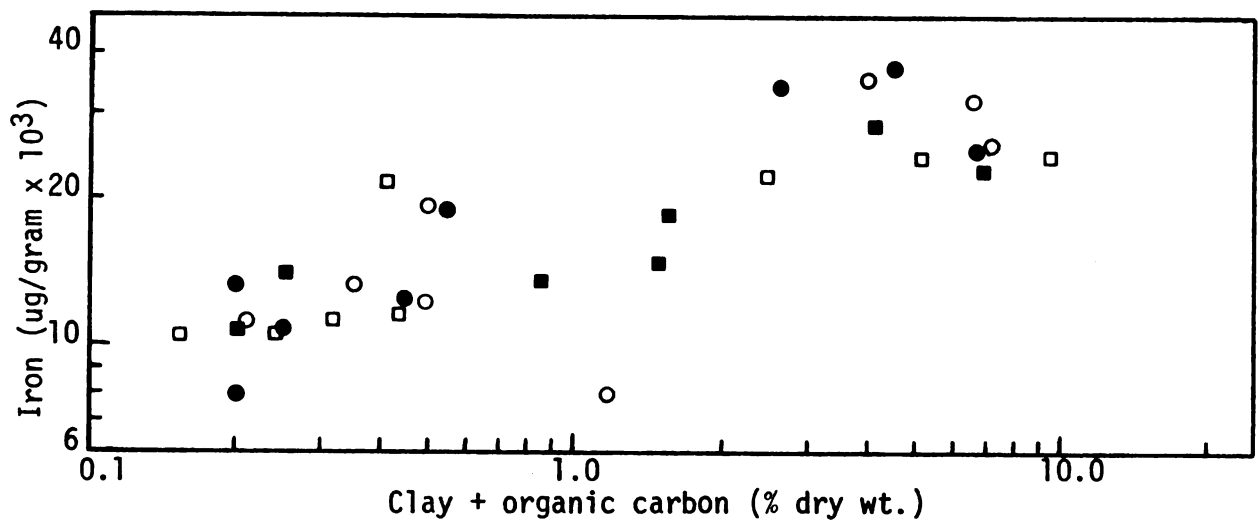
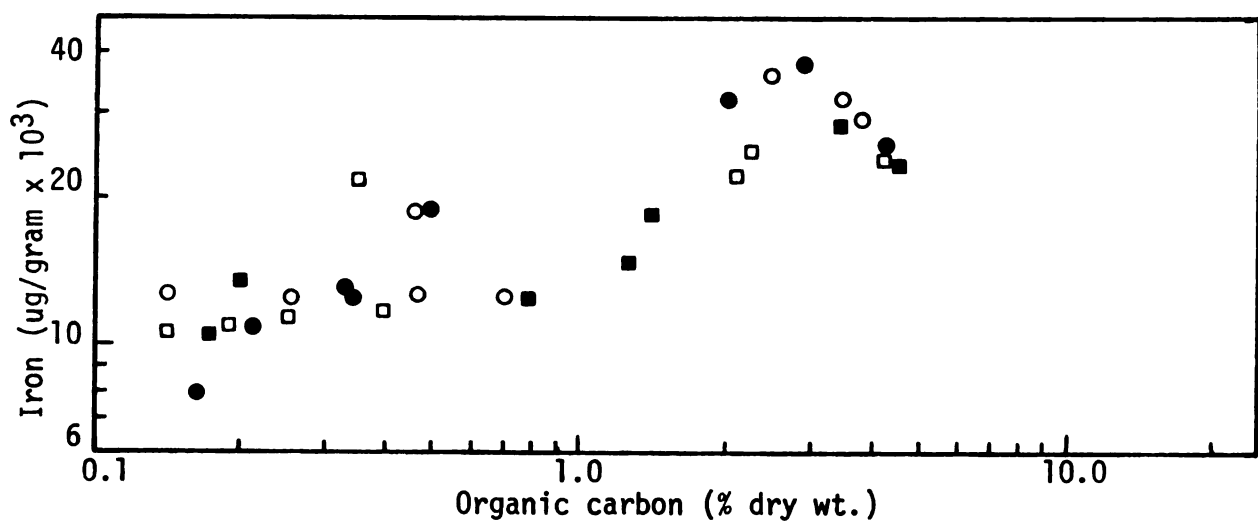
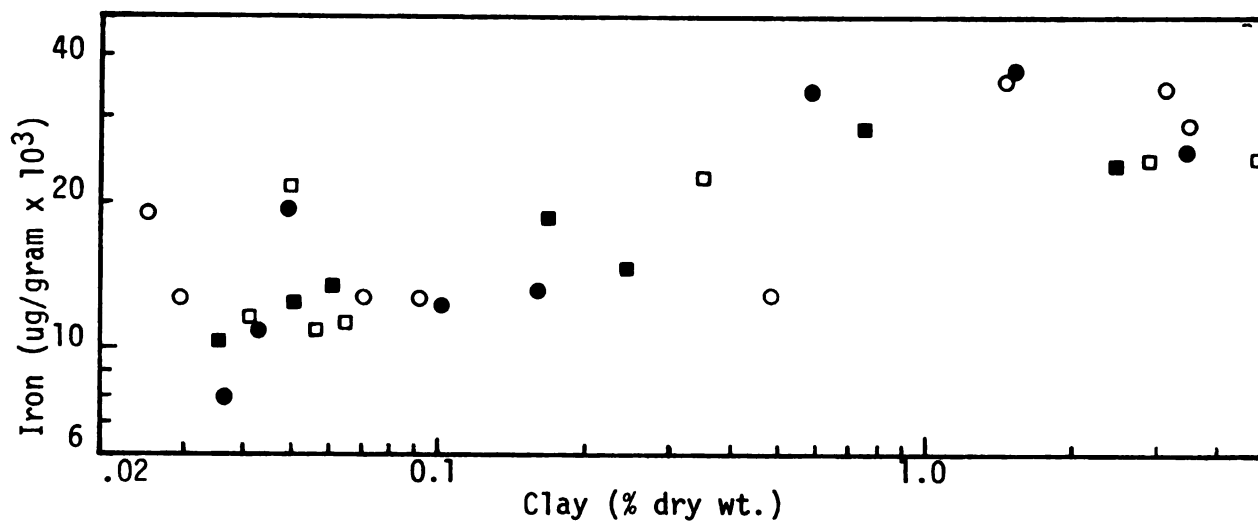


Figure A-5. Iron-sediment relationships for June-December 1973.
($\square$ -June, $\blacksquare$ -Sept., $\circ$ -Nov., $\bullet$ -Dec.)

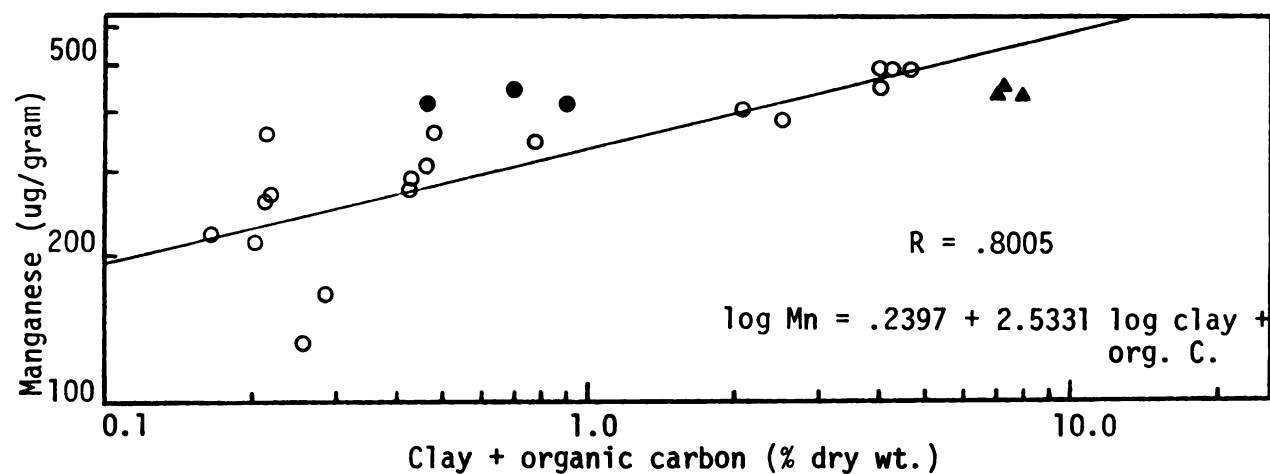
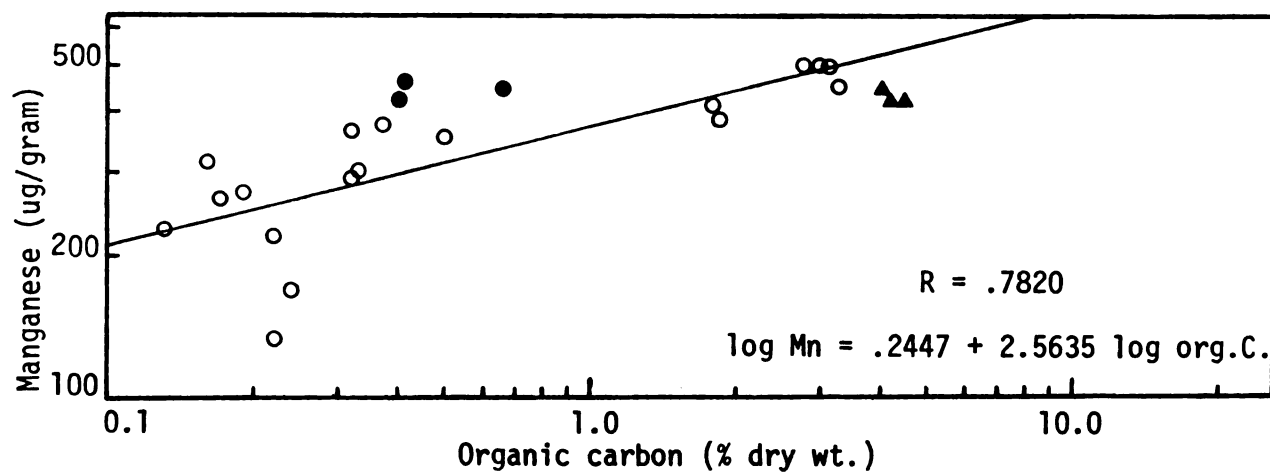
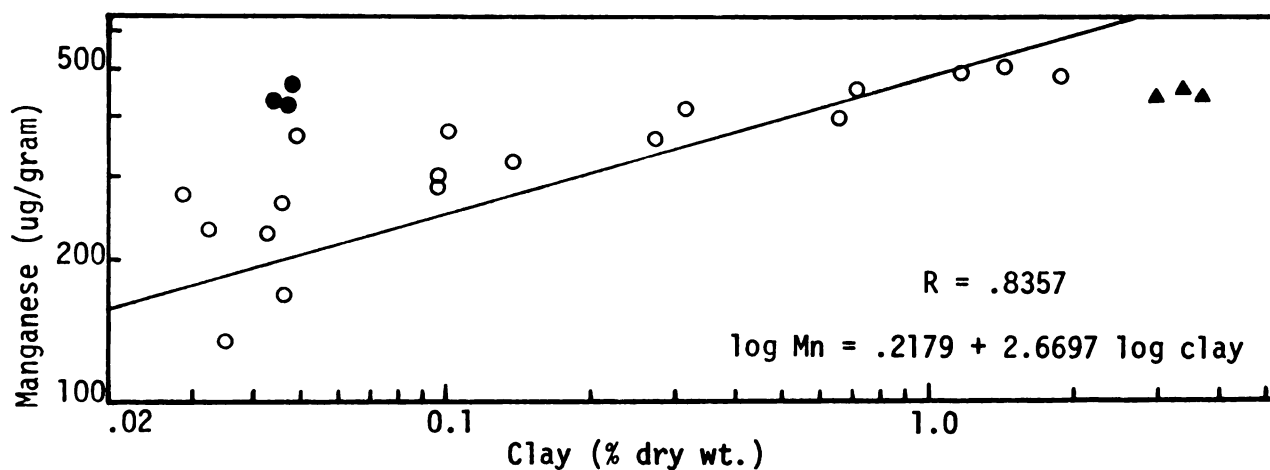


Figure A-6. Manganese-sediment relationships for December 1973.
 (▲-Station 1, ●-Station 5, ○-other stations.)

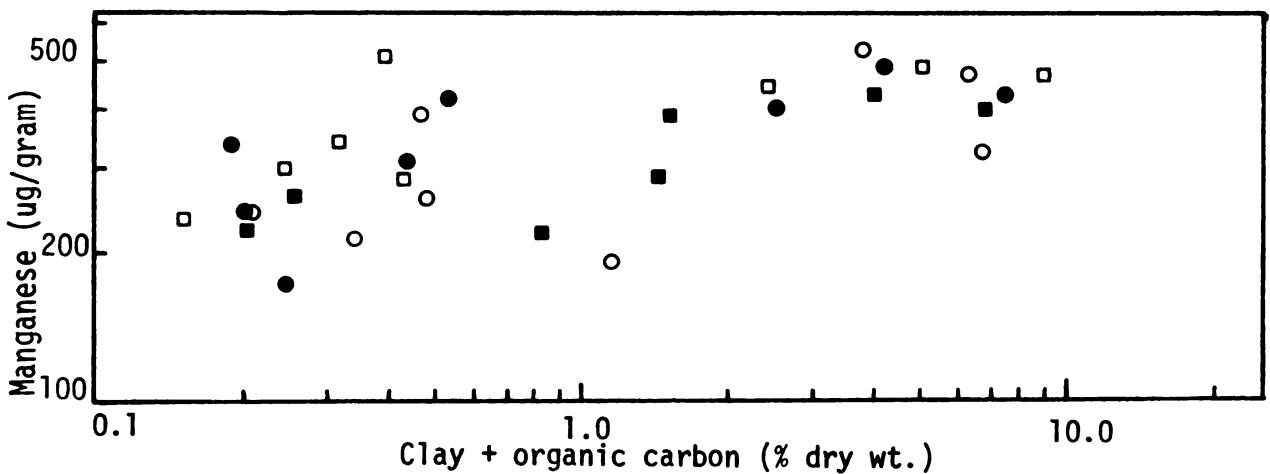
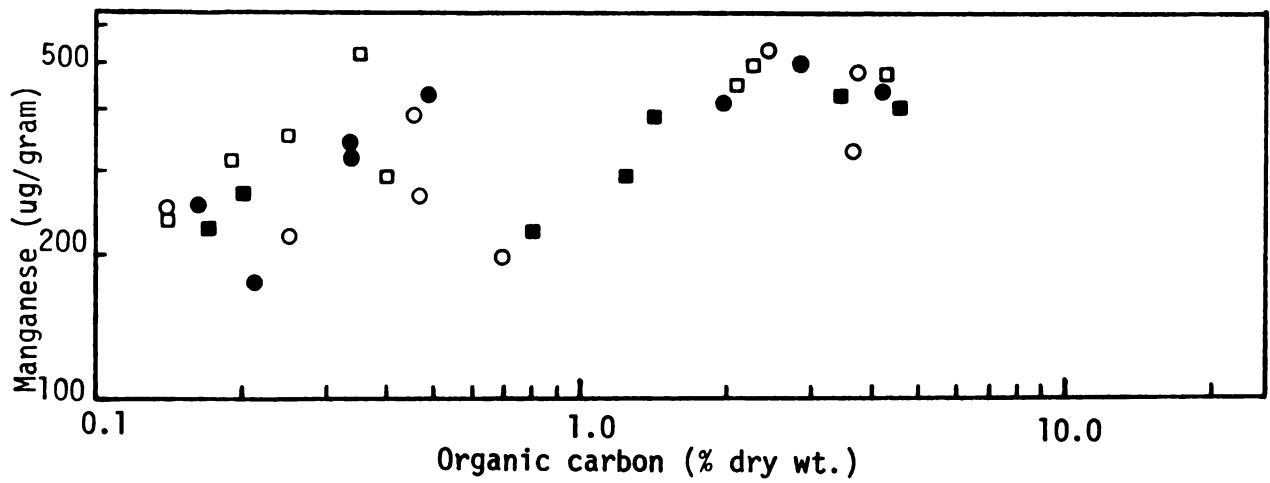
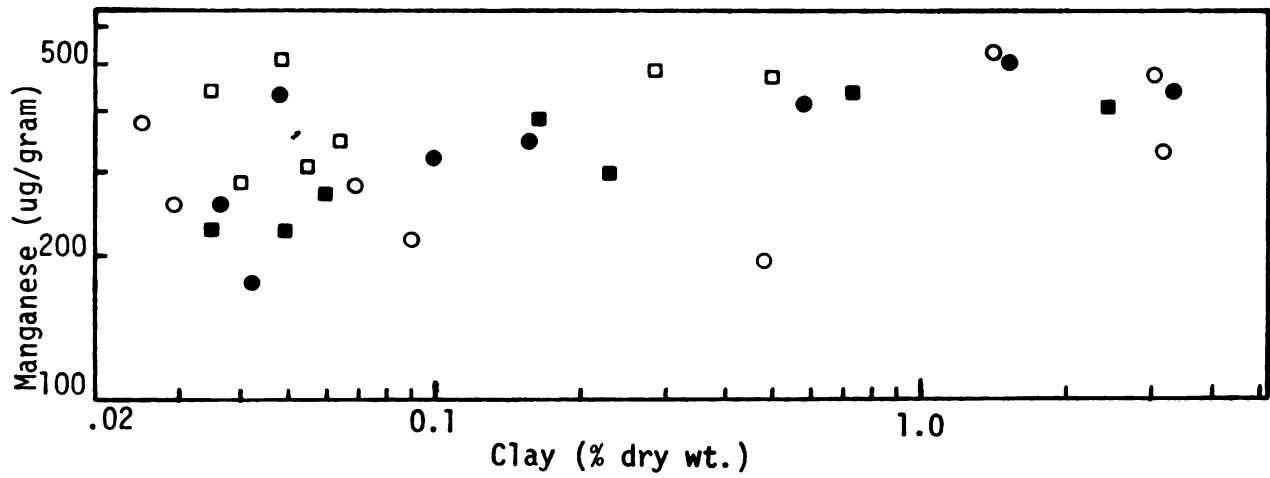


Figure A-7. Manganese-sediment relationships for June-December 1973.
(□-June, ■-Sept., ○-Nov., ●-Dec.)

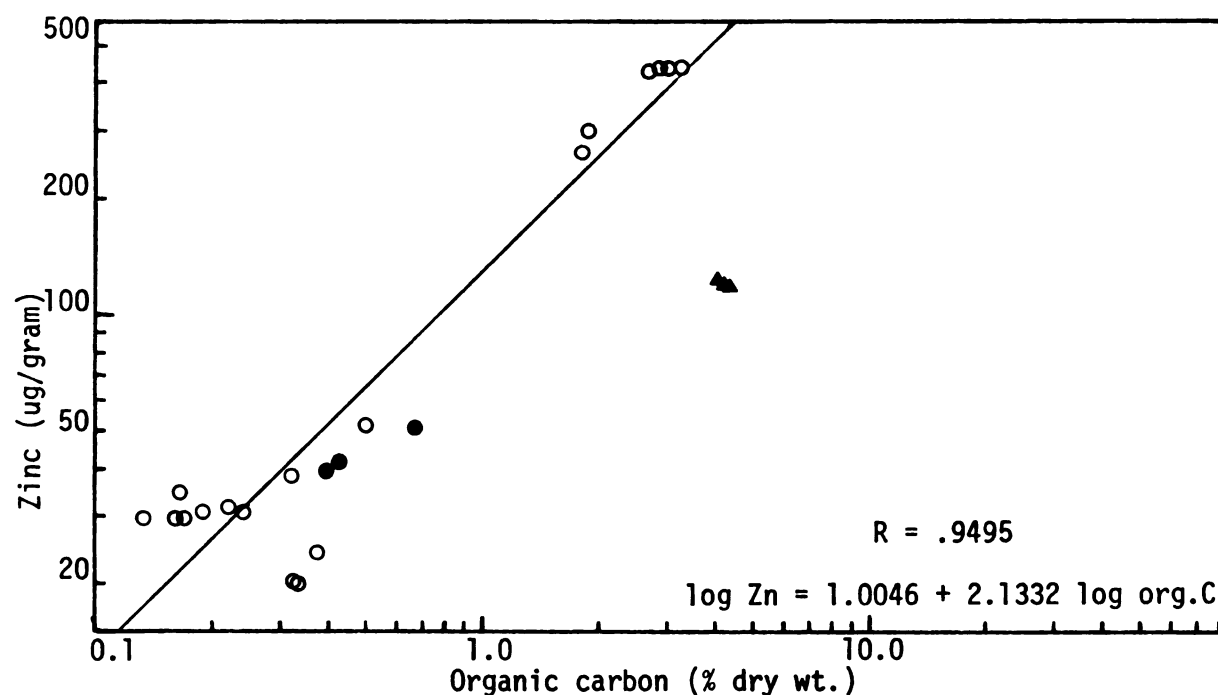
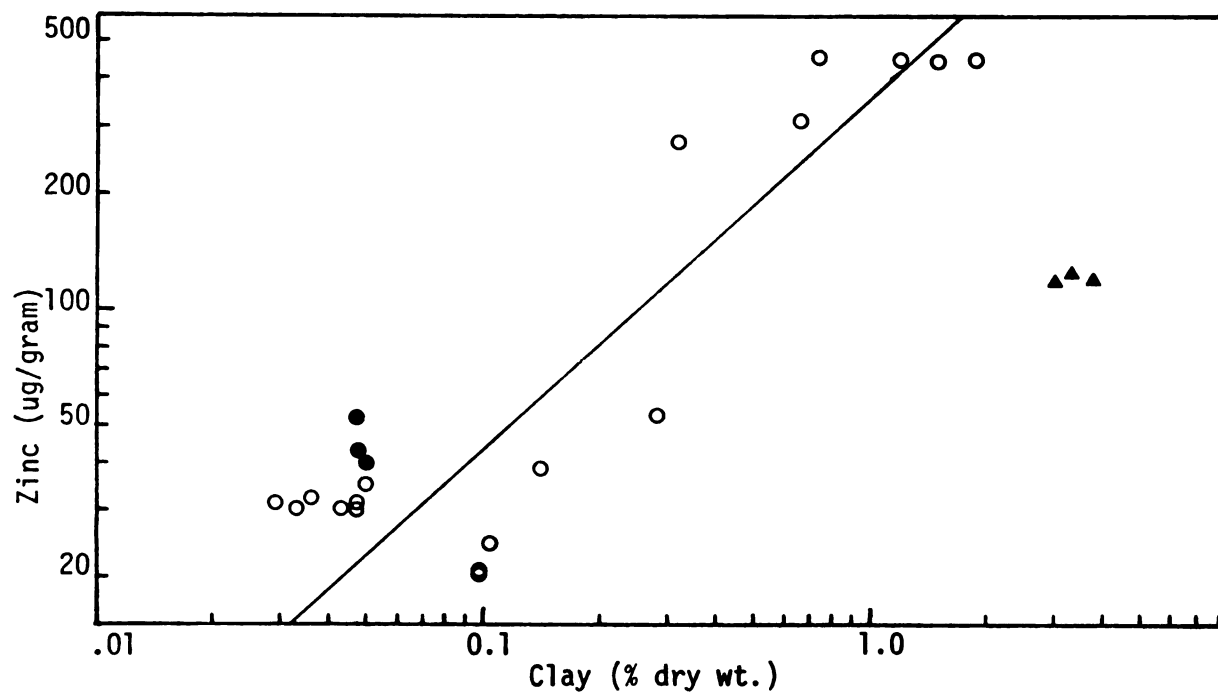


Figure A-8. Zinc-sediment relationships for December 1973.
(▲-Station 1, ●-Station 5, o-other stations.)

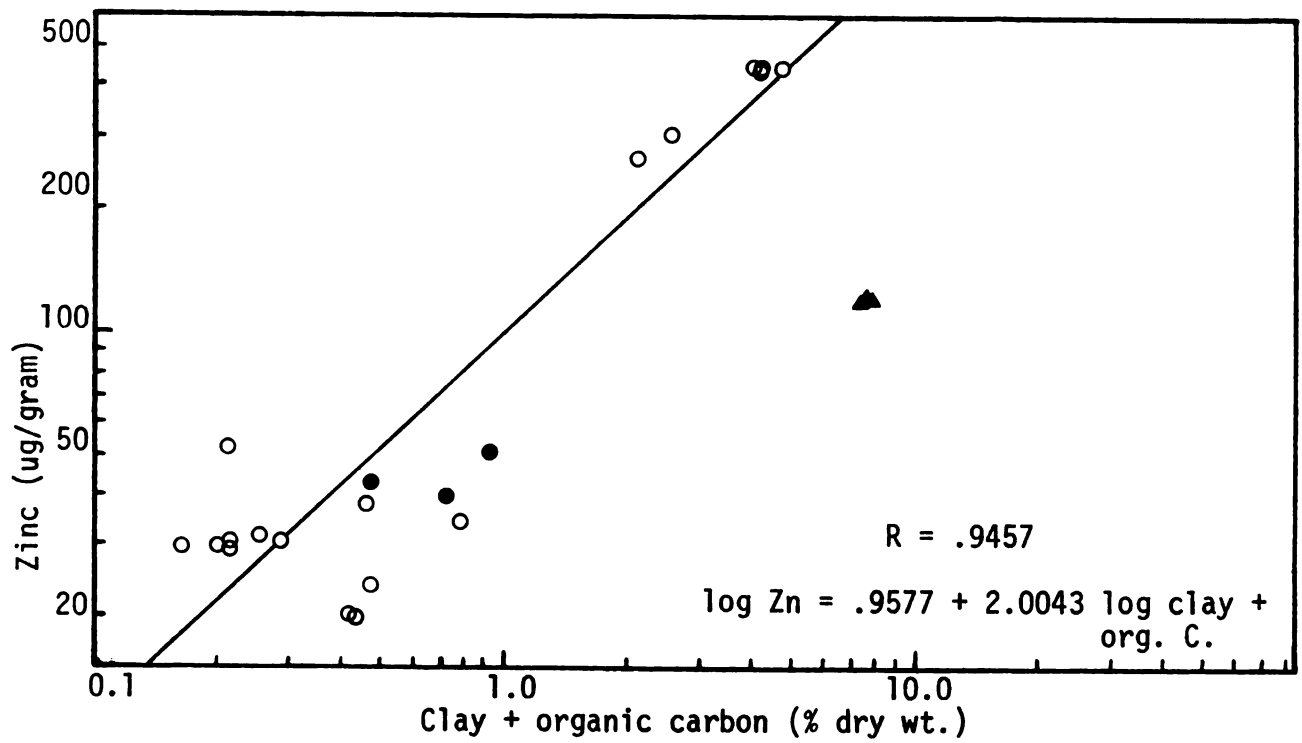


Figure A-8. continued.

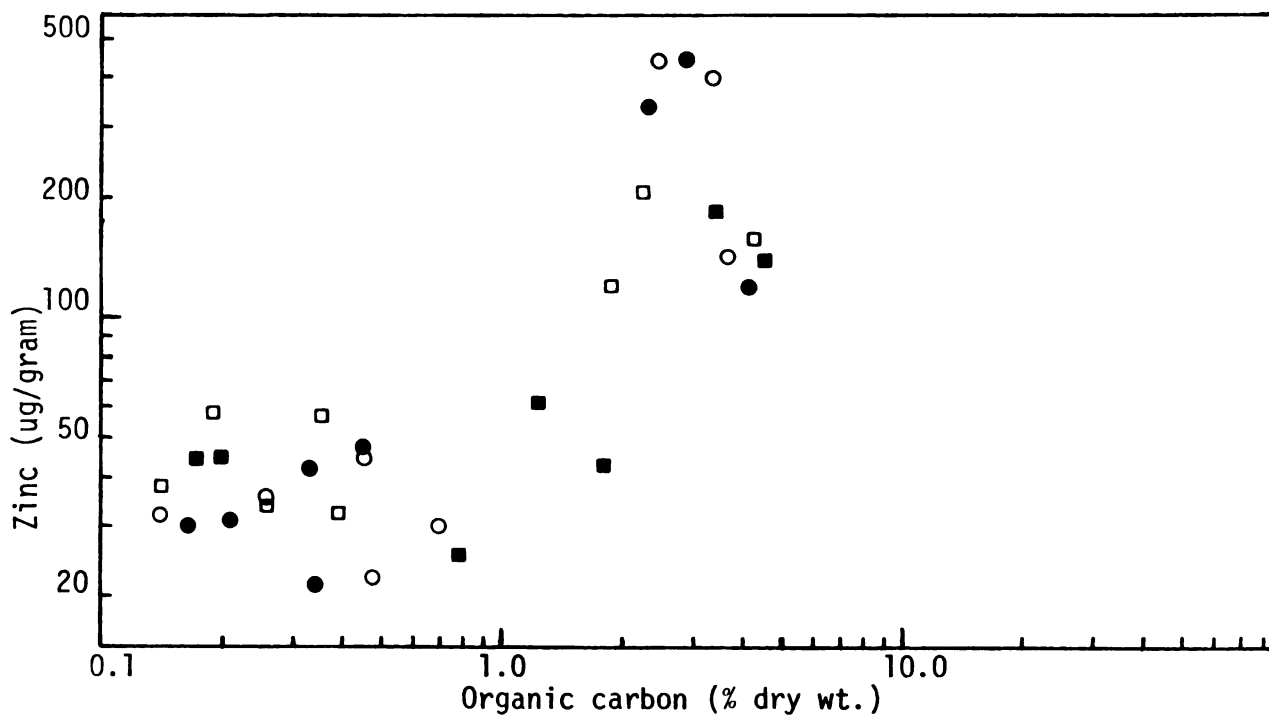
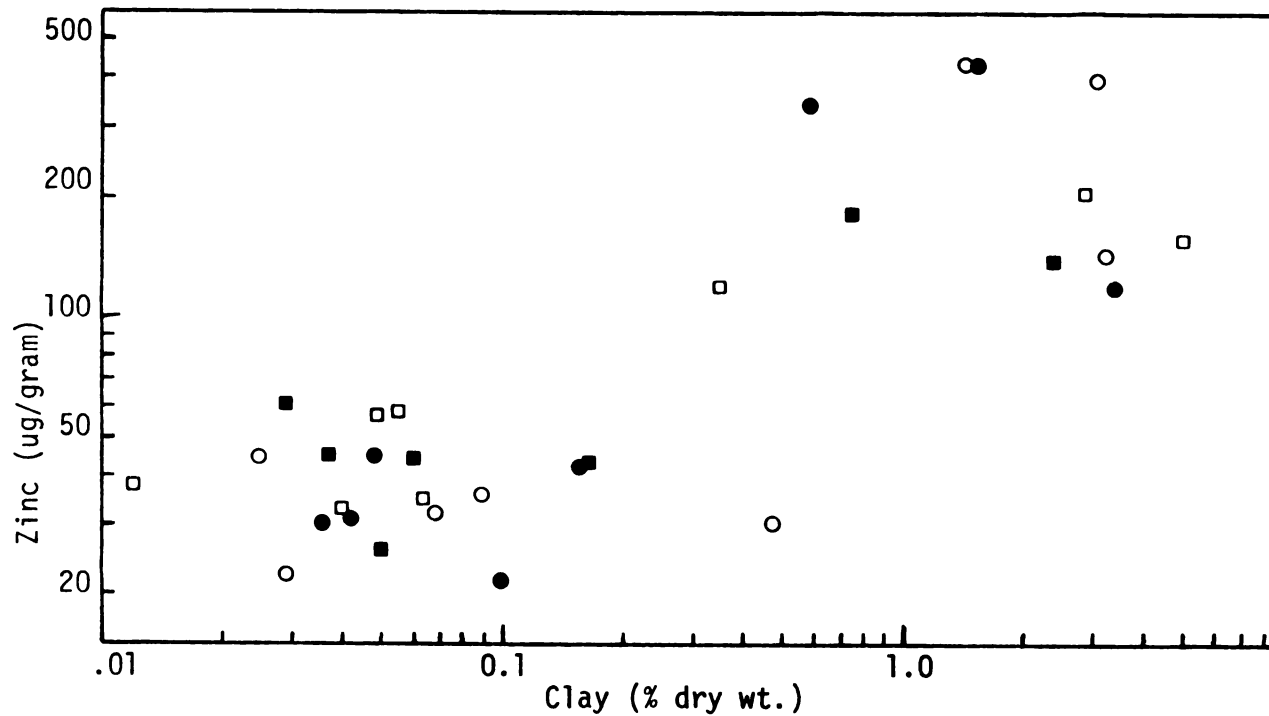


Figure A-9. Zinc-sediment relationships for June-December 1973.
(□-June, ■-Sept., ○-Nov., ●-Dec.)

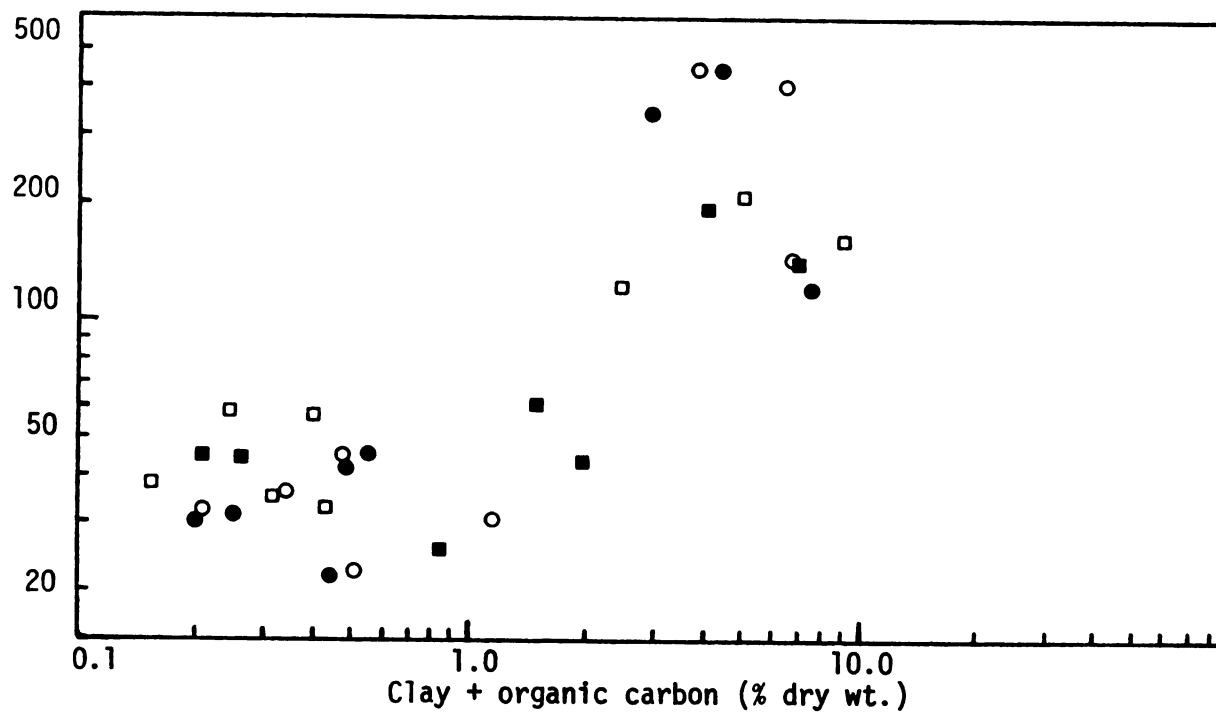


Figure A-9. continued.

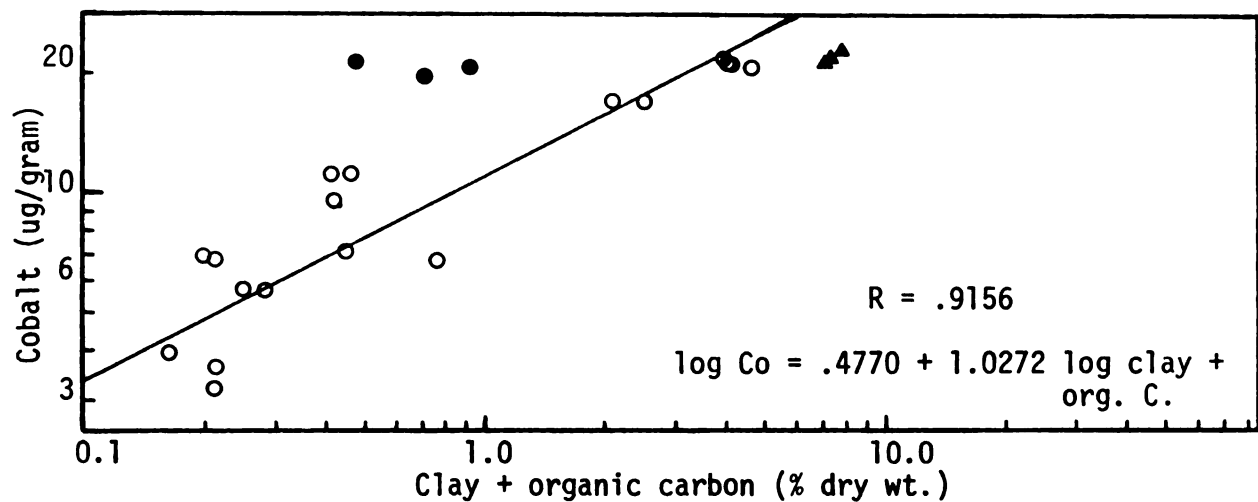
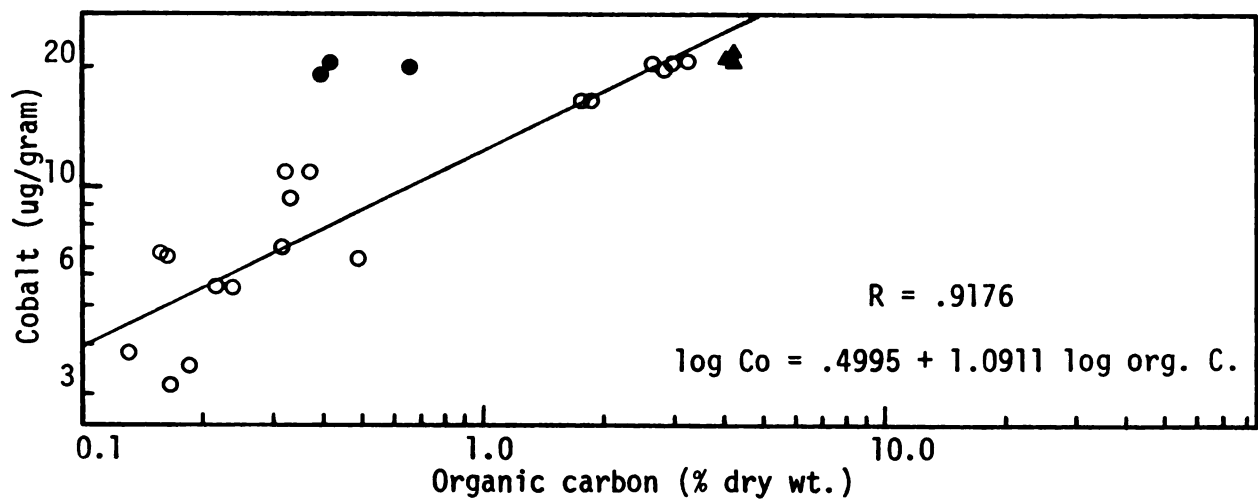
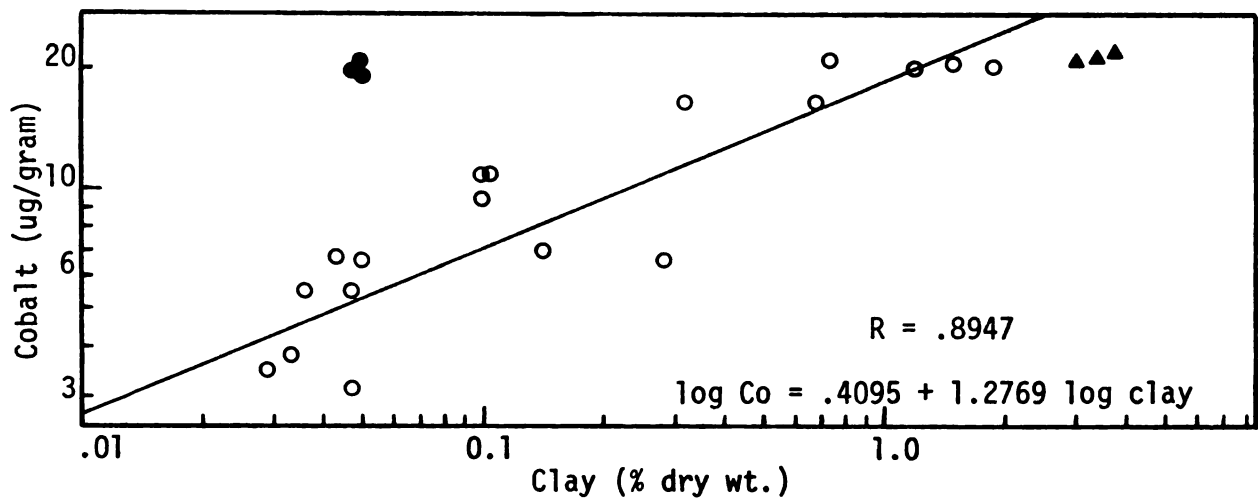


Figure A-10. Cobalt-sediment relationships for December 1973.
 (▲-Station 1, ●-Station 5, ○-other stations.)

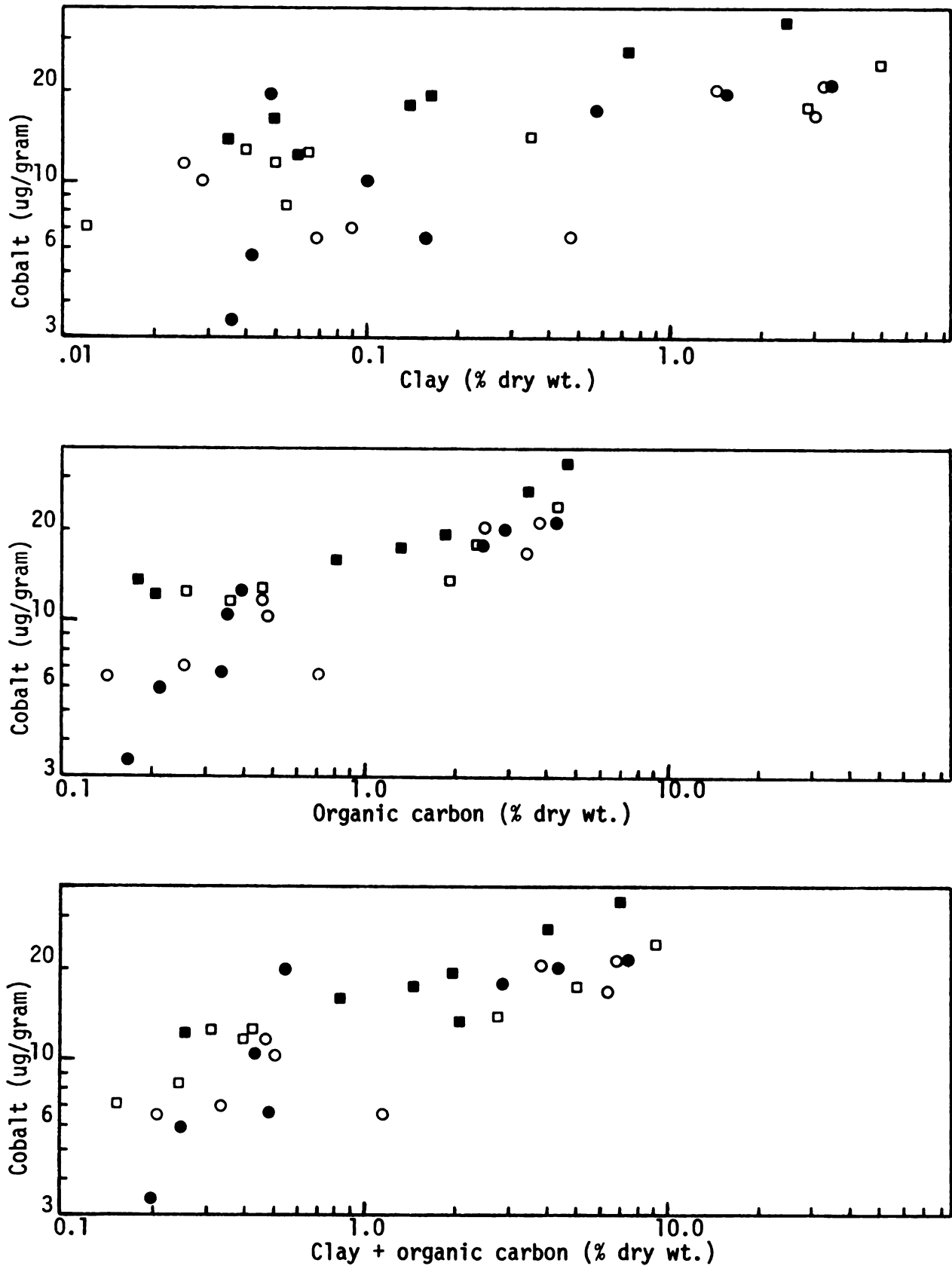


Figure A-11. Cobalt-sediment relationships for June-December 1973.
 (□ -June, ■ -Sept., ○ -Nov., ● -Dec.)

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