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The Effects of Acid Precipitation on Two Lakes in Southwestern Michigan

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THE EFFECTS OF ACID PRECIPITATION ON TWO LAKES IN SOUTHWESTERN MICHIGAN

by

Fardin Olyaei

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THE EFFECTS OF ACID PRECIPITATION ON TWO LAKES IN SOUTHWESTERN MICHIGAN

Fardin Olyaee, Ph.D.

Western Michigan University, 1986

The purpose of this study was to investigate the extent to which acid precipitation contributes acidity and heavy metals to lake enviroments. Asylum and Bonnie Castle Lakes, both located in the western portion of Kalamazoo County, served as the study sites. Precipitation samples were also taken at a site close to both lakes. Using the Hach Colorimeter, a preliminary study was undertaken to determine concentrations of the major cations (H^+, NH_4^+, K^+ and Ca^{2+}), and major anions (NO_3^-, SO_4^{2-}, and PO_4^{3-}). The main study dealt with the metal concentrations (Mn, Fe, Cu, Zn, and Pb) in rain/snow water, lakewaters, sediment, and aquatic vegetation of lakes. The data for the main study were provided by Atomic Absorption Spectrophotometry (AA), and Particle Induced X-ray Emission (PIXE) methods. For the water quality analysis by PIXE, the "vapor filtration" procedure was used to prepare the lakewater and rain/snow water samples. The sediments and macrophyte (<u>Chara</u>) samples used in the PIXE process were dried in order to make target pellets. The pellets were then analyzed by PIXE.

As a result of the study, the following conclusions

emerged:

1. The pH values for precipitation ranged from 3.9-5.82, with an event average of pH 4.67.

2. Although both receive similar amounts of acid deposition, Asylum Lake was alkaline, whereas, Bonnie Castle Lake remained neutral.

3. The acidity of precipitation was 800-1000 times greater than that of the water of Asylum, and 200-300 times greater than that of Bonnie Castle Lake.

4. Because of the groundwater flow characteristics around Asylum Lake, this lake did not receive a substantial portion of its total input as direct precipitation. However, the diluting effects of precipitation coupled with the absence of any contribution from hardwater sources such as groundwater, may be important in the water chemistry of Bonnie Castle Lake.

5. The acidic precipitation was associated with deposition of metals such as Zn, Fe, Cu, and Pb, resulting in elevation of their concentrations in the study lakes. Zn and Fe were the major elements present in precipitation.

6. Except for Cu, the concentrations of all heavy metals were higher in the solid phases, sediment and/or vegetatation, than in the lakewaters.

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Fardin Olyaee

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

The term "acid precipitation" refers to the acidic rain or snow that results mainly from polluting the atmosphere with compounds of sulfur and nitrogen. The acidity of rain, snow, and atmospheric particulates that fall on much of the world appears to have increased significantly within recent times (Angyal, 1980). The long term environmental, social and economic problems associated with acid precipitation and its control are particularly complex since the formation of such rain and snow is not constrained by existing political boundaries.

The consequences of acid precipitation have yet to be evaluated fully but, it seems to have had a far reaching environmental impact. It has been linked to sharp declines in many lakes and streams--in some cases to the point of total extinction--in the number of aquatic organisms. Evidence also suggests that acid precipitation may be damaging trees and other plants. In addition, the increased acidity accelerates the weathering and corrosion of materials and buildings. Some scientists also suggest that acid aerosols are a threat to human health (Angyal, 1980). Nevertheless, there is still considerable disagreement about the sources for the acid-forming components and the severity of the effects. The classic view of acidification and geochemical weathering in ecosystems focuses on the role of carbonic acid in rainwater. Now, however, strong acids such as sulfuric, nitric, and hydrochloric appear to have lowered the pH values of rain and snow falling over much of northern Europe and the eastern portion of the United States and Canada (Likens, 1976). These strong acids are thought to originate primarily from gaseous man made pollutants such as sulfur dioxide and nitrogen oxides produced by the combustion of fossil fuels.

As the standard of living has improved in industrially-developed societies, an unwelcome side effect of the greater energy consumption has been exhausts from automobiles as well as various pollutants from heavy manufacturing, metal smelting, and the generation of electricity. With the world's oil and gas reserves being depleted rapidly, and the development of alternate energy sources still in the distant future, the increased use of coal appears to be inevitable. Consequently it is estimated that sulfur and nitrogen oxide emissions will increase fivefold by the year 2000 (Angyal, 1980).

It is exceedingly difficult to estimate what proportion of atmospheric oxides is generated by human activity, for precipitation, without question, contains dissolved substances and particulate matter from natural sources such as sea spray, volcanic emissions, and terrestrial dust (Likens, 1976). Thus, an important question is what the pH of precipitation was before human activities began to alter it, particulary before the Industrial Revolution.

It is the purpose of this study to investigate certain relationships between acid precipitation and selected characteristics of lake ecosystems. Specifically the main objective is to identify the extent to which acid precipitation contributes acidity and heavy metals to a lake environment and also to determine any possible relationships between rain/snow water contributed metals and metal concentrations in the lake water, sediment, and vegetation.

Early Awareness of Acid Precipitation

Many features of the acid rain phenomenon were first observed by an English chemist, Robert Angus Smith, in the middle of the 19th century. In 1852, Smith published a detailed report on the chemistry of the rain in and around the city of Manchester, England. In this account, he called attention to the changes in the chemistry of precipitation as one moved from the middle of the highly polluted city to the surrounding countryside: "We may, therefore, find three kinds of air--that with carbonate of ammonia in the fields at a distance; that with sulfate of ammonia in the suburbs; and that with sulfuric acid or acid sulfate, in the town" (Smith, 1872).

Twenty years later, in a book entitled Air and Rain, the Beginnings of Chemical Climatology, Smith (1872) first used the term "acid rain" and enunciated many of the principal ideas that are part of our present understanding of the acid rain phenomenon. On the basis of detailed studies he demonstrated that the chemistry of precipitation is influenced by regional factors such as the combustion of coal, decomposition of organic matter, wind trajectories, proximity to the sea, and the amount and frequency of precipitation. He also noted the damage allegedly caused by acid rain to plants and materials in the industrial regions.

Although pH levels were not reported, detailed data on the chemistry of precipitation are available for the United States during the mid 1950's and can be used to calculate the H^+ concentration (Junge, 1958). These analyses indicate that precipitation in the eastern United States was already acid. Thus sometime between 1930 and 1950, the pH values of rain and snow appear to have dropped significantly in the eastern portion of the United States (Likens, 1976).

The first data measuring the pH value of precipitation for the entire United States were collected by the National Center for Atmospheric Research between 1964-1966. These data show that pH values varied from less than 4 in New England to well above 7 in many western states.

Currently the pH of precipitation in much of the northeastern portion of the United States ranges annually between 4.0 and 4.2. Furthermore, lower pH values of 2.0 and 2.1 have been observed for water from individual storms at specific locations (Liken, Bormann, and Johnson, 1972). This is 10-10,000 times more acidic than occurs under natural conditions. This acidification is a phenommenon of modern times, occurring especially in industriallized locations of the northeastern United States where the high degree of acidification has been measured.

There is evidence for the existence of long term changes in the acidity of precipitation in North America. These include changes in the acidity of surface water, changes in the amounts and patterns of fuel use in the United States and Canada since the Industrial Revolution began about 1850, and finally changes in the median annual pH value of precipitation in the years 1955-1956 and 1970 -1972 (Beamish and Harvey, 1972). At present, there is acid precipitation over the entire eastern half of the United States, the West Coast and Rocky Mountain states.

It was not until the 1960's and 1970's that enough evidence was accumulated to suggest a relationship between acid rain and acidification of surface waters. It was then suggested that the acidity of rain coincided with the enormous industrial expansions and almost exponentially rising consumption of energy after World War II (Angyal, 1980).

During that period, concern increased in that acid precipitation was causing damage to the natural environment throughout the world, particularly in Japan, Norway, Sweden, Canada, northern Europe, and the United States. As the acidity of precipitation in some regions had increased 200 fold since 1956, an estimated 10,000 lakes in Scandinavia are now without fish and another 10,000 are threatened. Moreover, according to recent projections, by the year 2000, an additional 20,000 lakes may be threatened (Hansen, 1982).

Although the consequences of the deposition of acidic rain and other air pollutants in the environment have not been fully evaluated, the impact is probably extensive. Likens, Wright, Galloway, and Butler (1979) reported that anthropogenic emissions of SO_2 and NO_2 are the major precursors of acid-forming anions in the atmospheric precipitation. Concentration of other anthropogenic pollutants in precipitation, including heavy metals and pesticides, are related directly to the distribution of acid precipitation. However, once the sources of the primary pollutant emissions are known, the major components of the precipitation that are derived from these sources should be evaluated.

A series of recent reviews (Last, Likens, Ulrich, and Walloe 1980; Overrein, Seip, and Tollan 1980) has indicated that, despite some questions concerning rates of reactions and of control mechanisms, enough is already known about the acidic deposition phenomenon to describe the general transport and formation of acid rain, the areas of impact, and the mechanism of effect. Figure 1 (p. 8) shows the flow relationships among the principal ecological consequences believed to result from fossil fuel emissions and the subsequent deposition of increased amounts of H^+, sulfate, and nitrate on the landscape and their final effects (Loucks, Usher, Millwer, Swanson, and Rapport 1982).

Chemical Composition of Acid Precipitation

Precipitation chemistry is influenced by the patterns of chemicals released to the atmosphere. Many of these chemicals are produced by naturally-occurring processes. Dust and debris carrying soil particles are swept from the ground into the air, giving precipitation a basic pH. Volcanic eruptions emit sulfur dioxide and hydrogen sulfide, both of which react with compounds in the air to form sulfuric acid. Lightning produces NO_x that in turn forms nitric acid. Decay of organic matter, sea spray, and fires also add rain-altering chemicals (Cowling, 1980).

The discharging of man made wastes into the atmosphere increases the concentration of compounds that contain C, N, and S, and adds to the variety of compounds such as

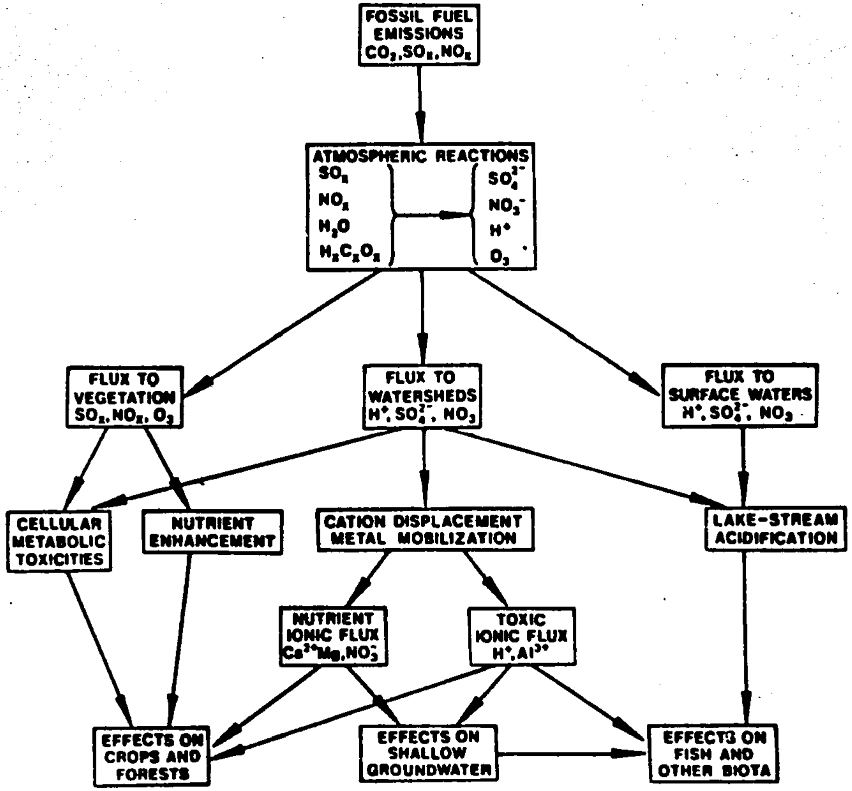

Figure 1. General Transport and Formation of Acid Precipitation and it Effect on Ecosystem.

anthropogenic organics (e.g., PCB'S) and heavy metals that are found in rainfall.

The general phenomenon of atmospheric deposition includes three major mechanisms by which substances are transferred from the atmosphere into the ecosystems:

1. absorption and adsorption of gases (dry deposition).

2. impaction and gravitational settling of fine aerosols (dry deposition).

3. Precipitation that contains both dissolved substances and particles that are removed from the atmosphere in rain, snow, hail, dew, fog, and frost (wet depostion) (Junge, 1958).

The relative importance of wet verses dry deposition depends on the distribution of the element or compound among the gas and particle phases, particle size distribution, intensity and duration of rain or snowfall, lakewater chemistry, and finally pollutant reactivity (Eisenreich, Thornton, Munger, Gorham 1981).

All the major anions and cations transferred into ecosystems when it is raining or snowing (wet deposition) are also contained in the gases and particulate matter that are transferred to the atmosphere into the ecosystem when it is not raining or snowing (dry deposition). Thus, in a chemical mass balance sense, it is impossible to distinguish the biological effects of "acid rain" (wet deposition) from the biological effects of dry deposition (Tamm, 1958; Oden 1976).

To understand the acidity of precipitation, it is essential to measure all the major anions and cations in precipitation. Changes in the acidity of precipitation reflect changes in the balance among the major cations (H^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+) and anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) in precipitation.

Among all the proton (H^+) sources that might contribute to the acidity of precipitation, sulfuric, nitric, and hydrochloric acids are the strongest donors in rain and snow (Likens et al., 1979). The ratio of sulfate to nitrate ions in precipitation varies with time and location. In much of eastern North America the average equivalent ratio of sulfate to nitrate varies from about 3.3:1 in summer to about 0.7:1 in winter. The average annual ratio of sulfuric acid to nitric acid is currently about 2:1; but nitric acid is becoming progressively more important as compared with sulfuric acid (Likens, 1976; Likens et al., 1979). Peterson (1983) reported that falling snow usually had a much higher nitrate than sulfate level even when compared with a winter rain. Snow appears to be an efficient scavenger of NO_3^- and other components from the atmosphere. However, since NO_3^- and SO_4^{2-} track together so closely, it is relatively impossible to determine the specific anion that originally caused the acidity.

Eisenreich et al., (1981) reported that the long winter season in some regions produces a deep snow cover that persists for several months, thus inhibiting the insertion of soil particles into the atmosphere during the winter months. With the H^+ ions deposited on snow, acidity increased. On the other hand, the very dry and dusty fall months result in a decrease in the acidity of precipitation. Therefore, the seasonal quantity and quality of precipitation are important for determining the potential for acidic impact on the environment. Acid pollutants accumulating in the snow pack have a higher potential for causing deleterious effects on organisms and habitats. These effects are due to the rapid flushing of accumulated acid during snow melt. Thus, the distribution of precipitation during the year, the temporal behavior of rainfall and the location of pollution sources within rainfall pathways are linked to the potential for damage to the ecosystem.

The potentially injurious substances in dry and wet deposition include not only acidic substances but also certain toxic gases, organic substances, inorganic materials, and heavy metals. This latter category includes Zn, Cu, Fe, Al, Pb, Ni, Cd, Va, and Hg. Whereas elements listed above are needed by living organisms in small amounts, higher concentrations of them can be toxic to plants and animals (Eisenreich, Hollod, and Langevien 1978).

Heavy metals are defined as those having a specific gravity greater than five (Giddings, 1973). These metals originate, at least partly, from natural background sources. But, most of them that are deposited from the atmosphere over wide areas of the globe are a direct result of human activities.

Although less attention has been focussed on the trace metals in rain and snow, the potentially deleterious impact of trace metal deposition by precipitation is important. High temperature industrial processes release many of these trace metals that, like acid, eventually appear in the rain and snow and subsequently in streams and lakes.

Eisenreich et al., (1981) reported that an analysis of the precipitation collected during a year's study indicated a wide range of metal concentrations with Al, Ca, Mg, and Fe ions varying most greatly. These elements are usually associated with larger particles in the atmosphere. Thus their concentrations would be most affected by the volume and intensity of rainfall than would the other metals. Eisenreich et al., (1978) found that Al, Ca, Fe, and Mn were associated with larger atmospheric particles (> 4.5 mu). These particles have high deposition velocities and consequently a low residence time in the atmosphere. The metals, Al, Ca, Fe, Mn, and Mg are major elements in the earth's crust and were found to have higher concentrations in rainwater than were other metals.

Trace metals are defined as those not in abundance in the earth's crust, namely Cr, Ni, Cu, Zn, Cd, and Pb. According to Eisenreich et al., (1981), The above metals vary less in concentration and are therefore much less abundant in the precipitation. These metals are usually associated with aerosol-sized particles in the atmosphere (< 1.0 mu), have lower deposition velocities and have longer atmospheric residence times. Futhermore, the acidity of precipitation may affect the solubility, mobility, and toxicity of certain cations in soil. This also increases the leaching of nutrient cations, including those of K, Ca, and Mg. These nutrient ions are transferred from soils into surfacewater and groundwater (Oden, 1976).

The Effect of Acid Rain on the Leaching of Elements From Sediment Into Water

There is increasing concern about the effect of acid rain on the release of elements into water. The effect of acid precipitation on the kinetics of release of anions and cations from sediments was investigated by Sparks and Curtis (1983). The kinetics of elemental release were evaluated by leaching the sediments with simulated acid rain at pH levels of 2.5, 3.4, 4.3, and 5.6. Leachates were collected until an apparent equilibrium was reached. At all pH levels, quantities of basic elements were released in the following order: Ca > K > Mg > Na. As acidity of rain increased, the total quantity of each released element increased. In all cases, a rapid initial release of each element was followed by slower release rates. Anionic release, including Cl^-, SO_4^{2-}, NO_3^- was also evalvated and found to be negligible.

Wiklander (1973) reported that acid rain enhances the rate of leaching of NO_3^-, SO_4^{2-}, and heavy metals into the groundwater. According to Wiklander, acidity of minerals in soils that could release large quanities of Al^{3+}, Fe^{3+}, and Si^{4+} into the groundwater, would make such water unfit for human consumption.

Hall, Likens, Fiance, and Hendrey (1980) reported that the experimental addition of sulfuric acid caused Al, Ca, Mg, and K ions to be released into the water. The increase in the cations may have been the result of their replacement by H^+ presumably via cation exchange with the sediment. This cation exchange exemplifies the typical chemical weathering reactions in mountain watersheds. This phenomenon has been observed in a number of Scandinavian and North American watersheds that receive substantial amounts of acid precipitation (Likens et al., 1979). Cronan and Schofield (1979) indicated that increased Al in solution may be due to solubility changes and not to cation exchange. Such increases in cation concentration may be of significance to aquatic communities since these nutrients could be important to attached plants and would, in turn, affect the organisms feeding on those plants.

In an attempt to determine what happens in acidified lakes when pH increases, Dillon, Yan, Scheider, and Conroy (1979) have experimented with the addition of neutralizing materials to several acidic lakes. The neutralizing agents chosen were $Ca(OH)_2$ and $CaCO_3$ because they can effect an increase in basicity with a minimum of other changes in lakewater chemistry (Grahn, Hultberg, and Landner 1974). The addition of bases reduced Cu, Ni, Zn, Mn, Fe, and Al levels substantial ly, probably by a precipitation mechanism. Cu was reduced from 500 to 100 mg/l, Ni from 1400 to 400 mg/l.

Several studies have shown that the nutrient levels, particularly that of potassium, increased after the addition of bases. Addition of P, however, caused substantial reduction in total N content of the water, either because of increased uptake by phytoplankton or increased rate of denitrification (Dillon et al., 1979).

The property of a metal and its behavior depend on many environmental factors such as ambient pH and the nature of the binding agents such as organic substances (Jackson, Kpphut, Hesslein, and Schindler 1980). Most metals are strongly complexed by mud and sediments and only some can be redissolved by cation exchange. Acidification of a lake, however, interferes with the accumulation of metals by sedimentary binding agents (Schindler, Hesslein, Wagemann, and Broecker 1980).

In an aquatic environment the stability of a complex increases with the degree of its covalent character and is therefore a function of the electronegativity of the metal (Douglas and McDaniel, 1965). This may account for the relationship between electronegativity of a metal and the percentage of a metal extracted from the sediment and also for the preference of metals for extraction from the sediment. In general, metal behavior involves the partitioning of metals between water and sediment. The larger cations showed a greater affinity for the aqueous phase than did the small cations (Jackson et al., 1980). This raises the possibility that metal ions of a large ionic radius may be preferentially released from lake sediment to the overlying water column.

The most important metal-binding agents in water and sediments are the plankton and other organisms, humic matter, and other forms of non-living organic matter. In nature, all the above are scavengers of trace metals. Acidification appears to interfere with the uptake of most metals by suspended particles (Schindler et al., 1980) and could reflect competition between the H^+ ion and the metal cations for binding sites.

Many studies including Hall et al (1980), Overrein et al. (1981), and Jackson et al. (1980) have shown that acid rain is responsible for an increase in dissolved metals. Zinc concentrations were positively related to the pH values, being released more strongly in acidified water due to the fact that zinc dissolves more readily in such waters (Schindler, 1980). In nonacidified lakes of pH values greater than 6.0, the zinc concentration remains under 10 mg/l (Beamish, 1976) and varies between 15 - 80 mg/l in lakes with pH values less than 5.3 (Henriksen and Wright, 1977) and present a mean value of 15 mg/l in lakes of pH 5.6 - 6.0 (Dillon et al., 1979; Yan, and Stokes 1978). These values show that higher zinc concentrations are expected in acidified waters.

Magnesium concentrations have also been found to be greatly increased in concentration in acidified lakes (Dickson, 1975; Beamish, Lockhart, VanLoon and Harvey 1975). This is attributed again to the leaching of soil by acid rain. In addition, Schindler et al. (1980) demonstrated the recruitment of magnesium from lake sediment during the experimental acidification of a lake. The concentration of magnesium in the water ranges from an average value of 3 mg/l in lakes with a pH greater than 6.0 (Beamish, 1976) to between 50 - 400 mg/l in lakes with a pH of less than 5.3 (Beamish, 1976; Dickson, 1980). In contrast to zinc, dissolved magnesium concentrations depend on the redox condition in water and thus vary with depth and the period of the year.

The strontium concentration also follows the same trend as zinc. Therefore, Sr dissolves more readily in acidified waters and is released more strongly in such waters. Hall et al. (1980) reported that the concentration of Zn, Sr, and Mg appear to be useful indicators of increased acidification of a lake.

In summary, an acidic lake can be characterized by its low pH value, elevated SO_4^{-2}, Ca, Mg, Na, and K levels and lake water concentrations of Cu, Ni, Zn, Mn, Fe, and Al.

Effects of Acid Precipitation on Aquatic Ecosystems

It is well known that the atmosphere is the major input pathway for the introduction of nutrients (P, N, C, S), acidity (H^+), trace metals (e.g., Cu, Cd, Pb, and Hg) and anthropogenic organics (PCB'S) into natural waters. The chemical composition of lakes and streams is determined in part by the chemical composition of wet and dry deposition. The chemical composition of precipitation is modified by chemical and biological weathering and exchange processes as precipitation washes over vegetation, percolates through the soil, interacts with the underlying bedrock of the drainage basin, and adds to the runoff over the soil surface (Oden, 1976).

The addition of acidic pollutants to a lake ecosystem is a complex and uneven process. Last et al. (1980) discussed the variables involved and noted that the H^+ ion deposited with precipitation, and originated by other components of precipitation, may have four fates in the lake system.

1. Where carbonates are present, the H^+ will be consumed, with the release of bicarbonate and Ca or Mg;

2. H^+ may be exchanged for various metallic cations in soils with appreciable cation exchange capacity;

3. H^+ may react with minerals, releasing metallic cations; and

4. A H^+ ion not neutralized by the above processes will enter aquatic ecosystems in association with a mobile anion, usually sulfate.

The first three processes alone account for the observation that surface waters are less acidic than the precipitation they receive. However, other considerations include the mobility of anions such as sulfate and the breakdown of ammonium ions yielding acidity. Alteration of waters appears to represent a combination of the above factors.

Surface water sensitivities to acidification vary among watersheds. The sensitivity of aquatic systems depends on buffering factors internal to both watersheds and surface waters. Important watershed factors include soil particle size, texture, ionic absorptive capacity, chemistry, depth, bedrock geology, soil drainage, land form relief, and vegetation. Surface water factors include alkalinity levels, sediment bicarbonates, weak organic acids, sulfate reduction, surface area, water volume flushing rates, respiration levels, and nutrient levels. The relative importance of these factors can differ among watersheds and among surface waters.

The region of greatest susceptibility to the effects of acid precipitation are usually recently glaciated areas. The large areas of exposed granitic and other noncalcareous bedrock and thin soils that are low in buffering and cation exchange capacity are sensitive to acid precipitation (Cowling, 1980). These soils and freshwaters are low in alkalinty and calcium; consequently, they are poorly buffered and are vulnerable to input of acidic pollutants. Thus this airborne acid particularly affects the characteristic chemistry of poorly buffered soils, lakes, and streams in Scandinavia, northeastern United States, and eastern Canada.

Because it is generally assumed that acid precipitation falling on nonsensitive regions is quickly neutralized, the effects of this process have not been studied and thus remain unknown. The first and unique reported case of "lake alkalinization" occurring as a consequence of acid precipitation was presented by Kilham in 1982. Kilham reported that acid precipitation appeared to have a marked effect on aquatic ecosystems in non-sensitive areas. In these regions accordingly acid precipitation is making lakes more alkaline rather than more acidic. Increasing alkalinity, like increasing acidity, represent a drastic environmental change. Weber lake near Hardwood in Dickinson County in upper Michigan has experienced a nearly 20-fold increase in proton loading from acid precipitation in the past 25 years. According to Kilham (1982), acid precipitation appears to play a major role in determining the present summertime alkalinity level of the lake. Owing to alkalinity production by ecologically mediated processes (nitrate uptake by plants and sulfate reduction by bacteria) and increased carbonate weathering, acid precipitation has doubled the alkalinity, raised the equilibrium pH, and made this softwater seepage lake more eutrophic. This means it has gone from oligotrophic to mesotrophic. Alkalinity production, resulting from nitrate uptake and sulfate reduction, is sufficient to neutralize completely the hydrogen ions entering the system from acid precipitation. This also includes biologically mediated hydrogen ion production. The chelation of strongly reducing conditions within a lake increases the availability of phosphorous and the lake would probably become more eutrophic than it was originally.

Kilham (1982) further reported that the alkalinity of Weber Lake has doubled primarily as a result of increased rates of weathering in the watershed. Weathering rates have increased as an indirect result of acid precipitation

The work of Peterson (1983) may also provide similar information of lake alkalinization due to acid rain. He reported that the minerals present in the soil react with the incoming acidic substances carried by the water, thus neutralizing the acids. The minerals themselves are "weathered". He believed that the present rate of weathering may have increased somewhat due to acid precipitation.

However, the effect of acid precipitation on lakes is more widespread and complicated than previously assumed. Softwater lakes seem to be particularly susceptible to the effects of anthropogenic mineral acids. In sensitive regions softwater lakes are subject to acidification and in nonsensitive regions, alkalization. Both processes change the species composition, but acidification kills fish whereas alkalization makes lakes more eutrophic which also reduces the fish population because of reduced oxygen. Neither is a desirable effect.

Effect of Acid Precipitation on Organisms

Increased surface water acidity affects lakes in many, far-reaching ways, changing them physically, chemically, and biologically. Therefore, one expects a direct effect on aquatic organisms from changes in the physical or chemical environment or indirectly from changes in food supply, competition, or predation.

Acidification results in the modification of communities of aquatic flora and fauna at all levels of the ecosystem. The number of species is reduced, and a shift from many species to a few dominant ones at a low pH value has been reported for freshwater animals and plants (Almer, Dickson, Ekstrom, and Hornstone 1978; Beamish, 1976; Hendrey and Wright, 1975; Hendrey, Baalsrud, Toraaen, Laake, and Ruddum 1976). Decomposition of leaf litter and other organic substances is also hampered, nutrient recycling is retarded, and nitrification is inhibited at pH levels frequently observed in acid stressed waters. Thus acidification decreases species diversity, increases representation of community dominants, and decreases the complexity of the food web (Hall et al., 1980).

Healthy lake water may have a pH value as high as 8 because of the presence of calcium bicarbonate. Acidification removes the calcium and at pH 7, the declining carbonate levels may affect the hatching of the fish eggs in the water. As the pH value lowers toward 6, snail and small crustaceans begin to disappear. The number and kinds of species that form the lake's complex food web decline rapidly and the phytoplankton at its base begin to die. Bacteria important in the decomposition process also are killed and organic materials tend to accumulate at the bottom.

Changes in the calcium carbonate balance also disrupt ion exchange across the gills of fish and prevent fish eggs production. Toxic metals that are released by the increasing acidity pose an additional threat to the fauna and flora. As the pH value approaches 5, acid-loving mosses, fungi, and algae choke out the lake's other plants and as a result more fish species die. At pH 4.5 all the fish and most of the other aquatic organisms and insects are dead. The lake is clear and blue and nearly lifeless (Angyal, 1980).

Effect on Primary Production

Acidification brings about a simplification and reduction of the primary production and biomass of pelagic and benthic algae. The biota of an acidic lake are quantitatively and qualitatively different from those in non-acidic lakes. The numbers of aerobic heterotrophic bacteria are low whereas numbers of aciduric bacteria are high. The species composition of phytoplankton had been drastically altered by acidification with Dinophyceae (dinoflagellates) and Chrysophyceae dominating (Almer et al., 1978; Hendrey et al., 1976). This shift in community structure is also supported by the results of other research (Dickson, 1975; Yan and Stokes, 1978; and Dillon et al., 1979).

Acid precipitation may influence primary production by reducing the limiting nutrient for growth and reproduction. Two potential growth limiting compounds in softwater lakes are dissolved carbon (DIC) and dissolved inorganic phophorous (Conway and Hendrey, 1982). Algae require an abundant source of DIC to grow and reproduce in aquatic systems. However, the solubility of CO_2 decreases dramatically as H^+ concentration increases (e.g. at $pH < 5$ the solubility of CO_2 is 0.24 mg C /l but at pH 9 this value increases to 60 mg C/l) (Calloway, Likens, and Edgerton 1976).

Phosphorous by virtue of its growth limiting status may also control biomass in many acidic lakes. It may indirectly control biomass in many biogeochemical processes associated with acidification, including decomposition of organic matter, nutrient cycling, and aluminum release from soils (Yan and Stokes, 1979; Dillon et al., 1979). In the latter case aluminum that is found at elevated levels in acid lakes removes dissolved phosphorous from the water column by precipitation (Almer et al., 1978). Since watershed acidification greatly increases the amount of aluminum in water, aluminum complexing of phosphorous may actually increase (Dickson, 1980).

In water impacted by acid precipitation, major changes also occur within macrophyte communities. In acid lakes, essentially all available inorganic carbon is in the form of CO_2 or carbonic acid. Conditions are more favorable for sphagnum, an acidophile that simply outgrows the flowering plants under acidic conditions (Grahn, 1977). Sphagnum has a ion exchange capacity that results in the withdrawal of essential ions from solution thus reducing their availability to other organisms. Sphagnum actively transports Ca^{2+} from the water by exchanging two H^+ for each Ca^{2+}, therefore adding to the acidity and further reducing the buffering capacity.

The chemical factors required for growth of benthic algae are controlled by the interstitial water of the sediment. This gives benthic algae a competitive advantage over planktonic forms since their supplies of growth limiting elements (P, N, Si, N) are not strongly influenced by water column stratification. Thus these essential elements are found in the sediments at concentrations much higher than those in the overlying waters (Carignan and Kalff, 1980).

Effects of acid precipitation on zooplanktonic populations have been described a number of times during the last decade (Almer et al., 1978; Wright, Dale, Giessing, Hendrey, Henriksen, Joannessen, Muniz 1976; Kwiatkowski and Roff, 1976). The community structure of zooplankton, however, is substantially different from that of less acidic lakes. A consistent conclusion is that progressive acidification reduces the number of species comprising the zooplankton community. Species begin to disappear as the pH values falls below 6.0, but by pH 5.5 to 5.0 and below, the rate of loss is much more rapid.

Of the biotic changes associated with acidification, the decline and disappearance of fish populations have received the most attention. Fish are especially vulnerable to changes in acidity because they have several critically sensitive life stages such as spawning, egg development, fry hatch, and early development.

In the acidified lakes and streams, partial or complete loss of fish populations is well documented (Beamish and Harvey, 1972; Almer, Dickson, Ekstrom, Hornstone, and Miller 1974; Schofield, 1976). Despite such large scale loss the mechanisms that caused these reductions are only partially understood. The most common causes of extinction appear to be the failed recruitment of new age classes (Ryan and Harvey, 1980; Rosseland, Sevaldrud, Svalastog, and Muniz 1980) brought about by reduced egg and larval survival (Schofield, 1976), failed maturation (Mount, 1973) or reduced spawning success (Beamish et al., 1975). Older fishes are also lost from the fish populations (Harvey, 1980; Rosseland et al., 1980). The greatest damage appears to occur in the spring during times of spawning or hatching. This period often coincides with snowmelt that rapidly flushes H^+ from the snow pack, ions accumulated from both atmospheric deposition and soil de- composition. The result is a rapid pulse of increased acidity in waters that can cause acute stress that at times becomes intense enough to kill adult fish, apparently by upsetting the salt balance in their bodies (Oden, 1976). Schofield (1976) also indicated that the episodic input of H^+ ions during spring snowmelt caused the pH value to drop rapidly and last for only a short time. Mortality and extinction of fish and other aquatic population were observed in regions with short term acidification episodes (Hultberg, 1976; Schofield, 1976).

Beamish (1976) also reported the seasonal fluctuation of the pH value in the aquatic ecosystem. In an acidified lake, he observed that the pH value dropped in the early spring, followed by a brief winter rise, and a drop again in the summer. Therefore, the episodic input of H^+ ions during the initial part of the snowmelt period may be adequate to alter community structure and function of poorly buffered aquatic ecosystems.

According to Hall et al. (1980), increased H^+ concentration may act :

1. Directly by affecting the physiology of organisms.
2. Indirectly by increasing heavy metal concentrations that prove toxic to individuals.
3. Indirectly by reducing primary production and/or bacterial decomposition.

Sutcliffe and Carrick (1973) support the third hypothesis listed above (i.e. that a decrease in pH value indirectly diminished the food supply). Hall et al.

(1980) found, however, that an immediate reduction of invertebrates took place before any diminution of the food supply. In some species growth was reduced despite an adequate supply of preferred food items (Beamish, 1976). A physiological response to increased acidity, either directly through ion exchange mechanisms or indirectly a more plausible explanation for observed changes than diminished food supply (Moreau, Barbeau, Frenette, Saint-Onge, and Simoneau 1983).

It is important however, to consider that the elevated concentration of heavy metals occurs because of increased weathering and solubility due to acidification of soils and lakes. If this is true, it is practical to think of aquatic populations as being stressed by an association of factors of which acid is the principal stressing agent as well as controlling the concentrations of the other factors such as heavy metals and food supplies.

In summary, this chapter dealt with a qualitative and quantitative assessment of the magnitude and importance of atmospheric input of pollutants to the natural waters and its impact on lakewater quality and also on aquatic organisms. Characterization of long-term effects of acid precipitation on the lake acidification and source-effect relationships require increased attention to quantify and detail the sequence and mechanisms involved.

In an effort to seek more data, this study was undertaken to investigate certain relationships between acid precipitation and selected characteristics of lake ecosystems. The standard techniques for such investigations will be described in the next chapter.

CHAPTER II

STUDY SITE, DESIGN, METHODOLOGY

The Study Site

Kalamazoo County, approximately 1481 square kilometers in area, is in southwestern Michigan. The County is on I-94, the main motor transportation route between Chicago and Detroit, approximately midway between these two midwestern metropolises. Since being settled almost 150 years ago, the region has undergone the commonplace transition from a farm-oriented community to an urbanized and industrialized county of over 200,000 people (Heller, 1978). The surficial earth materials and landscape of Kalamazoo County are the products of recent glaciation.

There are approximately 356 ponds and lakes in Kalamazoo County. They range in size .04 hectares for several unnamed ponds to those of 800 hectares (Harrison, 1978).

The climate of the county is described as primarily continental, although it is modified by the presence of Lake Michigan to the west. Mean monthly temperatures range from -3 degrees Celsius in February to 23 degrees Celsius in July. The average annual temperature is about 10 degrees Celsius. The mean annual precipitation is about 87 centimeters (Eichenlaub, 1978). Due to the presence of Lake Michigan, precipitation is generally greater in the western upland portion of the county than elsewhere (Allen, Miller, and Wood 1973). Precipitation in Kalamazoo is usually gentle and thus has a diluting effect on surface waters (Fenner, 1981). Wind velocity, humidity, and temperature, however, are important climatic variables that vary from lake to lake as well as seasonally at any one given lake (Wetzel, 1975).

The two lakes chosen for this study are located in the western portion of Kalamazoo County, situated within the Kalamazoo River Basin (Fig. 2, p. 33). The lakes were chosen on the basis of lake morphometry and also, on the availability of previous data concerning the water chemistry of the lakes (Fenner, 1981). One of these lakes (Asylum) is a very hardwater lake with a basic pH; whereas the other lake (Bonnie Castle) has softwater with a neutral to slightly acidic pH.

Both lakes have similar wetland vegetation around their borders, with characteristic plants being wild cherry, elderberry, mulberry, aspen, grapevine, maple, and birch. Aquatic vegetation also consists of a rather typical assemblage for the lakes of this region. Chara as a submerged alga (Chlorophyta: Characeae) dominates the littoral zone in most areas, often being present in pure stands. In many regions, Chara forms a mat nearly half a meter thick. Macrophytes other than Chara were

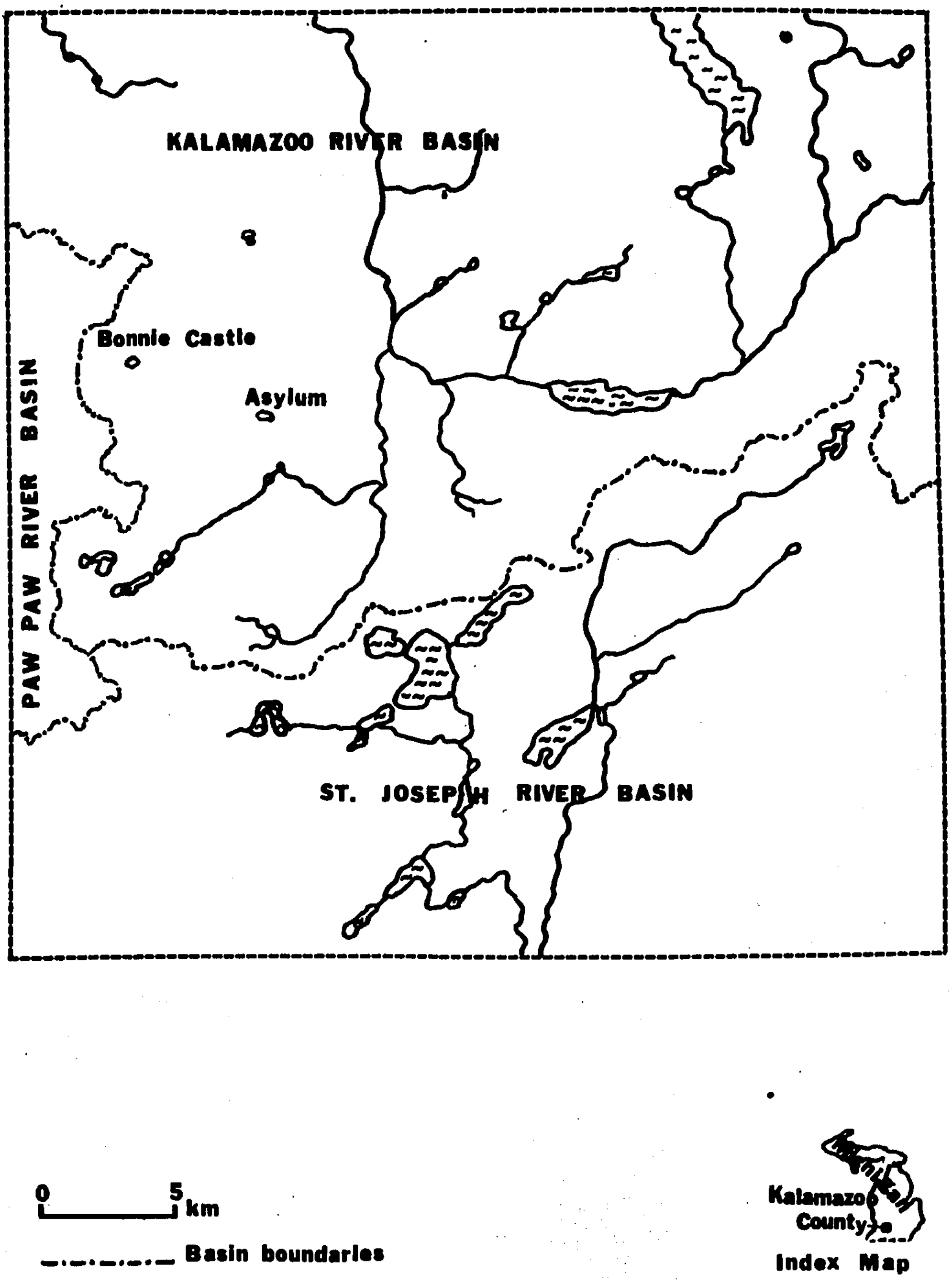

Figure 2. Location of the Study Lakes in Kalamazoo County

Potamogeton, *Anacharis*, and *Certatophyllum*. *Utricularia* was also widely distributed. Floating leaved macrophytes such as *Nuphar* and *Nymphaea* were scattered in the shallow areas of both lakes. The duckweeds, *Lemma* and *Wolffia* were abundant in the Asylum lake and are useful index organisms of hardwater habitats. *Scirpus*, as an emergent macrophyte, was common primarily in Asylum Lake from the middle of the littoral shelf to the shore where it was replaced by *Typha* as the most common emergent plant. Other emergents included *Cephalanthus* that occur marginally with *Decodon* and *Sagitarria*, *Eleocharis*, and *Nasturtium*.

Benthic invertebrates such as the fingernail clams, did occur in the sediments. *Physa*, *Helisoma*, and a few smaller snails were found associated with some vegetation or as empty shells near the shoreline. A relatively small number of leeches and a moderate number of aquatic insects were observed. Amphipods, midges, caddisflies, and a variety of hemipterans also were observed during the study period.

A typical variety of warm water fish has been reported in the lakes by local fisherman. Fishing has yielded bluegills, sunfish, largemouth bass, and perch.

Design

Maps of the lakes were obtained and the surface areas were divided into smaller areas near and away from the shore. Although there were differences in depth, the primary basis for selection was their distances from the shore. A preliminary study was done to evaluate selected physical, chemical, and biological parameters, including temperature, pH, carbon dioxide, dissolved oxygen, sulfate, sulfite, nitrate, nitrite, phosphate, and ammonia nitrogen. One shallow and one deep water sampling station were established for each lake. Based on the results of previous studies it were well known that heavy metals, like acids, find their way into rain and snow and subsequently into lakewaters. Therefore, acidic precipitation and heavy metal deposition have severely affected the aquatic ecosystems. However, the main study was designed for evaluating heavy metal concentrations in water, sediment, and aquatic vegetation. Sampling and analyses were undertaken to determine the following:

1. The extent to which the atmospheric deposition contributes heavy metals, namely, Pb, Cu, Ni, Cr, Cd, Fe, Mn, and other identified metals to the lake environment.

2. The concentration of heavy metals in wet deposition (rain or snow), lakewater, sediment, and aquatic vegetation.

3. Possible relationships between rainwater-contributed metals and metal concentrations in the lakewater sediment and aquatic vegetation.

Methodology

A preliminary study was undertaken for the evaluation of selected physical, chemical, and biological parameters. Analyses for the determination of chemical components were undertaken using the Hach Colorimeter Method Manual (1977). In addition to determining the pH values, these analyses involved quantitative determinations for dissolved oxygen, carbon dioxide, phosphate, sulfate, sulfite, nitrogen nitrate, nitrogen nitrite, nitrogen ammonia, manganese, and iron. Observations such as water and air temperature were also recorded at the study areas. As indicated earlier, the main study, as proposed was designed for evaluating the heavy metal concentrations in the wet deposition samples, lakewater samples, lake substrates, and the submerged macrophyte Chara.

A Beckman Model DB, Prism Atomic Absorption Spectrophotometer (AA) was used to make the metal determinations in the water samples. Stock solutions were prepared according to methods described in the U.S. EPA Methods for Chemical Analysis of Water and Wastes (1979). From these stock solutions, standards were prepared on the day of analysis at various concentration ranges for use in AA determinations of samples. Standards for Pb, Zn, Cr, Cd, Ni, Cu, and Fe were prepared, ranging from 1 ppm to 10 ppm in order to produce a working comparative curve in the concentration range of the samples to be analyzed.

The basic principle of atomic absorption involves aspirating the sample directly into the absorption cell-in this case by means of a Beckman burner. The metal atoms are reduced to their elemental state in the flame and are then passed through a path of light that is emitted from a lamp with a cathode of a specific metal. The atoms of metal contained in the sample will absorb a quantity of the light and the absorbance can be read on a meter.

The analysis of the reagent blank gave an indication of the amounts of heavy metals in the acid reagents and the effects of the acids on atomic absorption. The reagent blank reading of absorbance was subtracted from the sample readings. The heavy metal content of each sample was obtained from the standard curve. Total metal content in ppm was calculated for each sample.

Further information on the elements targeted for study was provided by Particle Induced X-ray Emission (PIXE). PIXE is a process of multielemental analysis of samples using the Tandem Van de Graff accelerator in the Department of Physics at Western Michigan University. The process has the advantage of analyzing for as many as 13 elements simultaneously.

The process itself, involved a production of a high energy proton beam with the Van de Graff accelerator. A

PIXE spectrum is then produced by the protons striking a sample target. When hitting the target, the protons in the beam interact with the electrons in the target atoms producing vacancies in the inner atomic shells. In the deexcitation process that follows, X-rays are emitted. These are detected by a lithium-drifted silicon (Si(Li)) detector that produces voltage pulses proportional to the energy of the incident X-rays. Since atoms of different elements have different electron configurations and binding energies, "characteristic" X-rays are produced for all detectable elements. In short, the energies of the X-rays are matched with those from the elements from which they were emitted. The X-rays emitted are thus an indication of the elemental makeup of the target. The voltage pulses from the detector are processed electronically to produce a visual pulse amplitude (energy) spectrum (Fig. 3, p.39). Since the detector plus impulse counter acts as an energy analyzer and information accumulator, the analysis is multielemental in nature. In terms of the present study, the PIXE process found and measured as many as 13 elements in most of the samples.

For background information, the spectrum produced in the PIXE process is then compared with a spectrum produced by a sample of pure silicon dioxide (for solid samples) or a spectrum that has been obtained from a piece of cellophane that has no contaminants (for water samples). A

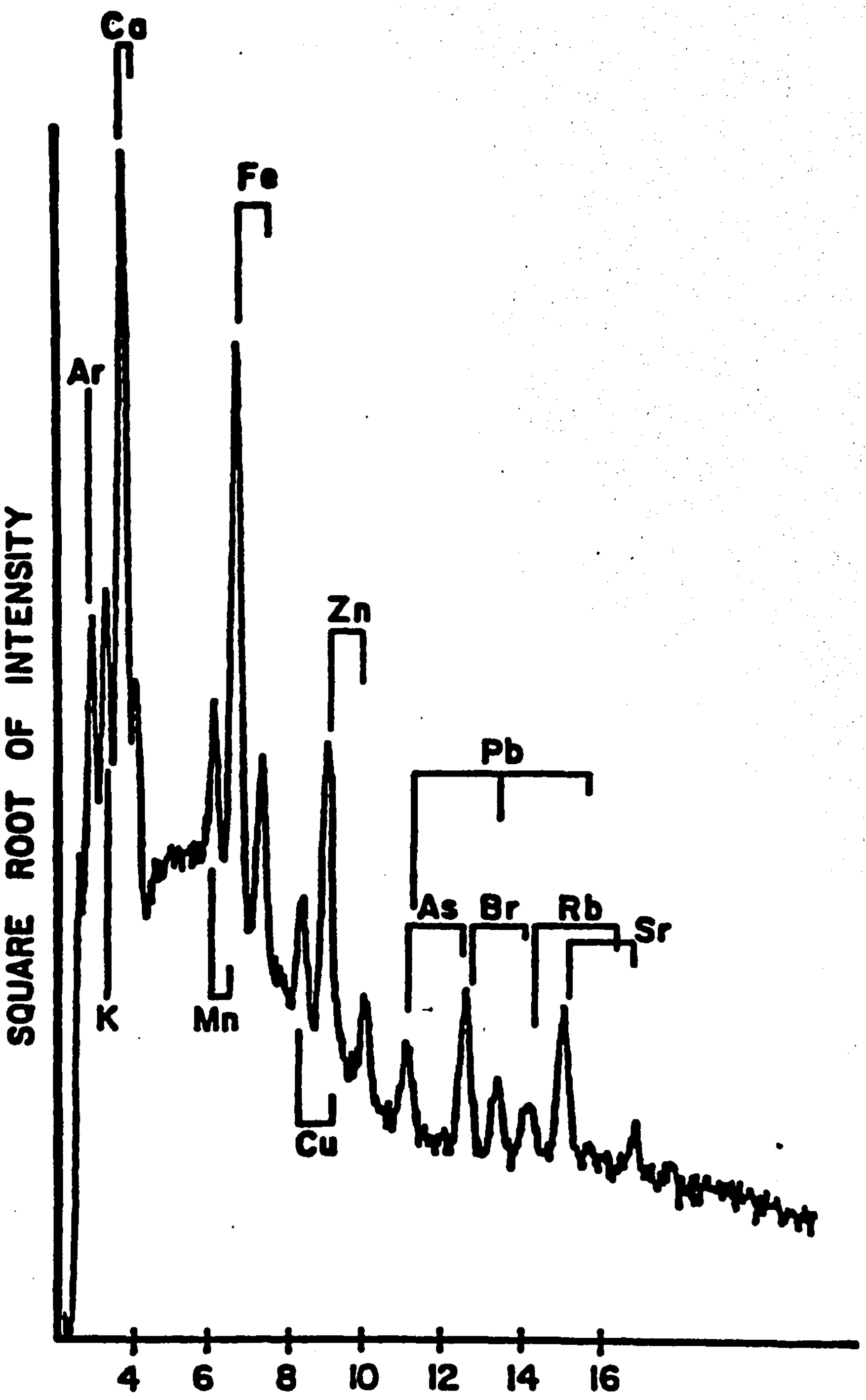

Figure 3. Typical PIXE Spectrum for Dried Sample Pellet

computer program has been prepared to subtract background values and calculate proportionate spectral areas for numerous elements. Since an area under the curve can be calculated and is proportional to the amount of the element present in the sample, the computer program prints out a quantitative value for each element whose specific X-rays are detected (for more detail see Simms and Rickey, 1978).

Sample Preparation for the Waters

Sample preparation played a particularly important role in this study since using PIXE for water quality analysis is a new process. The heart of the preparation procedure is a process termed "vapor filtration". When water samples are analyzed, it is usually the trace contaminants that are being measured, rather than the water. Vapor filtration removes the water from the sample and deposits the dissolved and suspended contaminants on a piece of cellophane that then can be used as a target.

Vapor filtration is done by pumping the water through a disk of cellophane that is permeable to water vapor but not to liquid water. Thus water evaporates only at the cellophane so that every non-volatile contaminant in the water is deposited on the cellophane. The filtration apparatus consists of two parts, a tube for holding the sample and a target support. This apparatus is resistant to HNO_3 which is necessary as all cleaning is done in an acid bath. A three-quarter inch circular disk of cellophane is placed on the target holder. This disk becomes the target for the accelerator protons once the contaminants are deposited on it. The tube is then placed on top of the target support and held in place by three spring clamps. A carefully measured amount of the sample (5 ml) is slowly poured into the tube in such a way that air bubbles do not develop. A piece of aluminum foil is placed over the top of the support to eliminate dust particles and the apparatus is opened to a vacuum.

Since the cellophane is permeable only to water vapor, any contaminants are deposited on the top of the cellophane. After approximately 48 hours, the water has been completely pumped out of the sample. The cellophane with the deposited contaminants is lifted out by attaching it to a support ring with vacuum grease placed in a specially made target holder that holds six targets at one time. The target is then ready for analysis.

The target holder is inserted manually into the chamber and the samples are bombarded one at a time. The detector then converts the energy of the X-rays into voltage pulses that are processed electronically into an energy spectrum of the sample. The initial analysis is done by a PDP-15 computer located in the accelerator facility. For more detailed analysis, the spectra were stored on tapes holding 20 spectra each and processed by the University's PDP-10 computer.

Preparation of Dried Sample Pellet

The sediment and macrophyte (Chara) samples used in this process must be homogeneous and dry in order to make a target pellet. The beam hits a three-eighth inch section on the pellet. The area on the pellet then gives off the X-rays and produces the X-ray spectrum. If the material is properly prepared, an average composition can be estimated by the process. For this reason, all samples were thoroughly ground with an acid-washed mortar and pestle before the pelletizing procedure. The pellet-making process used a hydraulic press to produce compacted pellets of approximately one-half inch in diameter. These pellets were then mounted in the target beam path. The mounting device is constructed in such a way that six pellets can be held at one time. A PIXE spectrum is obtained for each target pellet and the result calculated in parts per billion using the WMU PDP-10 computer system. An initial PIXE run was performed using National Bureau of Standards orchard leaves for comparision (Table 1, p.43)

Wet Precipitation Sampling

Wet deposition (rain and snow) was collected on an event basis from September 1983 through July 1984. The

Table 1

A Comparison of PIXE and NBS Orchard Leaf Values

	PIXE	NBS
K	16235.5	14700
Ca	24133	20900
Mn	84.5	91
Fe	469.5	300
Cu	11.5	11
Zn	32.5	25
Pb	48	45
As	9	10
Rb	14.5	12
Sr	41	37

event precipitation sampler was located on private land approximately five kilometers from each study area. Care was taken to ensure that the selected site was relatively close to the study area and would represent a background data base for the region. Rain and snow were collected in an uncapped, acid-washed plastic bucket that had been rinsed with deionized water. The collector was set up immediately at the beginning of each precipitation event. Care was taken to exclude any dirt or debris from the study site. The snow samples were melted and treated in the same manner as were the rain samples. The samples collected were drawn through a 45 u filter and stored in acid-washed 125 ml polyethylene bottles at 4° Celsius.

The pH and the chemical components, namely nitrate, nitrite, sulfate, sulfite, phosphate, ammonia nitrogen, iron, and manganese were measured immediately after each precipitation event according to the procedures described in the Hach Colorimeter Methods Manual (1977). Samples were then preserved in a freezer to await further analyses for metal ion concentrations. Analyses for Fe, Cr, Cd, Mn, Cu, PB, and Ni were made by using direct aspiration. All analytical methods used are described in the EPA (1979) manual. All samples were then subjected to PIXE analysis that showed the various concentrations of thirteen elements.

Lake Water Samples

Lake water sampling area included (I) an area near shore, under which the water was approximately .25 m deep; and (II) an area away from shore, in the middle of the lake, under which the water was approximately 1 m deep.

The samples were collected from September 1983 until July 1984 whenever a precipitation event occurred. The collection of lakewater samples before heavy snow and ice covered the lakes and also after the snow melted was on a weekly basis. During the winter period of ice cover, the lakewater was collected on a biweekly basis by breaking the ice.

Water temperature, air temperature, carbon dioxide, and dissolved oxygen were determined in the field. For further analyses, the lake water samples were treated in the same manner as the precipitation samples.

Aquatic Vegetation and Sediment Sampling

Plant sampling involved the benthic alga *Chara* (Chlorophyta: Characeae), a submergent aquatic plant found in dense growth clusters beneath the surface of the water. The common name "stoneworth" was suggested by the fact that many species of this genus become encrusted with calcium carbonate. It is one of the few genera of plants that is without roots. *Chara* dominated the littoral zone in most regions, often occurring in pure stands.

An aquatic net was used for collecting the plant samples. Surficial sediments (0-5 cm.) were collected with the same net and from the stations corresponding with regions of plant collection. Samples of the plants and sediment were collected during the entire period of the study (October 1983-July 1984), except during those winter months when the lakes were covered with heavy ice and snow.

Samples were then placed in sealable polyethylene bags. After drying them for 48 hours at 100 degrees Celsius, approximately 10 grams of each sample were homogenized, using an acid-washed mullite mortar and pestle. The resulting powders were stored in 10 gram glass sample bottles. Two grams of the homogenized sample powder were subjected to 5000 PSI in the pelletizing hydraulic press. The pellets were then analyzed by the PIXE process.

In summary, two lakes located in Kalamazoo County were chosen for this study. A precipitation sample was also taken at a site close to both lakes. Using a Hach Colorimeter, a preliminary study was undertaken in order to evaluate of the chemical composition of lakewater and rainwater samples. The main study however, dealt with the metal concentration in the rainwater, lakewaters, and aquatic vegetation. The data for the main study were provided by AA and PIXE procedures.

For the water quality analysis by PIXE, the "vapor filtration" procedure was used to prepare the lakewater and rainwater samples. The sediment and macrophyte (Chara) samples used in the PIXE process were dried in order to make a target pellet. All samples were then analyzed by the PIXE process.

CHAPTER III

RESULTS AND DISCUSSION

The results presented here are based on the preliminary study that extended from October 1983 through July 1984. This study dealt mainly with the chemical compositions of lakewaters and rainwater samples. However, the emphasis of the main study that was undertaken during the same period, dealt with the metal concentrations of the samples.

The monthly mean concentrations of the major chemical species are listed in Table 2 (p. 48) (see Appendices A, B, and C for the weekly values of chemical parameters in precipitation, Bonnie Castle Lake, and Asylum Lake, respectively). An examination of the raw data indicated that there was a wide range of concentrations for the parameters measured. Meteorlogical data such as wind direction, type of event, duration of event, and the intensity of the precipitation are some of the factors that affect the concentration of substances in precipitation and subsequently the chemistry of lakewaters (Eisenreich et al., 1981).

Precipitation Chemistry

All the ions that might contribute to the acidity of

Table 2

Chemical Parameters Measured in Preliminary Study of Precipitation, Bonnie Castle, and Asylum Lakes From October 1983 Through July 1984

Parameter (ppm)	Sample[a]	Oct. 83	Nov. 83	Dec. 83	Jan. 84	Feb. 84	Mar. 84	Apr. 84	May 84	June 84	July 84
Nitrate	I	1.43	1.24	1.49	2.60	1.75	1.56	1.52	1.18	1.05	1.20
	II	.93	.68	.55	.65	1.0	.43	.55	.53	.51	.80
	III	.69	.49	.65	1.45	.55	.49	.40	.50	.52	.60
Nitrite	I	.012	.011	.019	.015	.018	.010	.015	.009	.008	.008
	II	.010	.009	.015	.009	.007	.004	.003	.004	.003	.008
	III	.009	.012	.018	.021	.005	.011	.009	.007	.005	.002
Ortho-Phosphate	I	.188	.244	.153	.085	.163	.185	.269	.240	.225	.190
	II	.093	.105	.040	.090	.040	.070	.053	.085	.053	.020
	III	.076	.075	.210	.195	.095	.125	.030	.120	.130	.060
Sulfate	I	5.10	2.08	3.75	3.50	4.75	4.50	3.24	3.40	2.25	2.00
	II	3.83	2.45	3.50	2.00	2.50	4.75	.75	1.00	0.0	.20
	III	15.5	14.1	17.5	18.5	11.0	12.0	13.0	11.5	12.5	12.0
Sulfide	I	.011	.010	.001	.010	.014	.012	.010	.015	.001	.005
	II	.005	.002	.005	.006	.010	.015	.008	.002	.008	.020
	III	.008	.003	.001	.007	.020	.013	.010	.013	.015	.010
Ammonia Nitrogen	I	1.12	.84	.73	1.95	1.29	.84	1.16	.93	1.12	1.50
	II	.220	.18	.19	.20	.32	.17	.24	.14	.26	.25
	III	.243	.32	.70	.35	.62	.23	.17	.16	.12	.19
Iron	I	.076	.041	.068	.083	.210	.085	.073	.044	.060	.080
	II	.043	.037	.100	.050	.065	.290	.093	.090	.068	.050
	III	.040	.033	.010	.011	.040	.140	.100	.108	.048	.015
Manganese	I	.03	.032	.04	.11	.10	.07	.05	.067	.050	.06
	II	.08	.120	.10	.132	.09	.003	.010	.030	.100	.08
	III	.15	.170	.16	.200	.08	.020	.075	.100	.058	.10
Carbon Dioxide	I	--	--	--	--	--	--	--	--	--	--
	II	11.9	11.3	9.0	10.0	7.25	6.25	7.00	8.50	10.9	12.5
	III	24.3	23.5	21.0	23.5	20.0	14.0	14.0	15.0	16.3	17.0
Dissolved Oxygen	I	--	--	--	--	--	--	--	--	--	--
	II	9.94	13.1	15.0	13.4	11.6	14.1	13.0	9.00	9.06	7.75
	III	11.4	11.4	13.3	11.5	12.3	15.0	14.3	13.8	10.9	11.0

[a] I Precipitation
II Bonnie Castle Lake
III Asylum Lake

the precipitation sample must be identified in order to evaluate fully the chemistry of the sample. Thus to understand any changes in the acidity of precipitation caused by changes in the concentration among ions in the precipitation, the seven ions of most importance (hydrogen, ammonium, nitrate, sulfate, calcium, and phosphate) were measured. The chemical composition of precipitation was studied at a site close to both lakes. The pH and relative hydrogen ion concentration of precipitation, collected during the sampling period (October 1983 through July 1984), are reported in Table 3 (p. 50). Precipitation samples from forty rain and snow incidents were collected. Highly acidic events (pH < 4.5) occurred several times during the study period. The most acidic of these (pH = 3.9) occurred on a stormy day in May. The major variation in pH values of precipitation ranged from 3.90 to 5.82, with an event average of pH 4.67. The average pH refers to the average hydrogen ion concentration converted to pH. In most of the precipitation events, episodes of acid rain at pH 5.6 or less were observed. As shown in Figure 4 (p. 51), 29 of a total of 40 precipitation events had a pH value below 5.5. The remainder of the events were only small amounts of rain or snow. The washout of alkaline soil dust appears to be related only minimally to the pH of the light precipitations (Dash, Cadle, and Wolff 1984). Likens and Butler (1981) have also reported that the

Table 3

pH and its Related Hydrogen Ion Concentration in Precipitation

Date		pH	$[H^+] \times 10^{-7}$
October	8	5.72	1.91
	12	5.65	2.24
	13	5.71	1.95
	22	4.35	4.47
	23	5.6	2.5
November	2	4.8	50.1
	11	4.4	39.8
	15	4.5	31.6
	19	5.8	1.59
	27	5.81	1.55
	28	5.82	1.51
December	2	5.72	1.91
	6	5.45	3.55
	8	5.4	3.98
	30	5.8	1.59
January	18	5.2	6.31
	19	4.4	39.8
Febuary	7	4.4	39.8
	9	5.1	7.94
	18	4.3	50.1
	27	5.6	2.5
March	6	5.3	5.01
	12	5.82	1.51
	16	4.52	30.2
	21	4.2	63.1
April	3	4.1	79.4
	4	5.3	5.01
	12	5.3	5.01
	14	4.6	25.1
	17	4.25	26.2
	19	4.0	100.0
	22	4.45	35.5
May	18	5.0	10.0
	19	5.4	3.98
	22	4.8	15.8
	25	4.0	100.0
	28	3.9	26.0
June	5	4.9	12.6
	23	5.1	7.94
July	9	5.2	6.31

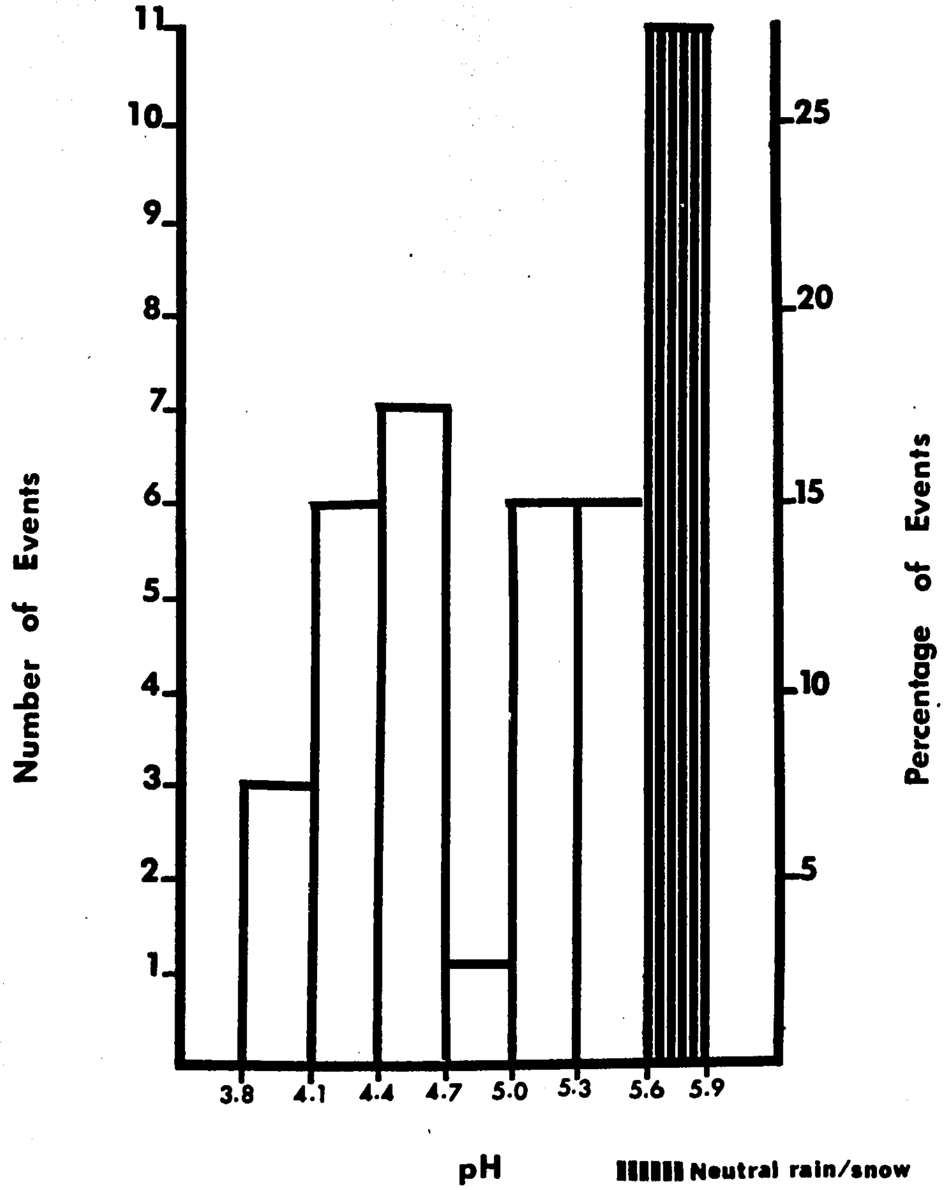

Figure 4. Frequency an pH of Precipitation

rainwater pH value in Michigan is much higher than the levels in northeastern states such as New York. According to the investigators, any effect from acid deposition in Michigan are somewhat ameliorated by the limestone-based soil that covers most of the state. The lower acidity exists, mainly because of neutralization with Ca^{2+} that is four times greater in Michigan's rains than in other states. As expected for soil-related species, Ca^{2+} is found mainly in large particles. In contrast species that originally caused the acidity (sulfate and nitrate ion) are in small particles. Also, as expected, the deposition velocities decreased with decreasing particle size. Therefore in rains of low intensity Ca^{2+} exhibited a higher deposition rate.

A comparison of the parameter of Ca^{2+} concentration with pH values for precipitation during the study period, indicated a similar phenomenon for these parameters. Thus it appears that the results of this study are consistent with those from the analysis of Likens and Butler (1981).

Precipitation chemistry is also influenced by the patterns of chemicals (S and N species) released to the atmosphere. the role of nitrogen pollutants appears particularly significant. Although sulfuric acid has been by far the dominant acid in rainfall in Michigan, (Dash et al., 1984) the increased deposition of hydrogen ion has been caused primarily by increased amounts of nitric acid in precipitation.

Figures 5, 6, and 7 (pp. 54-56) shows the concentrations of hydrogen, sulfate, nitrate, and ammonium ions in the precipitation. The acid-forming anions here are sulfate and nitrate. According to Figure 6 (p. 55) , the values for sulfate and nitrate ion are closely related as evidenced by a correlation coefficient of .81 between the two. This could indicate that they came from the same regional sources or that meteorological conditions caused them to rise and fall together. The concentration of hydrogen ions was also closely related to sulfate and nitrate concentrations.

Based on the data in Figure 6 (p. 55), it was estimated that sulfuric acid contributed more to the total deposition of acidity during this study period than did nitric acid. As shown in Figsures 5 and 6 (pp. 54-55), the peak acidity occurred primarily during periods of higher sulfate concentrations. However, since the concentration of nitrate and sulfate are closely related, it is difficult to determine the species that originally caused the acidity.

The pH gradient cannot be explained only by the sulfate and nitrate concentrations. Other contributory factors must also be considered. According to Eisenreich et al., (1981) the pH differences that parallel the patterns observed for those elements are believed to be caused by the suspension of crustal material, specifically Mn, and

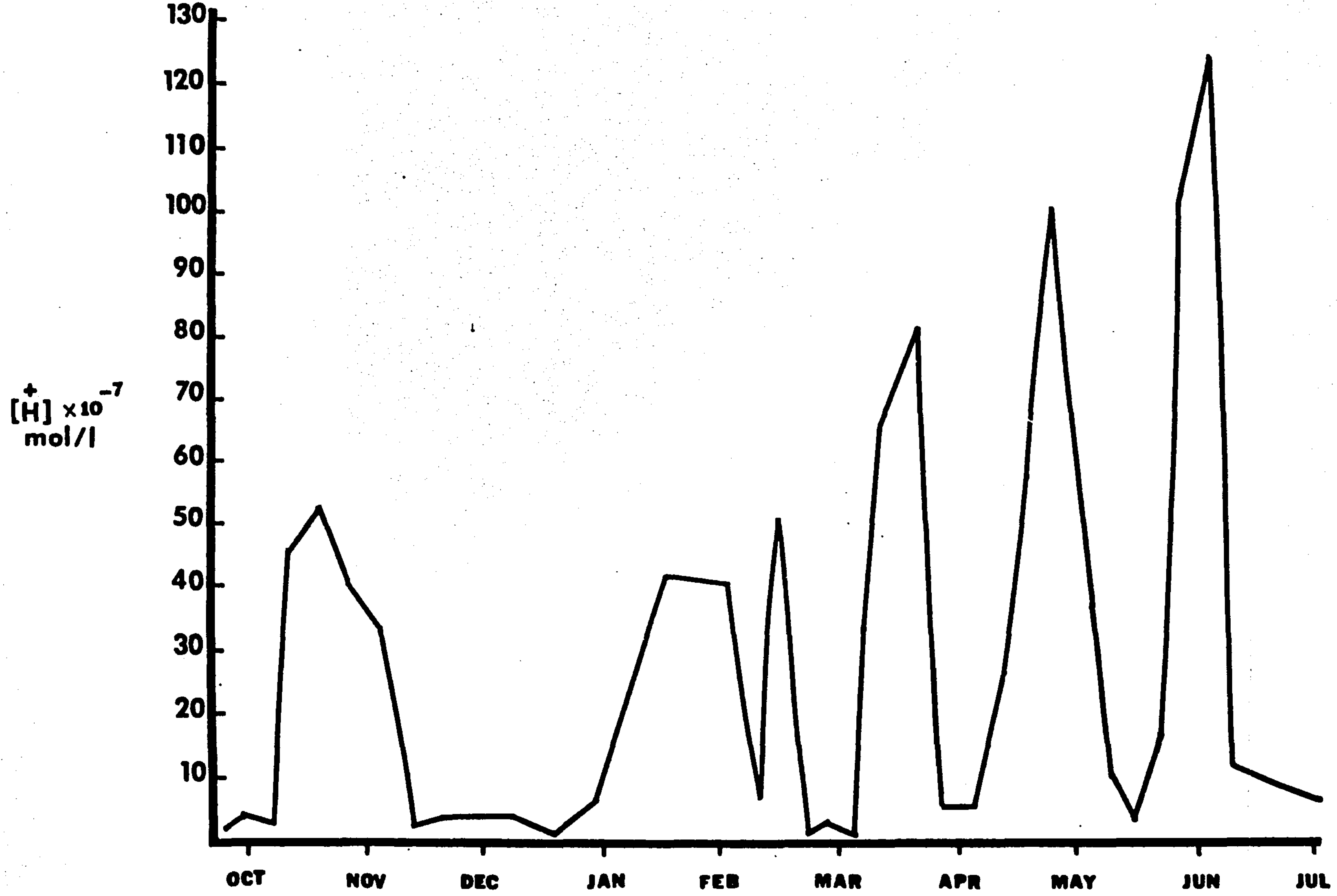

Figure 5. Hydrogen Ion Concentration in Precipitation From October 1983 Through July 1984.

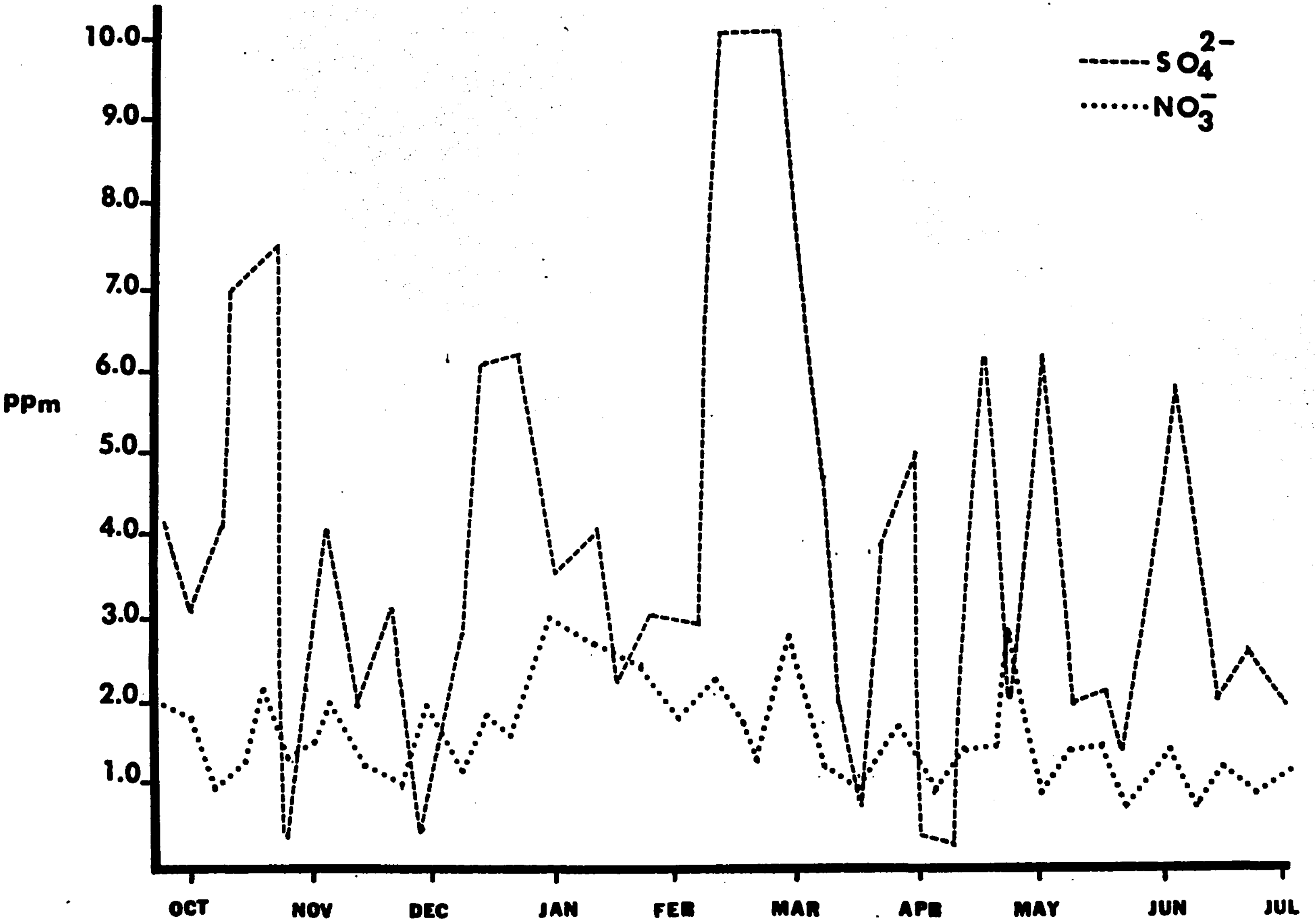

Figure 6. Sulfate and Nitrate Concentrations in Precipitation From October 1983 Through July 1984.

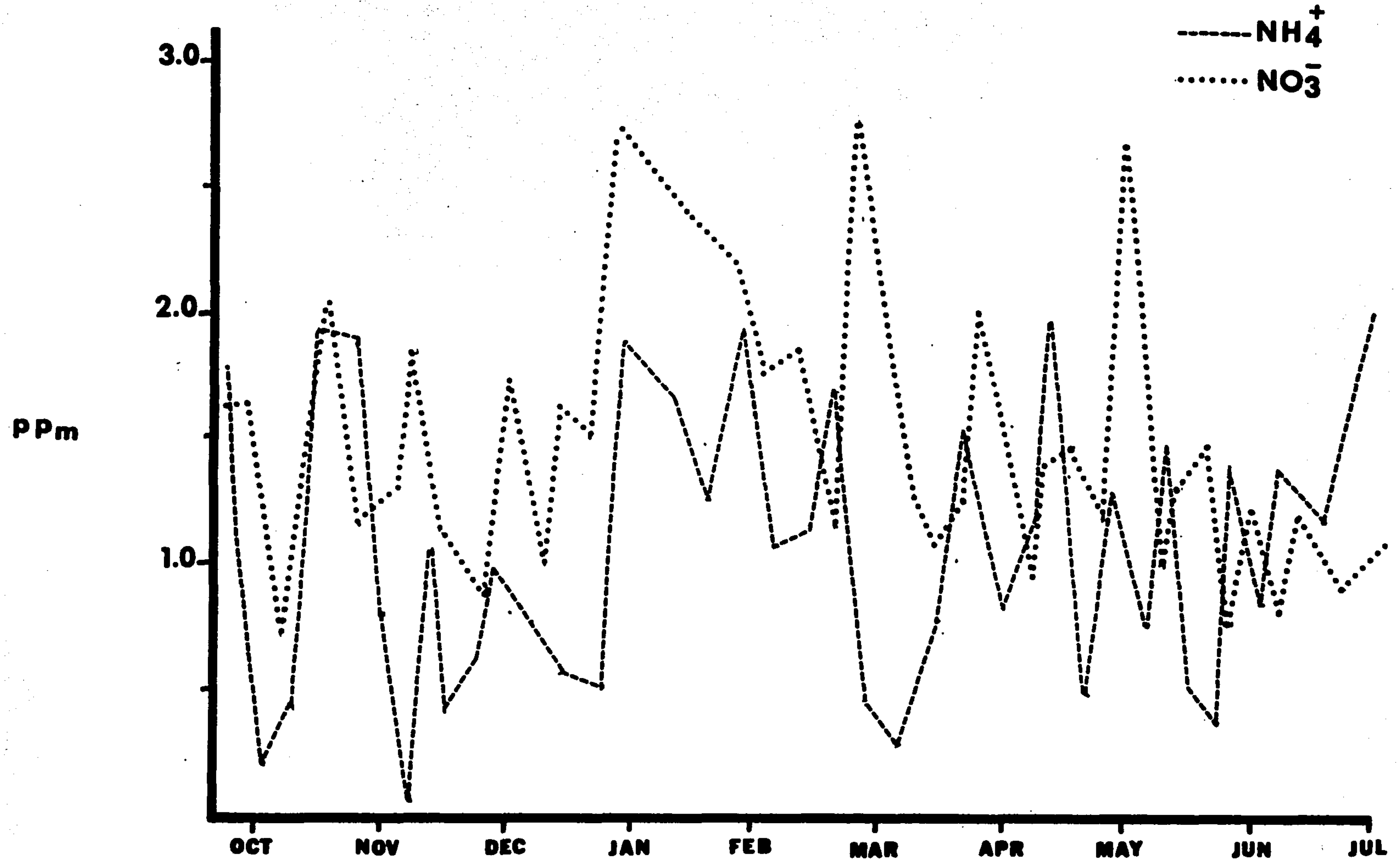

Figure 7. Ammonia Nitrogen and Nitrate Concentrations in Precipitation From October 1983 Through July 1984.

to some extent nitrate and ammonium ion.

The concentration of important nutrients, especially ammonia and nitrates in precipitation, have received much attention from scientists. Ammonia is considered to be derived mainly from biological activity in soil and water; whereas nitrate (and sulfate) are regarded as caused by both natural and human activities.

The manner in which the forms of nitrogen are distributed between wet and dry precipitation is an important consideration. Deposition of nitrate and ammonium ion by wet only input averaged 68% and 81% respectively of the total deposition (Junge, 1958). Thus for these two substances, wet precipitation was the main deposition mechanism. Atmospheric precursers of ammonium and nitrate in rainwater are gases (ammonia and nitrogen oxides) and secondary aerosol particulates formed by gaseous reactions such as ammonium nitrate, and ammonium hydrogen sulfate. These aerosols are small (> 1 mu) and thus do not settle from the atmosphere as dry precipitation. They are hygroscopic and consequently serve as condensation nuclei for raindrop formation (Junge, 1958). Figure 7, p. 56, shows that nitrate and ammonium ions exhibited seasonal patterns for precipitation similar to one another. As shown in Figure 7, concentrations of both nitrate and ammonium ion are greater in winter and lower in spring than in other seasons. Highest concentrations of both nitrogen' compounds in winter are associated with heavy rain and snow and also with a more efficient washout of substances (Hendry and Brezonik, 1980). These may also be related to the physical differences between rain and snow and their relative abilities to scavenge components from the atmosphere (Peterson, 1983). An increase in concentrations of nitrate and ammonium ions observed in summer may reflect increased biogenic emission of gaseous nitrogen compounds caused by higher summer soil temperatures and also by milder rain events than during other seasons (Hendry and Brezonik, 1980). The higher values likely reflect atmospheric buildup of contaminants during these dry periods. Since ammonia is the primary alkaline gas in the atmosphere, it is considered to be a source of neutralization for hydrogen ions in precipitation (Dash et al., 1984).

As shown in Figs. 5 (p. 54) and 7 (p. 56), the seasonal trend in pH of precipitation is similar to that of ammonium ion concentration. The peak of acidity in precipitation occurred most often during the period of low ammonium ion concentration. Therefore, ammonia could be at least partly responsible for the reduction in precipitation acidity during October, November, December, June, and July.

In so far as nutrients occur in rainfall, it is well known that precipitation is also an important source of phosphorus (Dillon et al., 1980). However, dry fall input of phosphorus, that accounts for 80% of total deposition, is more important than wet precipitation. Only 15% of organic phosphorus is deposited via rainfall. Since compounds of phosphorus are usually nonvolatile, the cycle of phosphorus generally is limited to rock-soil-water phases. Atmospheric deposition of phosphorus therefore occurs primarily by gravitational settling of particles that enter the atmosphere as a result of various phenomena associated with agriculture, mining, and fires (Dillon et al., 1980).

Potential Alteration of Lake Waters

In addition to the parameters already mentioned as being dealt with in the preliminary survey, the survey also provided an initial understanding of the relationship between acid precipitation and lakewater composition as a function of existing ions and nutrient deposition. Measurements concerning these conditions were made at both lakes during the entire period of the study beginning October 1983 and extending through July 1984. The data suggested that if the rate of acid precipitation changes, a variety of constituents in both lakes will respond (e.g., SO_4^{2-}, base cation [BCs], and alkalinity). However, by comparing the chemistry of Bonnie Castle Lake with its low alkalinity with the chemistry of Asylum Lake with its high alkalinity from a similar geological area, it may be posible to gain some insight into the changes that have occurred.

Geological Influences

The ability of lakewater to resist a reduction in pH when acid is added, depends on its alkalinity or buffering capacity. Although the rainfall in Michigan is nearly as acid as rainfall on the rest of eastern North America, the lakes here are not so acid as might be expected. The difference is the vast buffering system (Leupold, 1985). As mentioned previously, most of the state of Michigan is covered with limestone-based soil containing minerals that are easily dissolved and enter the aquatic system as buffers (Liken and Butler, 1981). Buffers in these lakes can neutralize acids that enter them so that the pH shows little or no change. Oliver and Kelso (1983) reported that the acid-neutralizing or buffering capacities of natural waters are considered to depend on the carbonate-bicarbonate buffer system. Henriksen (1982) also suggested that since the alkalinity of water is derived essentially from the weathering of carbonate materials, the calcium and magnesium content should balance the bicarbonate component in systems unaffected by acid precipitation. In general, the classic view of acidification and geochemical weathering of the ecosystem focuses on the role of carbonic acid (H_2CO_3) in rain and groundwater. Carbon dioxide dissolves in water to produce a slightly acidic solution, that in turn, dissolves the minerals of the earth's crust, including Ca, Mg, Mn (likens, 1976).

Galloway, Norton, and Church (1983) indicated that the the acidification of freshwaters is the result of a series of complex, interrelated processes. The series begins with the increased emissions of sulfur to the atmosphere. This is followed by "instantly" increased deposition in the terrestrial ecosystem and increased concentration of sulfate in the aquatic system that also must result in decreased alkalinity and increased base cation [BCs] (Ca^{2+}, K^+, Mg^+, Na^+) concentrations or a combination of both. An initial increase in sulfate concentration may result in proportionally large increases in [BCs] concentrations. This continues for some time until the easily weathered or exchangeable reservoirs of [BCs] in the soils associated with the hydrologic pathways through the terrestrial system are depleted with the base saturation approching zero. Then, the concentration of hydrogen ions increases more rapidly with a concurrent decrease in the alkalinity.

Although some reports assume that [BCs] do not change in surface waters during acidification (Almer et al., 1974), others assume that they do (Henriksen, 1982; Dillon et al., 1980). The magnitude of the changes in [BCs], however, depends on the characteristics of the aquatic system and on the residence time of the sulfate in the system. Therefore, before further discussion, it is appropriate to describe the general characteristics of each lake.

General Lake Characteristics

Information on the relationship of the hydrologic settings of lakes and water chemistry is important. In a study by Fenner (1981), the interrelationship of atmospheric, surface, and groundwater with certain aspects of lakewater quality in Kalamazoo County were analyzed. According to Fenner, the important hydrologic parameters that control lakewater chemistry are (a) lake size; (b) presence or absence of streamflow or outlets; (c) elevation of the lake with respect to the groundwater elevation; (d) groundwater quality; and finally; (e) position of the lake in the regional groundwater flow system. Other factors that may affect the chemistry of lakewater are ion exchange with bottom sediments, effect of vegetation due to the aereal capture of salts, and the decomposition of vegetation (Gorham, 1961).

The hydrologic conditions at each lake were identified with the use of existing information (Fenner, 1981), in order to determine the extent of the relationship between the hydrologic variables and the alkalinity and hardness of the lakes (Table 4, p. 63).

Carbonate hardness is the concentration of calcium and magnesium ions dissolved in water (mg/l of $CaCO_3$). It was thought that the hardness might indicate the primary

Table 4

Hydrologigal Data for Asylum and Bonnie Castle Lakes[1]

	Asylum	Bonnie Castle
Size (hectares)	13.3	17.8
Hardness (mg/l)	224.0	56.0
Interchange		
inlet	no	no
outlet	yes	no
Elevation of lake	263 m	278 m
Groundwater elevation	263.6 m	274.3 m
Difference between lake and groundwater levels[2]	-.6 m	+3.7 m
Glacial Landform	Alluvium	Moraine

1. Data from Fenner, 1981
2. (+) above, (-) below

source of the lakewater because of the relatively large difference in the concentration of this parameter in the rainwater (6.4 mg/l) and groundwater (160-560 mg/l) (Allen et al., 1972). However, the primary factors believed to control lakewater hardness are described as follows:

1. Atmospheric--Two important variables related to the atmospheric interchange with a lake are precipitation and evapotranspiration. The size and shape of the lake basin are also significant variables (Gorham, 1961). Lakes with relatively large surface-to-volume ratios

generally have large evaporative losses. Therefore, the depth and surface area of a lake represent precipitation/evapotranspiration balance and are related to the atmospheric interchange with the lake. According to Fenner (1981) precipitation in Kalamazoo County is very soft (hardness = 6.4 mg/l) and thus precipitation has a diluting effect on surface water. This factor can be responsible for lower concentrations of calcium in both lakewaters. When the amounts of precipitation were higher during March - June 1984 (Fig. 8, p. 65), the mean concentration of calcium during the period of study was lower for Bonnie Castle Lake (118.6 mg/l) than for Asylum Lake (458.1 mg/l). Since Bonnie Castle Lake has a larger area it will receive more rainwater and is probably more affected by precipitation than is Asylum Lake.

Numerous factors, control the precipitation/evapotranspiration balance of an individual lake and the effects on its water chemistry. Climatic variables are one of the examples of such factors that vary from lake to lake as well as seasonally at a given lake (Wetzel, 1975).

2. Surface water--whether water flows as superficial runoff or as groundwater may exert a profound effect on lakewater chemistry. In general, lakes are classified as open or closed systems. Drainage lakes, such as those that are dominated by surface water input, have been defined as lakes with at least one inlet. Seepage lakes

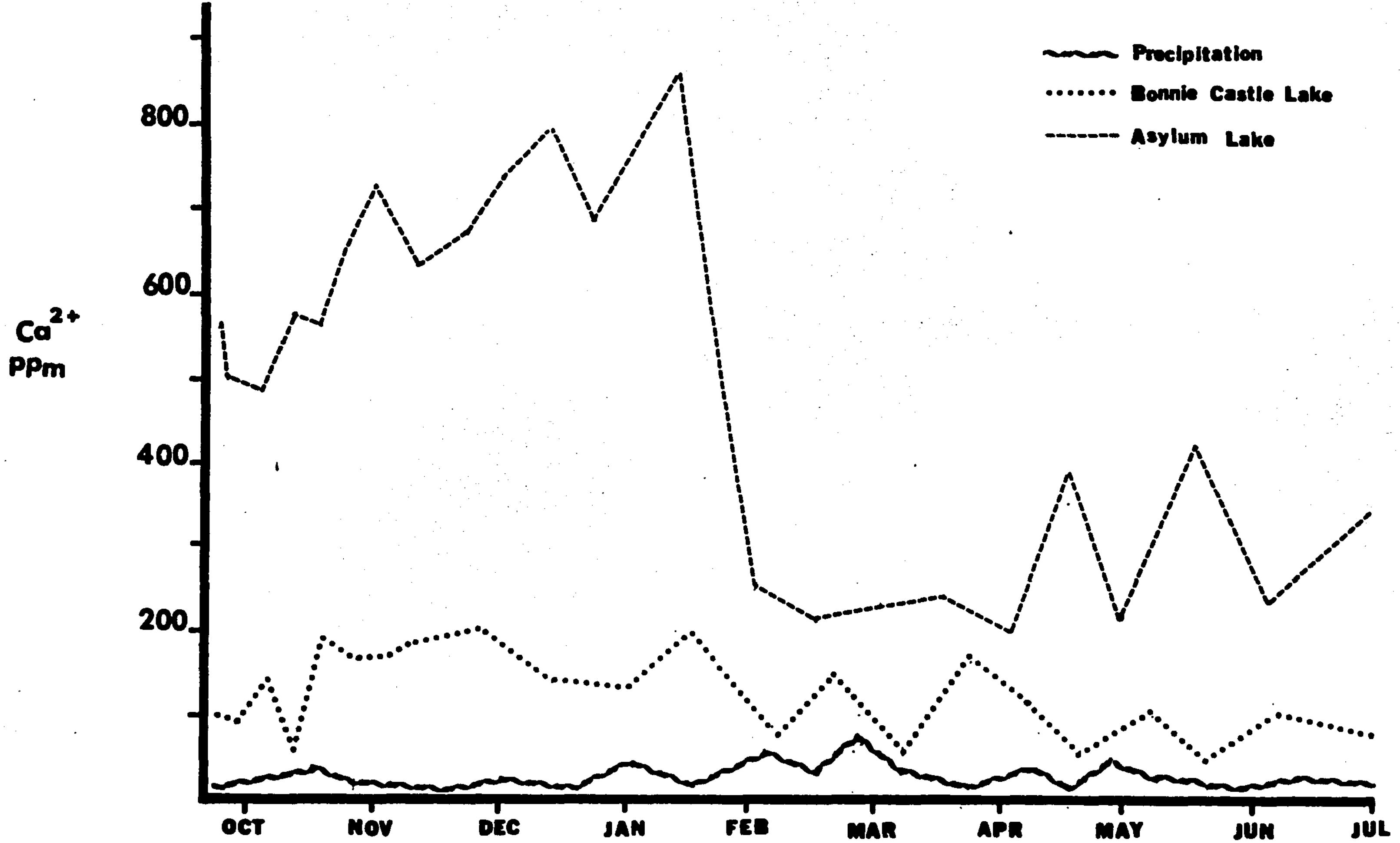

Figure 8. Calcium Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

are those with either an inlet or outlet, or neither (Born and Stephenson 1979). According to Table 4 (p. 63), both Bonnie Fenner (1981) reported that seepage lakes range from very soft (hardness < 60 mg/l) to very hard (hardness > 180 mg/l). Most seepage lake are presumably dominated by groundwater input (Born et al., 1979). The relatively high hardness concentration in Asylum Lake (224 mg/l) may be caused by the hardness concentration from the groundwater as well as the dominance of evapotranspiration or the lack of flushing of lakewater. Results of research in Asylum Lake were related to the recharge location of the groundwater inflow, support such a conclusion.

In a soft water seepage lake such as Bonnie Castle (hardness = 56 mg/l), that is not dominated by groundwater, precipitation and non-channelized runoff may be responsible for nearly all the water input (Fenner, 1981). Therefore, the diluting effect of precipitation coupled with the absence of any contribution from hardwater sources such as groundwater, may be important in the water chemistry of Bonnie Castle Lake.

On the contrary, Asylum Lake does not receive a substantial portion of its total input as direct precipitation. Groundwater can constitute a significant fraction of the water budget of Asylum Lake.

3. Groundwater--one of the factors that controls the nature and degree of communication between a lake and the

groundwater is the position of the lake in the groundwater flow system (Born et al., 1979). It was not feasible, in the present study, to analyze all the factors believed to control every aspect of groundwater interchange with a lake. So the factors considered include the groundwater elevation relative to the lake elevation and the position of the lake in the regional groundwater flow system. The difference between lakes and groundwater (Table 4, p. 63). Fenner (1981) reported that lakes in which the surface is at least two meters above the estimated groundwater elevation, are soft to moderately soft (hardness < 120 mg/l). These lakes are presumably recharged lakes that contribute to the groundwater system through the entire lake bottom. In contrast, lakes in which the elevation is at least .5 meters beneath the approximate groundwater table are all hard (hardness > 180 mg/l). Fenner indicated that these hardwater lakes can be discharge lakes by receiving groundwater through the entire lake bottom and their high hardness concentrationare caused by groundwater input.

It appears from the results of the Fenner's study, and the data presented in Table 4 (p. 63) that Bonnie Castle Lake falls into the former category, since the difference between lake and ground water elevation equals +3.7, and hardness equals 56 mg/l. Therefore it could be a recharge lake. However, Asylum Lake fits in the latter category since the difference between elevation of the lake and groundwater was -.60 m and the hardness was 224 mg/l. Therefore it appears to be a discharge lake.

According to Born et al. (1979), spring runoff can raise lake levels before there is an appreciable rise in the water table level and can result in a groundwater recharge. This causes a reduction in hardness and consequently the concentrations of calcium and potassium decrease. This principle may be related to the sharp decrease in cation concentrations of both calcium and potassium, specifically in Asylum Lake. That lake has been affected mainly by groundwater quality (Figs. 8 and 9, pp. 65,69). During summer and fall, evapotranspiration can lower lake levels relative to the water table and result in a transition to a discharge condition (Born et al., 1979). This can contribute to the hardness of water and consequently higher concentrations of calcium and potassium in the lakewater during the months of July, October, and November (Figs. 8 and 9, pp.65,69).

Lake Chemistry

The preceding discussion involved the factors of groundwater input and quality that are believed to control lakewater qualities. In order, to examine the relationship between lake pH and atmospheric loading of acidic pollutants, the concentrations of major ion components of

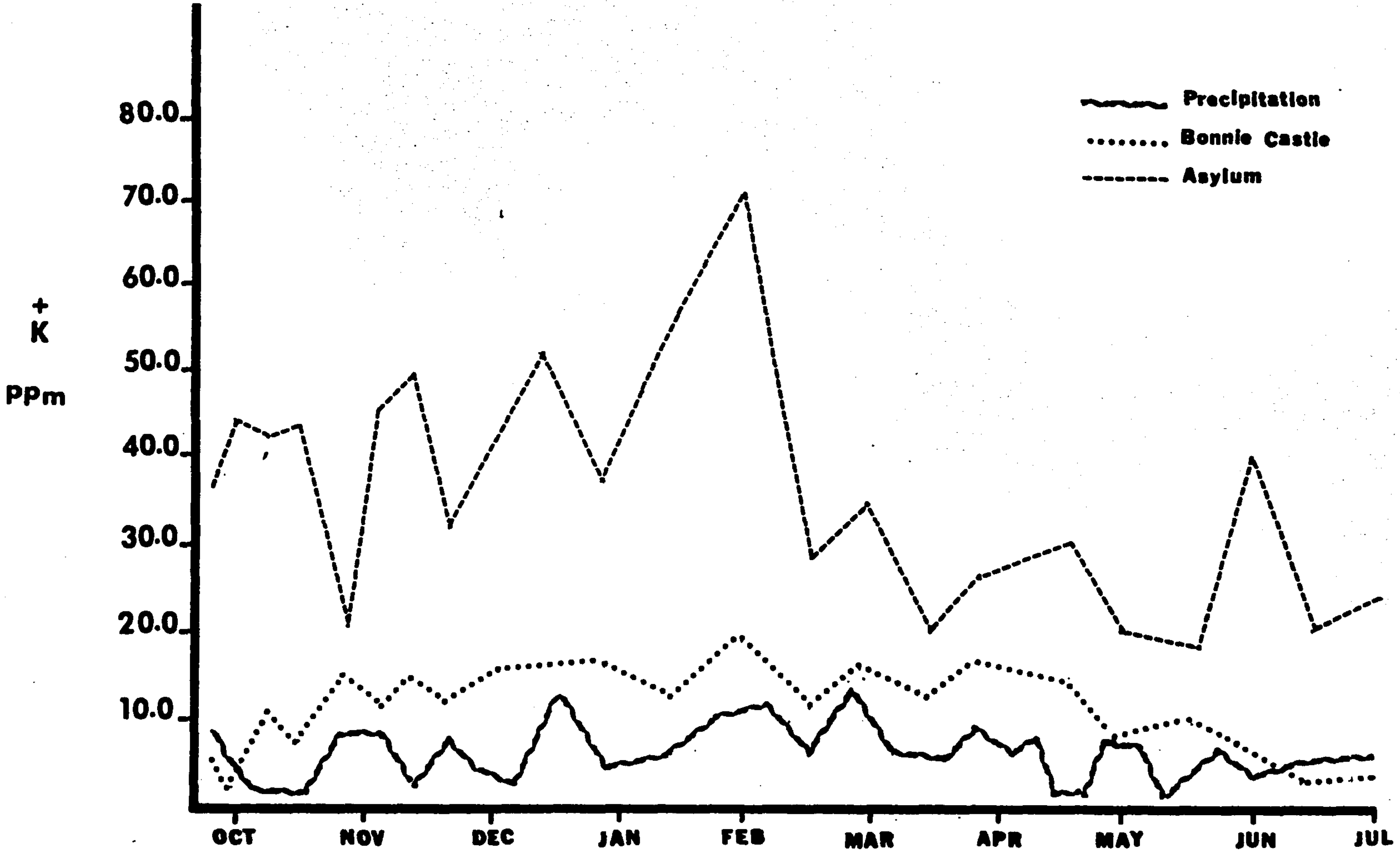

Figure 9. Potassium Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

each lake were also determined and the results are presented in Table 5 (p. 71). Figure 10 (p. 72) compares monthly variations in precipitation pH and lakewater pH. The results indicated that the pH of Asylum Lake ranged from 7.0 to 9.05, with the average pH (average hydrogen ion concentration converted to pH) of 7.67, whereas the pH of Bonnie Castle Lake varied from 5.9 to 7.9 and an average pH (average hydrogen ion concentration converted to pH) of 6.9. This indicates that the acidity of precipitation (average pH = 4.67) is 800-1000 time greater than the water of Asylum Lake and 200-300 times more acidic than that of Bonnie Castle Lake.

According to Last et al. (1980), in the lake watershed system in which carbonates are present, the hydrogen ion generated by precipitation will be consumed with the release of bicarbonate and calcium. Or, hydrogen ions may be exchanged for various metal cations in soils. Finally they may react with minerals, releasing metal cations. Therefore, the above process may account for the observation that lakewaters were less acidic than the precipitation that they received.

The distinguishing feature of rainfall in the lakes being studied is their possession of elevated calcium concentrations, such concentrations presumably being responsible for the high acidity. As shown in Figure 8 (p. 65), calcium is present in significantly higher concentrations

Table 5

Major Ion Components of Precipitation, Asylum, and Bonnie Castle Lakes From October 1983 Through July 1984

Ions	S[a]	Oct. 83	Nov. 83	Dec. 83	Jan. 84	Feb. 84	Mar. 84	Apr. 84	May 84	June 84	July 84
H^+[b]	I	106.0	210.0	27.6	231.0	251.0	249.0	395.0	512.0	103.0	6.31
	II	3.10	3.19	1.59	1.24	4.94	2.62	1.82	0.75	0.22	0.40
	III	0.59	0.74	0.50	0.66	0.60	0.50	0.40	0.38	0.05	0.01
NO_3^-[c]	I	1.44	1.24	1.49	2.60	1.75	1.56	1.52	1.18	1.05	1.20
	II	0.93	0.68	0.55	0.65	1.00	0.43	0.55	0.53	0.51	0.80
	III	0.69	0.49	0.65	1.45	0.55	0.49	0.40	0.50	0.52	0.60
SO_4^{-2}	I	5.10	2.08	3.75	3.50	4.75	4.50	3.29	3.10	2.25	2.00
	II	3.83	2.95	3.50	2.00	2.50	4.75	0.75	1.00	0.0	2.00
	III	15.50	14.10	17.50	18.50	11.00	12.00	13.00	11.50	12.50	12.00
NH_4^+	I	1.12	0.84	0.73	1.95	1.29	0.84	1.16	0.93	1.12	1.50
	II	0.22	0.18	0.19	0.20	0.32	0.17	0.24	0.14	0.26	0.25
	III	0.24	0.32	0.70	0.35	0.63	0.23	0.18	0.16	0.12	0.19
K^+	I	5.25	8.20	5.96	4.70	8.27	7.80	5.21	4.74	4.90	5.10
	II	7.81	15.02	17.27	14.75	15.81	14.85	15.74	9.12	5.93	4.43
	III	39.61	38.85	52.79	48.11	50.53	30.83	31.30	20.78	22.19	24.99
Ca^{+2}	I	7.36	8.29	8.34	16.26	29.45	33.67	18.13	14.47	12.15	10.54
	II	118.3	175.5	186.4	135.9	130.9	99.89	131.6	60.63	89.55	57.44
	III	538.7	665.1	768.2	577.4	642.8	246.9	309.7	303.0	234.0	300.0

[a] I: Precipitation
II: Bonnie Castle
III: Asylum

[b] Concentrations expressed as 1 x 10^{-7} M.

[c] Following concentrations are expressed as parts per million unless otherwise stated.

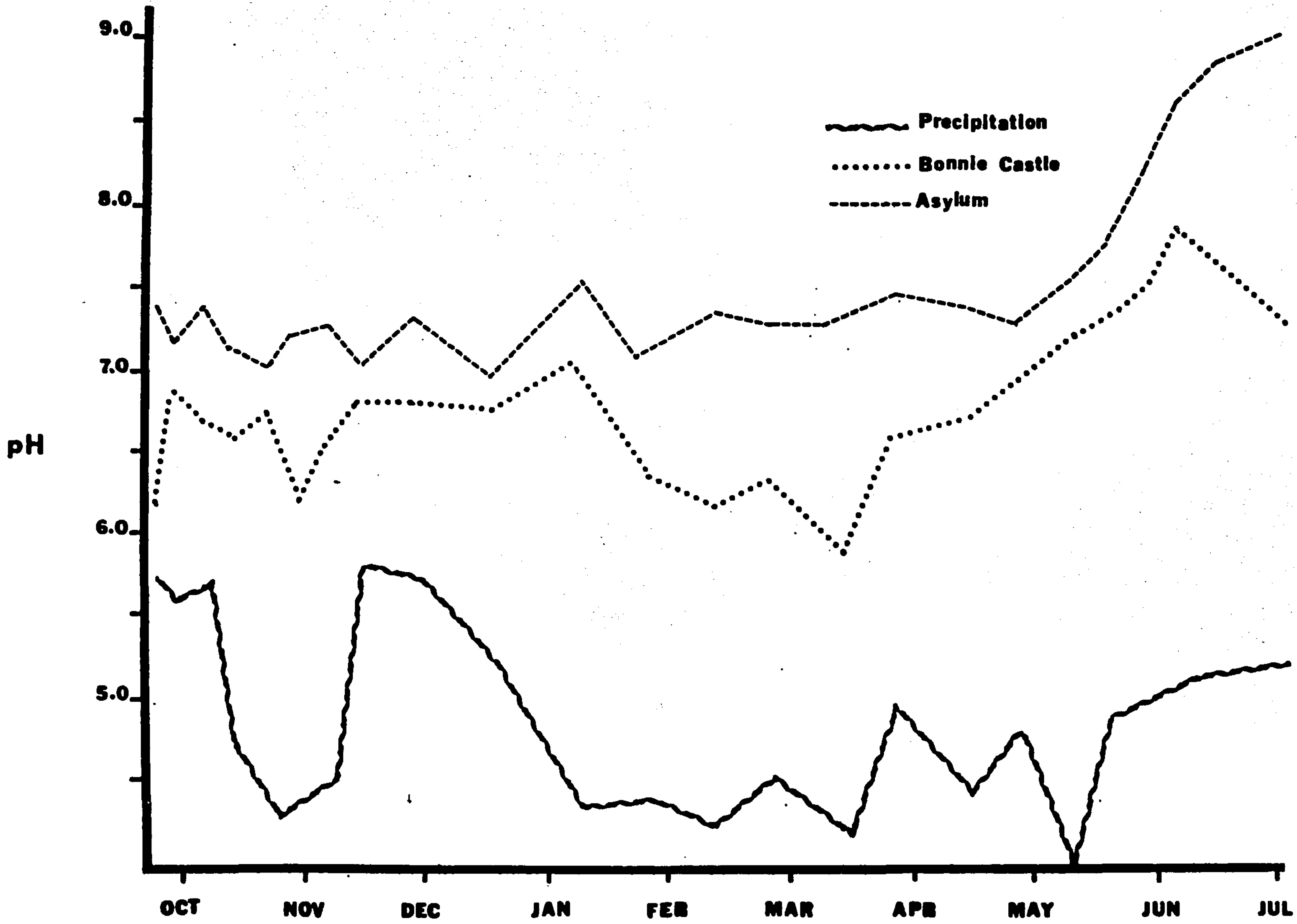

Figure 10. pH of Precipitation and the Study Lakes From October 1983 Through July 1984.

in Asylum Lake than in Bonnie Castle Lake. The higher concentration may be an indication of the groundwater flow characteristics around Asylum Lake. Although in both lakes, terrestrial processes mediate the lakewater acidification process, carbonate is the associated factor in Asylum Lake and is deposited in sufficient quantities to account for the pH difference between the lakes. In contrast to Asylum Lake, Bonnie Castle, with less basicity throughout the year, (pH values are 0.4 to 2.2 units lower than those of Asylum Lake samples), had concentrations of calcium relatively similar to those in precipitation. Similar results were noted by Beamish (1976) who found that a less acidic lake had a base cation concentration (Ca^{2+}, K^{+}, Mg^{2+}, and Na^{+}), with calcium concentrations double the values of the nearly acidic lakes. Both seasonal quantity and quality of precipitation are also important with respect to lakewater pH. With hydrogen ion deposited on snow, the acidity of the precipitation increased. Due to rapid flushing of accumulated acid during snow melt, the acidity of lakewaters will increase (Beamish, 1976). A similar trend was found for the study lakes. As shown in Figure 10 (p. 72), the pH fluctuation for the first three months of study (October-December) ranged from 7.05 - 7.35 for Asylum Lake and between 7.2 and 6.8 for Bonnie Castle Lake. A winter rise to 7.5 for Asylum and 7.05 for Bonnie Castle Lake was followed with a drop in the early spring, although greater for Bonnie Castle Lake that is more affected by precipitation. Finally there is a sharp increase in alkalinity during the dry period (May-July) to 9.05 for Asylum Lake and 7.9 for Bonnie Castle Lake.

It is important to consider the depositions of chemical species that originally caused the acidity (sulfate and nitrate) and their possible relationships to the acididity of the study lakes.

Figure 11 (p.75) shows the monthly trends for sulfate and nitrate concentrations for both lakes during the period of this study. Sulfate is present in significantly higher concentrations in Asylum Lake (10-21 mg/l) than in Bonnie Castle Lake (0-7.5 mg/l). This can be an indication of groundwater flow with its high concentration of sulfate around Asylum Lake. A comparision of sulfate concentrations in Bonnie Castle Lake with those of precipitation shows a similar monthly trend with a correlation coefficient of 0.72. This may indicate that precipitation has affected the acidity of this lake and that part of the sulfate that entered the lake was caused by precipitation. Since Asylum Lake does not receive a substantial portion of the total water input as direct precipitation, sulfate concentrations in the lake were not related to that of the rain.

A comparision of pH values (Figure 10, p. 72) of the

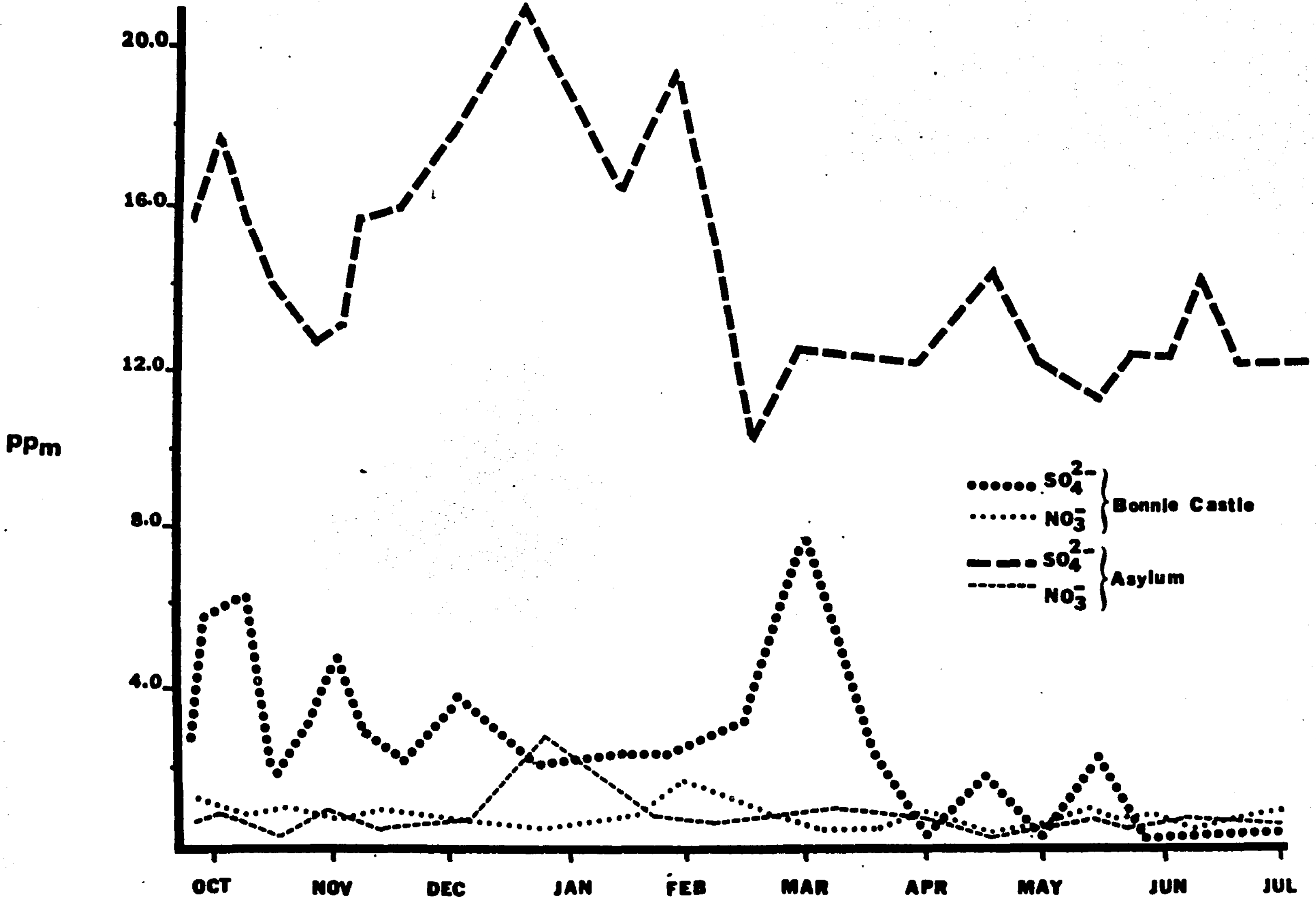

Figure 11. Nitrate and Sulfate Concentrations for the Study Lakes From October 1983 Through July 1984.

lakes with their sulfate concentrations (Fig. 11, p. 75) shows that the higher sulfate concentrations were related to high acidity. The highest values of sulfate were found during the winter period for both lakes with a sharp drop in early spring. The concentrations remained lower for the remainder of the study period, that encompassed dry periods. The lowest acidity values, however, were associated with lower sulfate during the dry periods.

As shown in Figs. 10 (p.71) and 11 (p.75), concentrations of nitrate are not affected by the pH fluctuations in the lakewaters as much as are those of sulfate. Galloway et al. (1983) also reported that sulfate is more important than nitrate in prompting long term acidification of aquatic systems.

Results of other research studies also show that sulfate concentrations are high in many acidified lakes (Gorham and Gordon, 1960; Beamish and Van Loon, 1977). According to Galloway et al. (1983), an initial increase in sulfate (or hydrogen ion) concentrations may result in proportionally large increases in base cation concentrations ($CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$) as compared with decreases in alkalinity in the aquatic system. This continues until the reservoirs of base cations are depleted. Then, the concentration of sulfate (or hydrogen ion) increases more rapidly with a concurrent decrease in alkalinity.

Figures 8 and 9 (pp. 65, 69) show that the concentratrations of both of these cations (K^+ and Ca^{2+}) are much higher in Asylum Lake where the sulfate concentration is also higher than in Bonnie Castle Lake. The monthly fluctuation of both cations are similar to those of the sulfate concentrations in Asylum Lake. The gradual increase from fall through winter in concentrations of calcium, potassium, and sulfate was followed by a sharp decrease in the middle of March, and the concentrations remained lower for the rest of the study period. The correlation coefficients between the sulfate concentrations and calcium and potassium were found to be .75 and .70 respectively. Therefore, it may be assumed that increased sulfate or hydrogen ion concentration is related to an increase in base cation concentration in Asylum Lake without decreasing the lake's alkalinity.

The similarity between base cations (Ca^{2+}, K^+) and sulfate concentrations was less apparent in Bonnie Castle Lake. The figures indicate that the above concentrations of ions in Bonnie Castle Lake and their concentrations in precipitation were related. This may indicate that the higher concentrations of SO_4^{2-}, Ca^{2+}, and K^+ in Bonnie Castle Lake are related to those of the precipitation.

The magnitude of the changes in base cations, however, depends on the characteristics of the aquatic system. The variety of potential sources of buffering, water flow patterns, rate of acid deposition and, finally flushing, all tend to make each lake system unique. Precipitation, however, delivers from 1%-35% of each lake's annual nitrogen input. Lakes with greater surface area, not necessarily deeper, receive a greater percentage of their ions through rainfall owing to their larger surface areas (Messer, 1978).

Figures 11 (p. 75) and 12 (p. 79) show the seasonal patterns of nitrate and ammonium ion for each lake. These parameters exhibited similar trends, each having higher concentrations in winter and at the beginning of spring, and lower concentrations during dry periods.

Ammonia is derived mainly from biological activity in soil and water. The ionization equilibrium for $NH_3 \rightarrow NH_4^+$ at the lakes depends on the pH and is imcomplete at slightly alkaline pH's. Lakes that are buffered (pH = 8) have NH_4^+ concentration ranges of .10 - .40 mg/l (Messer, 1978). Lakes with the lower alkalinity exhibit lower NH_4^+ (.07 mg/l) concentration. The concentrations of ammonium ions for Asylum Lake as buffered, ranged between .10 and .9 mg/l whereas Bonnie Castle, with its lower buffering capacity, exhibited lower concentrations of NH_4^+.

The results of this study, therefore are in general agreement with the data previously reported by Messer (1978).

The preceding discussions of precipitation chemistry involve the relative importance of precipitation as a source of available phosphorus to the lakes. According to

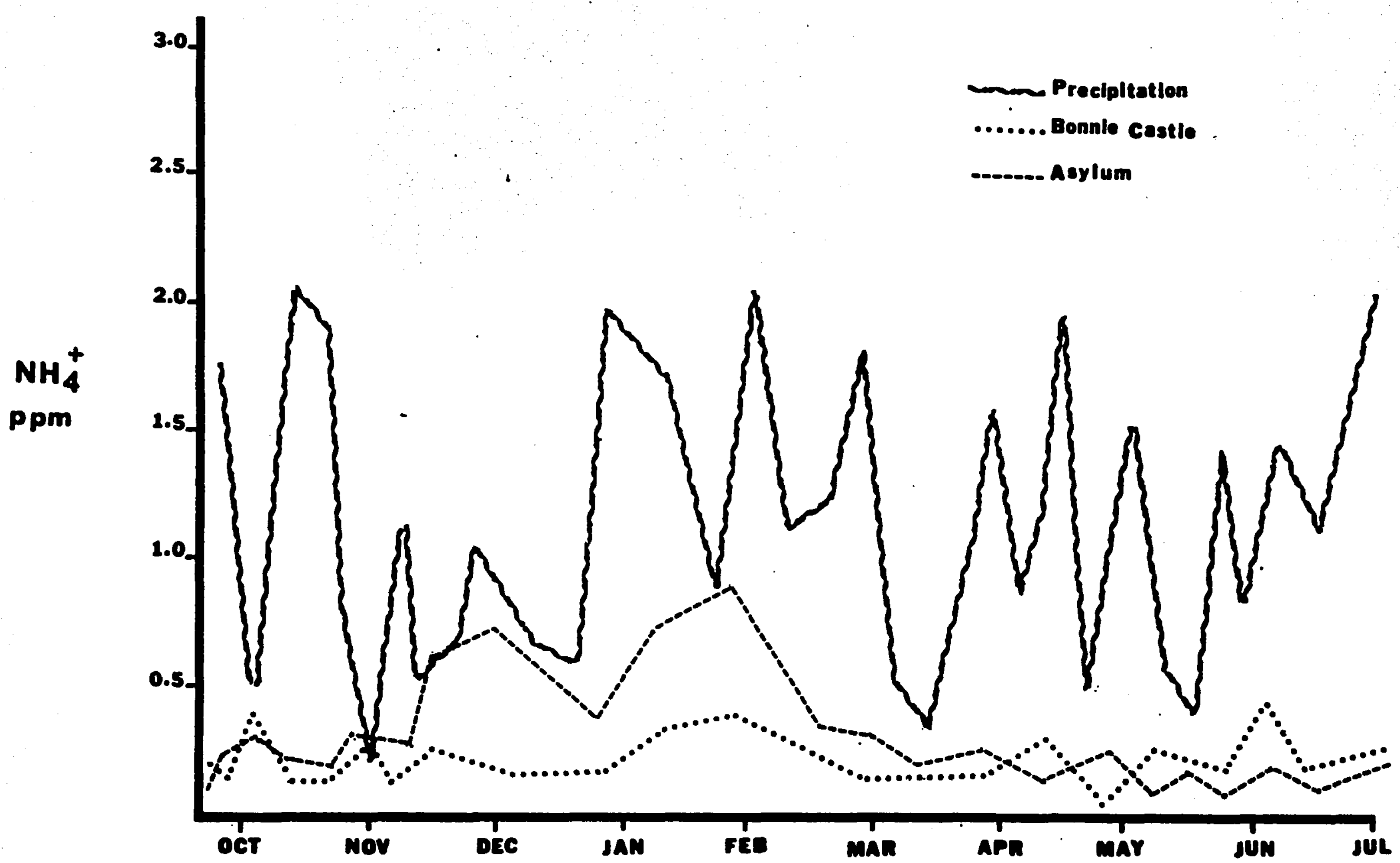

Figure 12. Ammonia Nitrate Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

Dillon et al. (1979) the phosphorus supplied by precipitation to many oligotrophic lakes is a vital factor in determining their trophic status. A significant portion of the total phosphorus in precipitation samples was available immediately for uptake by the phytoplankton and bacterial population of the lakes. Figure 13 (p. 81) shows that the highest deposition occurs during spring and summer for precipitation, whereas the least deposition ocurred in the winter months. Even though both lakes show seasonal variations for the phosphate concentration, they had high concentrations during winter (.20 mg/l for Asylum Lake, .09 mg/l for Bonnie Castle Lake). A sharp decrease occurred during summer (.06 mg/l for Asylum Lake, .02 mg/l for Bonnie Castle Lake). The lower values of phosphate during the summer periods reflect the larger and more active phytoplankton biomass in both lakes. Reduction in the phytoplankton and bacterial populations of the lakes during winter should be responsible for the higher values for phosphate in lakes.

The mean concentrations of phosphate, however, for Asylum Lake were higher than for Bonnie Castle. The runoff during winter may produce higher concentrations of phosphate in Asylum Lake. According to Hildbrandt and Wood (1982), the sources of water for Asylum Lake that were examined would seem to be capable of causing a highly eutrophic condition. Thus, the sources of pollution are

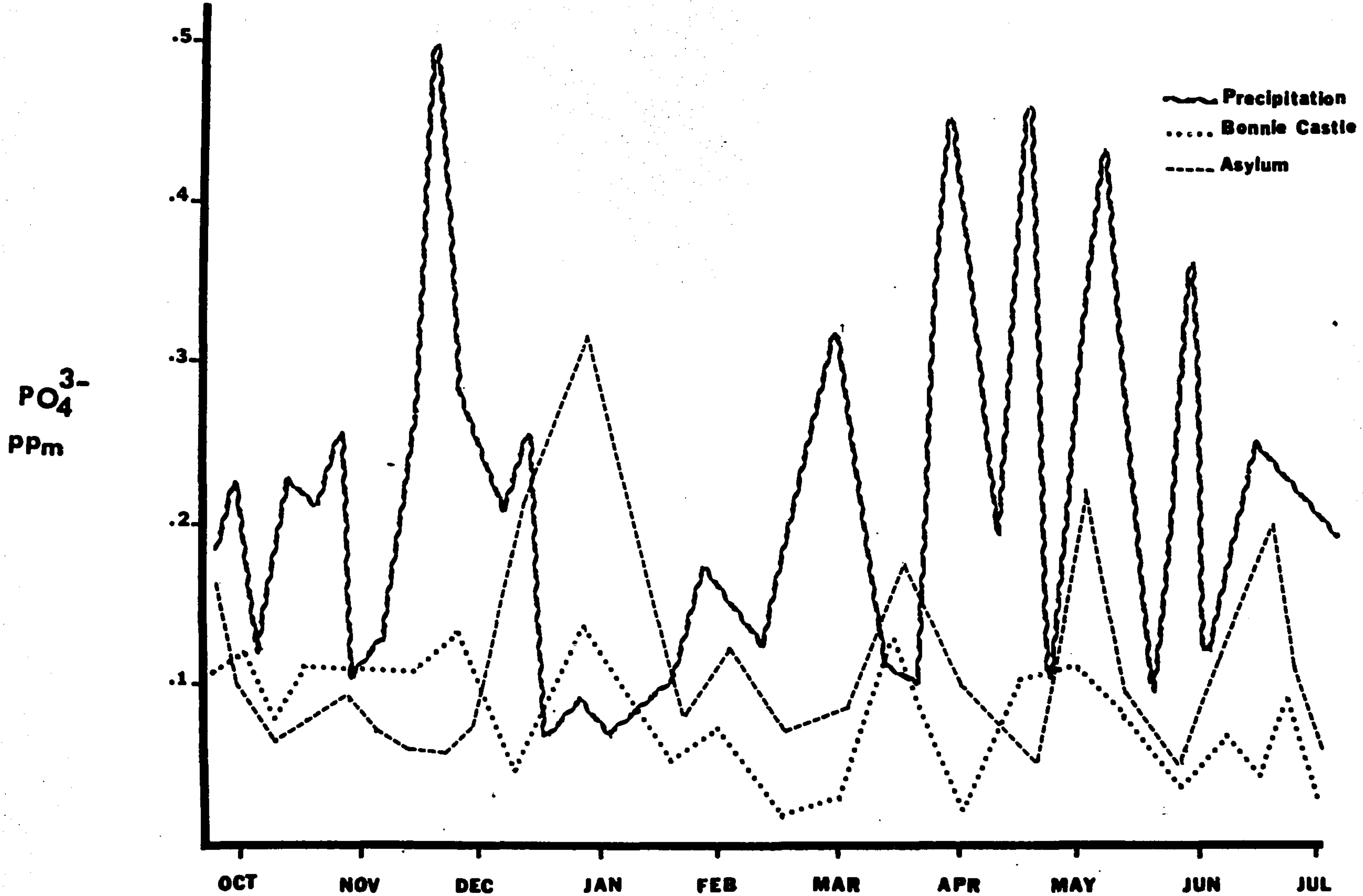

Figure 13. Phosphate Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

important factors for the future of Asylum Lake. Increased cultural eutrophication seems to be the major problem and it could greatly reduce the quality of this lake.

Dissolved Metals in Water

Many studies have shown that metal concentrations in a lake will be altered greatly during the acidification process (Beamish, 1976; Overrein et al., 1980; Jackson et al., 1980). Concentrations of metals in freshwater may be increased directly through deposition (Beamish and Van Loon, 1977) or indirectly through mobilization of metals from the sediments as a result of acidification (Wright and Gliessing, 1976).

In order to identify the major effects of acidification on the study lakes, metal concentrations in the precipitation and lakewater sediments, and the vegetation in the lakes, were investigated.

A combination of analyses, (AA and PIXE procedures) were used on selected elements of the samples. Details of these methods were reported in a previous chapter. PIXE values for metal concentrations were generally higher than those obtained by the AA method. This would be expected since the PIXE process is sensitive to all forms of the specific atoms whereas the AA method is not. The majority of the samples, however, did not show a detectable level of metal concentrations when using the less sensitive traditional AA procedure. Thus, the data for the metals under consideration will be those obtained using PIXE. The sample showed thirteen elements when using this method.

The concentrations of these chemicals are presented in Tables 6-8 (pp. 84-86). Appendices D, E, and F give the weekly concentration of metals detected by PIXE in precipitation, Bonnie Castle, and Asylum lakewaters, respectively. The data indicated that acidic precipitation in the study area is associated with the deposition of heavy metals, resulting in the elevation of their concentration in both lakes. Since many of the heavy metals are components of fossil fuels and metal ores, their occurrences in the study area may be linked defensibly with human activities and fossil fuel combustion.

The effect of precipitation acidity on the metal concentration in the lakes can be further addressed by comparing the monthly variations of pH with their related metal concentrations. As expected, the decrease in metal concentrations for most metals was related to an increasing pH.

Heavy Metals (Zn, Fe, Cu, Pb)

As mentioned previously, except for iron, precipitation showed the highest level of concentrations for heavy metals, and the study lakes had comparable amounts of each

Table 6

Monthly Mean Concentrations of Metals Detected by PIXE in Precipitation

Metal (mg/L)	Oct. 83	Nov. 83	Dec. 83	Jan. 84	Feb. 84	Mar. 84	Apr. 84	May 84	June 84	July 84
K	5.25	8.20	5.96	4.70	8.27	7.80	5.21	4.74	4.90	5.10
Ca	7.36	8.29	8.34	16.26	29.45	33.67	18.13	14.47	12.15	10.54
Mn	.009	.007	.011	.028	.034	.024	.013	.026	.019	.012
Fe	.067	.047	.062	.098	.129	.043	.040	.031	.036	.038
Cu	.010	.006	.009	.025	.035	.032	.016	.013	.012	.010
Zn	.025	.018	.031	.077	.100	.077	.060	.032	.029	.026
Pb	.010	.012	.014	.017	.019	.007	.012	.008	.007	.006
Br	.006	.005	.007	.012	.014	.009	.008	.007	.008	.007
Sr	.005	.007	.007	.006	.008	.007	.007	.005	.006	.005

Table 7

Monthly Mean Concentrations of Metals Detected by PIXE in Bonnie Castle Lakewater, Sediment, and Vegetation

Metal (mg/L)	S[a]	Oct. 83	Nov. 83	Dec. 83	Jan. 84	Feb. 84	Mar. 84	Apr. 84	May 84	June 84	July 84
K	I	7.81	15.02	17.27	14.75	15.81	14.85	15.74	9.12	5.93	4.43
	II	1.64	1.83	1.88	1.58	1.66	1.52	2.70	3.75	3.52	3.91
	III	6.82	11.63	10.29	9.85	9.41	8.20	12.01	19.08	19.40	12.00
Ca	I	118.3	175.5	186.4	135.9	130.9	99.89	131.6	60.63	89.55	57.44
	II	13.16	16.22	17.61	14.26	10 91	1.74	5.96	3.85	4.84	7.62
	III	15.42	21.03	14.23	12.52	10.10	9.37	9.80	7.74	8.31	9.30
Mn	I	.026	.038	.029	.040	.031	.009	.011	.014	.025	.022
	II	.329	.389	.295	.260	.225	.036	.110	.130	.109	.040
	III	.922	.994	.610	.750	.690	.600	.580	1.23	1.44	1.12
Fe	I	.080	.076	.120	.176	.188	.215	.192	.171	.120	.099
	II	5.41	6.15	4.85	4.38	4.10	3.40	4.90	5.76	6.14	7.04
	III	3.03	2.15	2.44	2.98	3.30	2.95	1.44	3.18	2.02	1.90
Cu	I	.007	.003	.005	.014	.009	.010	.007	.006	.005	.006
	II	.007	.009	.010	.009	.012	.008	.009	.007	.009	.011
	III	.007	.005	.006	.009	.007	.008	.004	.005	.007	.008
Zn	I	.014	.012	.015	.041	.030	.020	.026	.023	.022	.017
	II	.070	.086	.087	.065	.085	.076	.071	.058	.086	.120
	III	.057	.064	.076	.098	.082	.100	.087	.053	.088	.100
Pb	I	.003	.004	.003	.005	.007	.006	.016	.018	.013	.010
	II	.039	.069	.085	.069	.052	.042	.041	.034	.058	.082
	III	.006	.014	.023	.025	.026	.028	.044	.076	.042	.026
Br	I	.009	.010	.011	.008	.009	.010	.011	.010	.015	.016
	II	.047	.041	.025	.035	.038	.012	.030	.026	.020	.026
	III	.016	.017	.025	.023	.024	.025	.017	.019	.016	.019
Sr	I	.017	.029	.031	.020	.013	.010	.011	.008	.012	.013
	II	.028	.038	.034	.048	.052	.073	.084	.098	.087	.083
	III	.045	.031	.029	.035	.036	.038	.022	.019	.029	.033

[a] I: Water
II: Sediment
III: Vegetation

Table 8

Monthly Mean Concentrations of Metals Detected by PIXE in Asylum Lakewater, Sediment, and Vegetation

Metal (mg/L)	S[a]	Oct. 83	Nov. 83	Dec. 83	Jan. 84	Feb. 84	Mar. 84	Apr. 84	May 84	June 84	July 84
K	I	39.61	38.85	52.79	48.11	50.53	30.83	31.30	20.78	22.19	24.94
	II	4.01	4.39	6.20	2.20	2.30	1.00	2.84	3.23	2.28	2.23
	III	9.11	12.64	14.07	9.30	9.89	7.12	9.26	9.38	11.30	12.60
Ca	I	538.7	665.1	768.2	577.9	642.8	246.9	309.7	303.0	234.0	300.0
	II	115.2	73.86	40.90	45.35	49.80	15.20	29.17	24.42	47.15	54.48
	III	101.6	49.59	21.10	22.28	31.81	24.04	34.09	46.64	32.22	29.36
Mn	I	.043	.071	.061	.067	.029	.023	.026	.024	.022	.031
	II	.263	.202	.095	.087	.069	.025	.145	.167	.195	.210
	III	1.98	3.04	2.42	2.85	2.17	1.04	1.73	1.88	1.52	1.20
Fe	I	.059	.035	.045	.082	.100	.155	.127	.079	.053	.044
	II	6.55	11.01	9.70	8.55	6.55	3.20	8.24	13.48	9.59	7.96
	III	.980	2.46	2.36	3.28	3.82	5.34	2.52	2.56	1.13	.560
Cu	I	.001	.001	.001	.015	.014	.012	.007	.006	.008	.009
	II	.008	.013	.012	.010	.011	.005	.007	.014	.011	.009
	III	.008	.003	.007	.010	.009	.008	.007	.006	.006	.008
Zn	I	.009	.009	.012	.028	.032	.023	.025	.015	.018	.015
	II	.075	.170	.100	.120	.250	.060	.140	.280	.150	.140
	III	.048	.066	.081	.092	.102	.183	.085	.068	.039	.035
Pb	I	.001	.002	.004	.006	.012	.008	.013	.011	.010	.009
	II	.140	.530	.267	.560	.860	.590	.770	.760	.105	.120
	III	.059	.076	.119	.152	.218	.252	.036	.035	.025	.030
Br	I	.062	.055	.065	.050	.060	.068	.077	.070	.075	.081
	II	.049	.045	.022	.030	.042	.021	.032	.040	.045	.061
	III	.033	.036	.028	.024	.030	.042	.028	.022	.030	.024
Sr	I	.144	.153	.169	.121	.073	.082	.108	.113	.075	.076
	II	.182	.124	.140	.110	.090	.075	.109	.128	.109	.104
	III	.073	.065	.050	.045	.035	.040	.060	.073	.075	.080

[a] I: Water
II: Sediment
III: Vegetation

element (Fig 14,15,16,17 pp. 88-91). According to figures 11 and 12, zinc and iron, with the highest concentrations (Zn = 0.135 ppm; Fe = 0.140 ppm), were considered to be the major elements present in the metal fallout. Zinc concentrations for both lakes were about average (0.005-0.05 ppm) when compared with an average concentration of 0.049 that was obtained by Beamish (1976) for over 1500 samples from waters within the United States. There are, however, strong positive correlations between zinc concentrations in precipitation and those in the lakes ($\underline{r}_{\text{Asylum}} = .70$, $\underline{r}_{\text{Bonnie Castle}} = .79$). Although the concentrations of iron in precipitation were similar to those of zinc, the maximal values for this metal were found in Bonnie Castle Lake (0.40 ppm). A high positive correlation existed between zinc and iron in precipitation ($\underline{r} = 0.72$).

In general, the monthly values of heavy metals exhibited the highest concentrations for all samples during winter and after snowmelt. It is important to consider that the elevated concentrations of heavy metals and perhaps other substances may occur because of increased weathering and solubilty due to acidification of soils and lakes (Hall et al., 1980). Therefore, higher values of metals when the pH is lower, may be related to the above phenomenon. The average concentrations of lead in precipitation, however, were lower than those of iron and zinc (Fig. 16, p. 90). According to Galloway et al., 1983, the

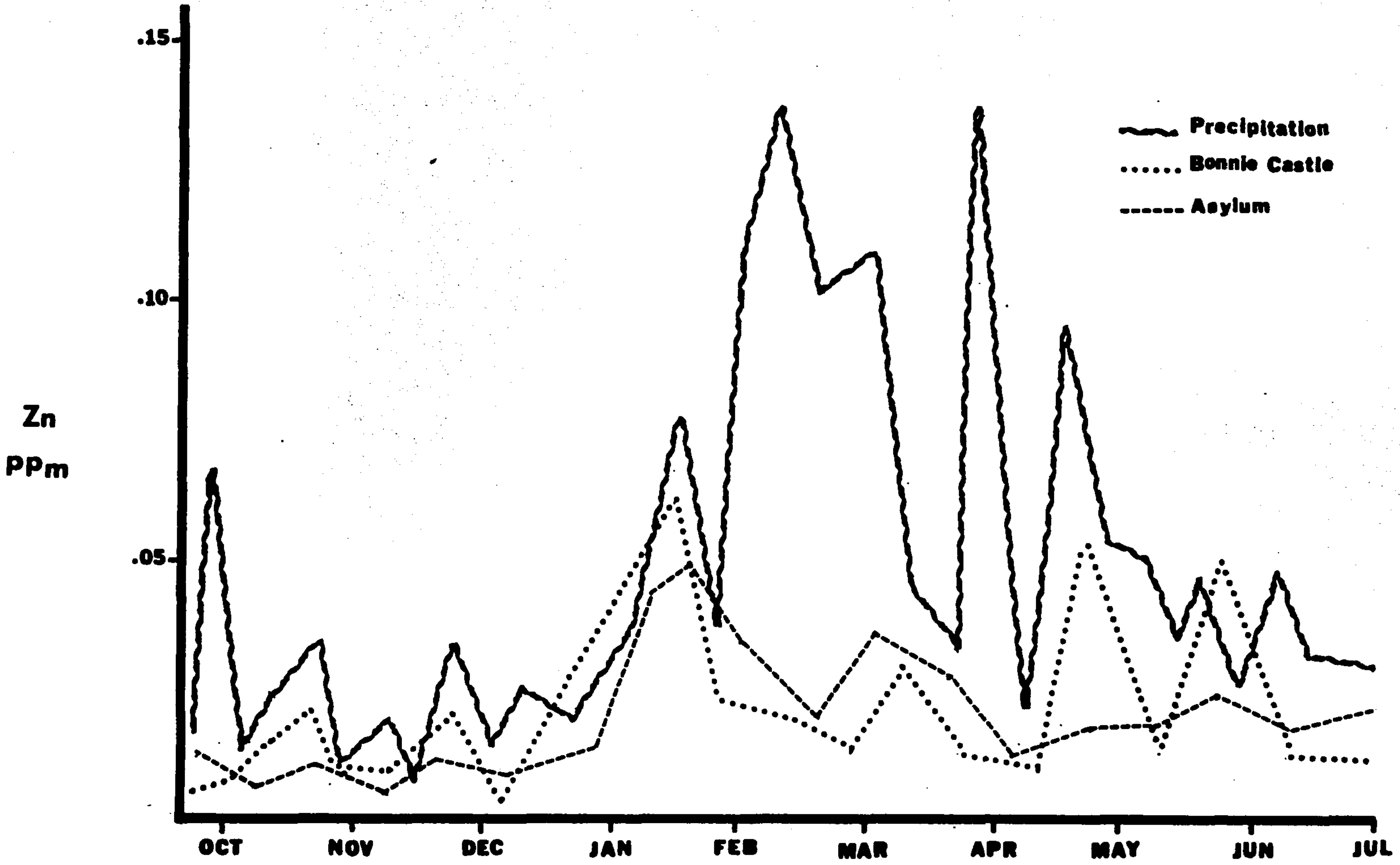

Figure 14. Zinc Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

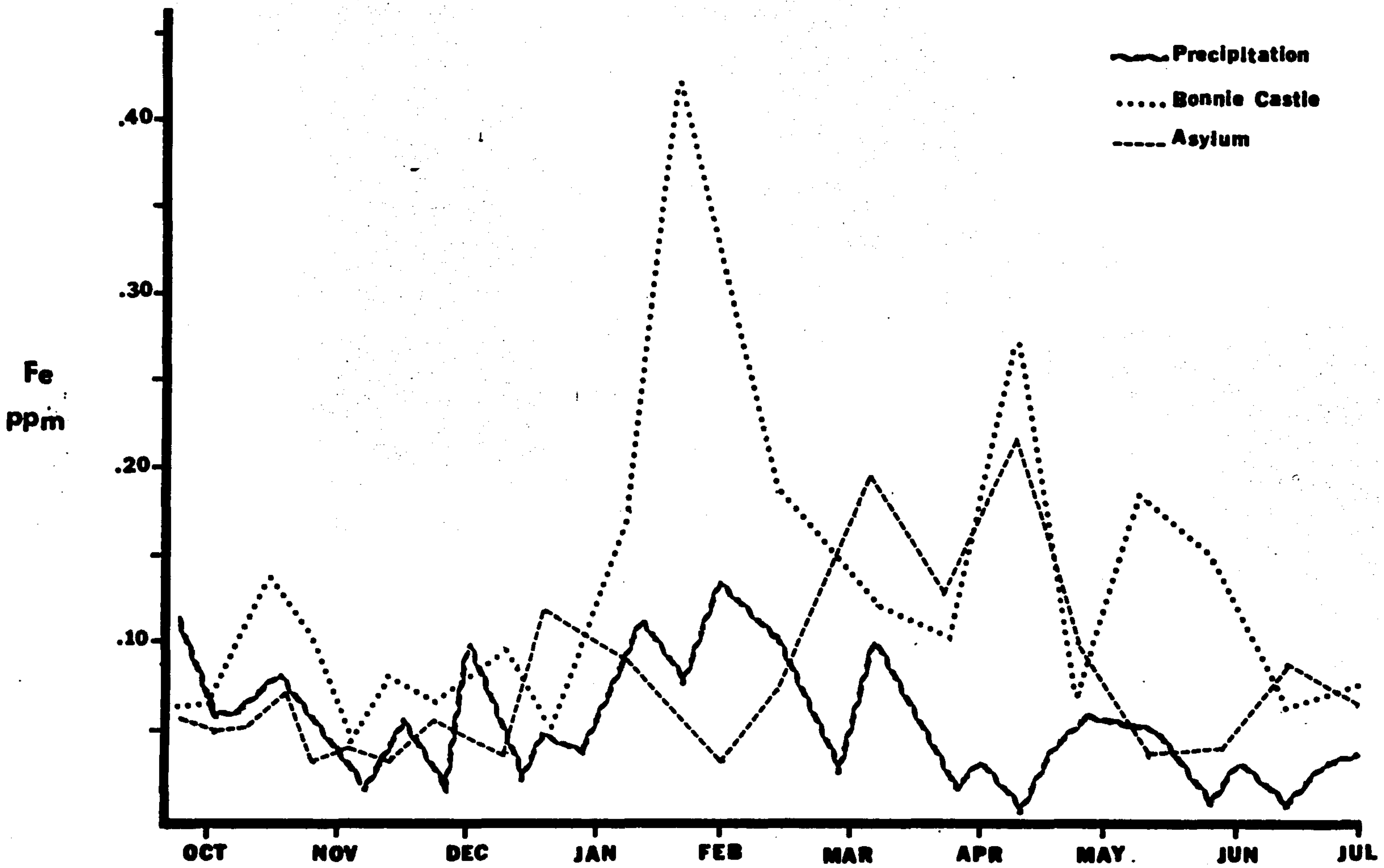

Figure 15. Iron Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

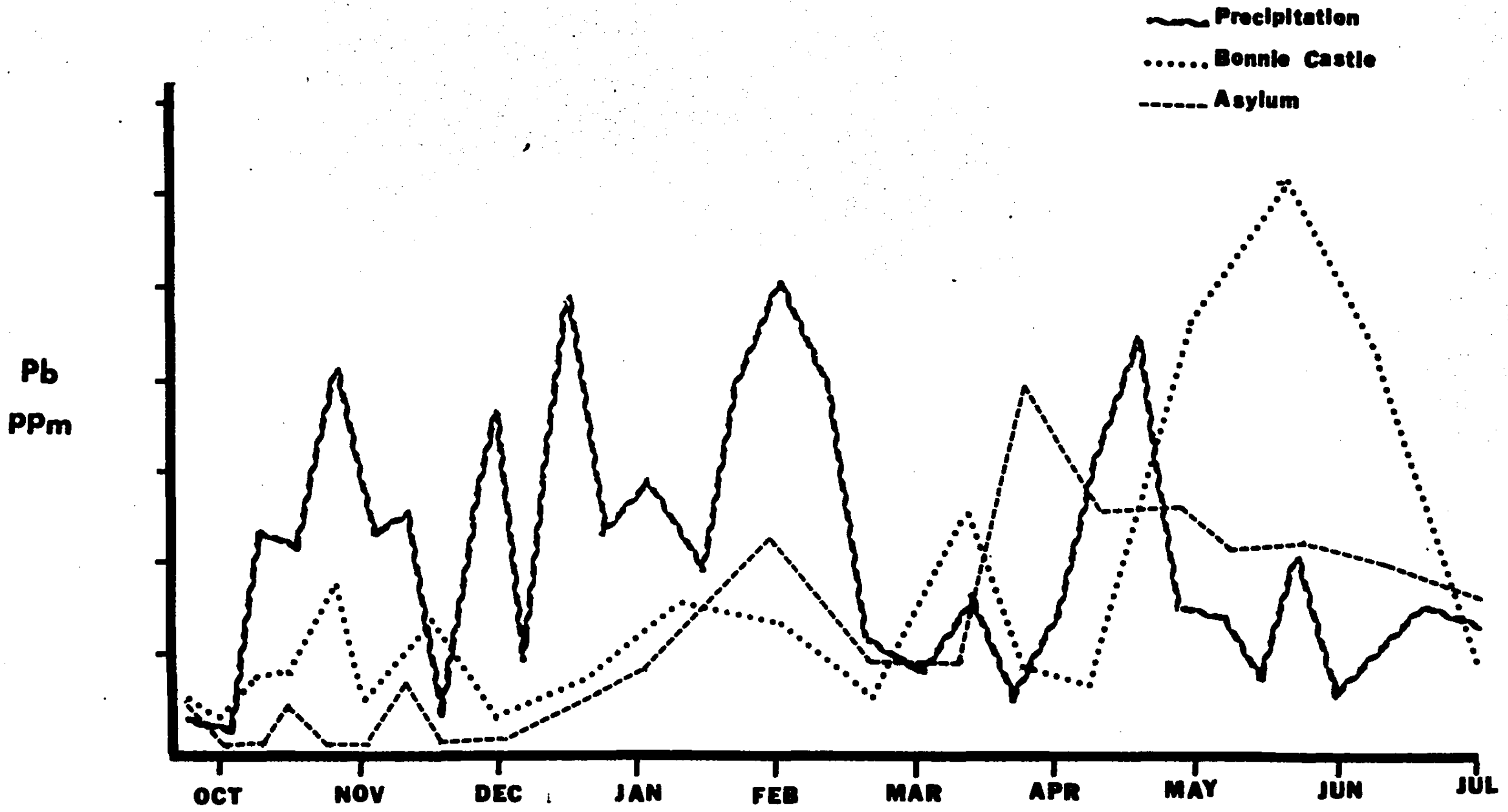

Figure 16. Lead Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

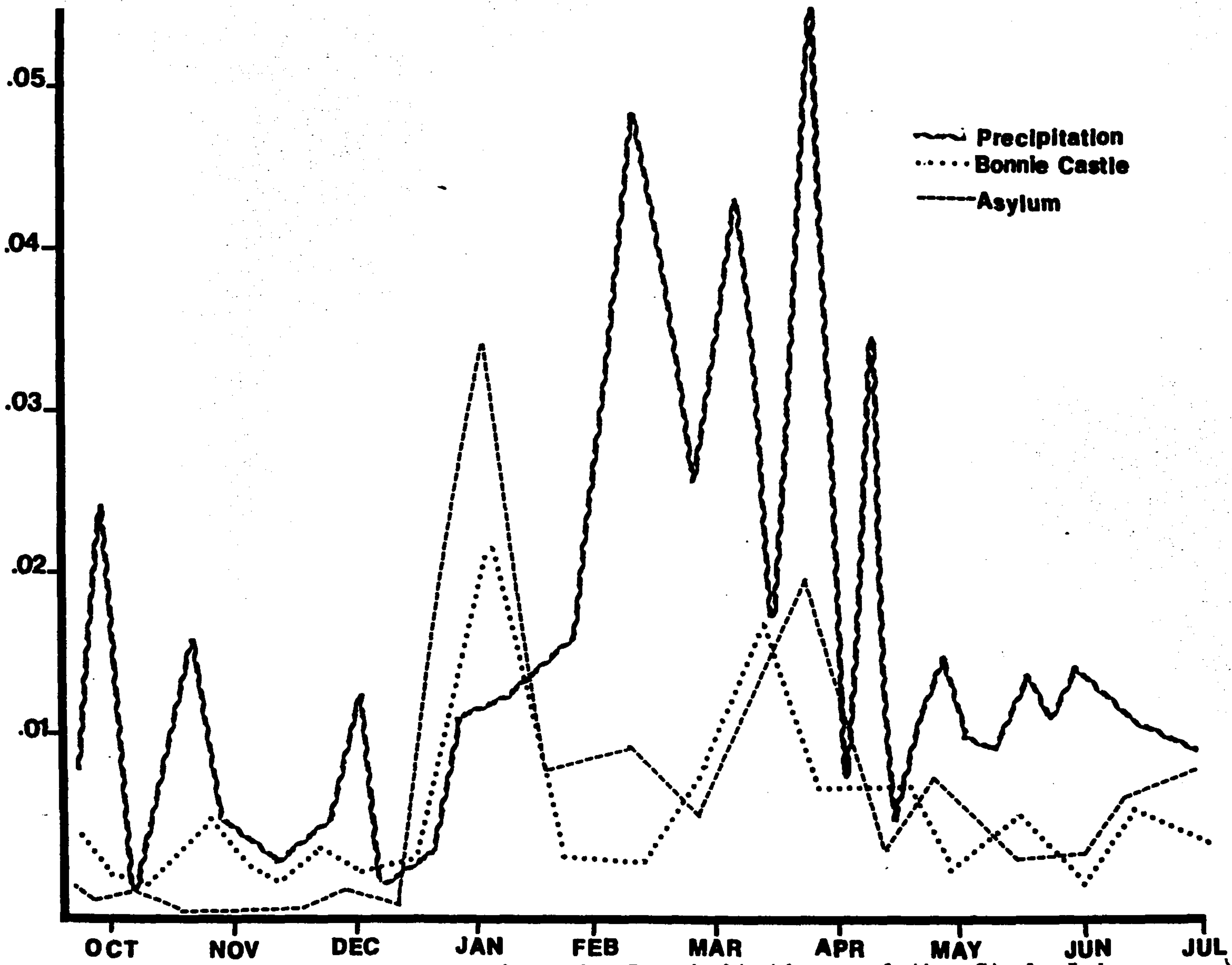

Figure 17. Copper Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

concentration of lead in precipitation is generally less than those of zinc and iron. There are, however, similar monthly trends, with less variability than those of other metals, for iron and lead in precipitation. A high positive correlation also existed between lead and iron ($\underline{r}$ = .90) in precipitation.

The distribution of copper in lakewaters showed elevated levels that corresponded with the copper concentrations in precipitation. The concentrations of this metal in both lakes showed similar trends that are also consistent with the pattern of its deposition by precipitation (Fig. 17, p. 91). A high positive correlation for copper existed between precipitation and lakewaters ($\underline{r}_{\text{Asylum}}$ = .86, $\underline{r}_{\text{Bonnie castle}}$ = .78). There were also high correlations between copper and zinc in precipitation ($\underline{r}$ = .95).

It has been suggested that calcium concentration in water may affect the uptake of some metals such as Zn, Sr, Mn, and Fe (Moreau et al., 1983). But the data in this study showed that only the Mn concentration was highly correlated with that of Ca, specifically in Asylum Lake ($\underline{r}$ = .82). As shown in Fig. 18, p. 93, Mn concentrations appeared to be slightly higher in lakes than in precipitation samples. This may be expected since Mn is usually associated with large particles that have a high deposition velocity and consequently a low residence time in the

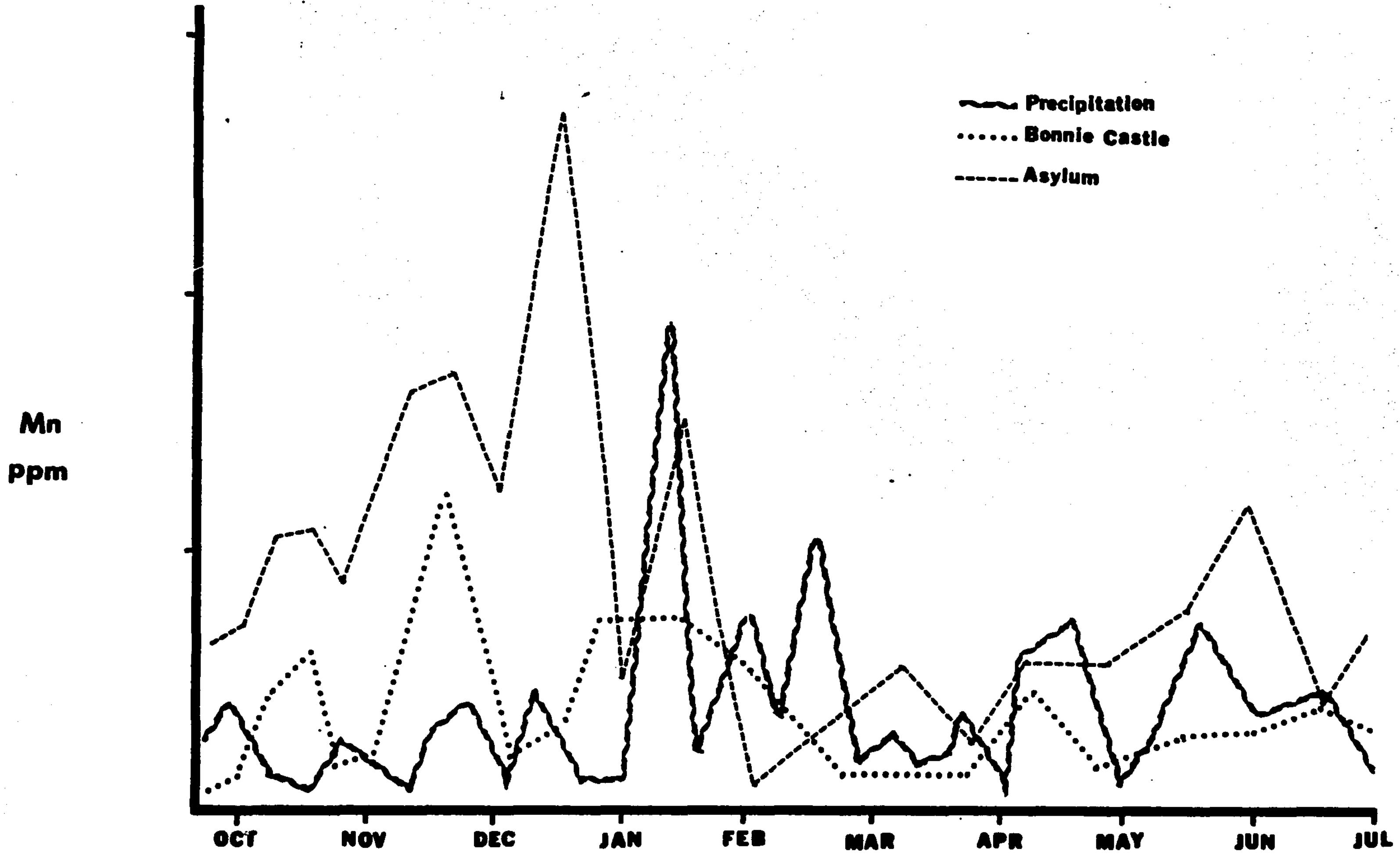

Figure 18. Manganese Concentrations in Precipitation and the Study Lakes From October 1983 Through July 1984.

atmosphere (Eisenreich et al., 1981). Mn showed higher concentrations during dry periods and a decrease in winter. This could be expected since the resuspension of soil and dust particles in the air contributed significantly to the concentration of this metal (Moreau et al., 1983). Dissolved Mn concentrations, however, depend on the redox condition (oxidation-reduction condition) in the water and thus vary with depth and period of the year (Dickson, 1980).

Metals in Sediments and Vegetation

The scavenging of metals by suspended particles and bottom sediment is not unexpected. According to Jackson et al. (1980), lowering the ambient pH enhanced the accumulation of heavy metals by suspended particles. This variation in heavy metal content of the sediment and vegetation is caused by increased atmospheric loading or leaching of metals from soil and sediment by acidic precipitation (Davis, 1979). Figures 19-28 (pp. 95-104) showed the monthly variation of metals in the water, sediment, and the vegetation of the lakes. According to these figures, the concentrations of all metals, except copper were higher in the sediment and/or vegetation than in the lakewater. Competition for copper among aqueous, solid, and organic (biological) phases is particularly strong, reflecting the chemical nature of copper. Copper has a

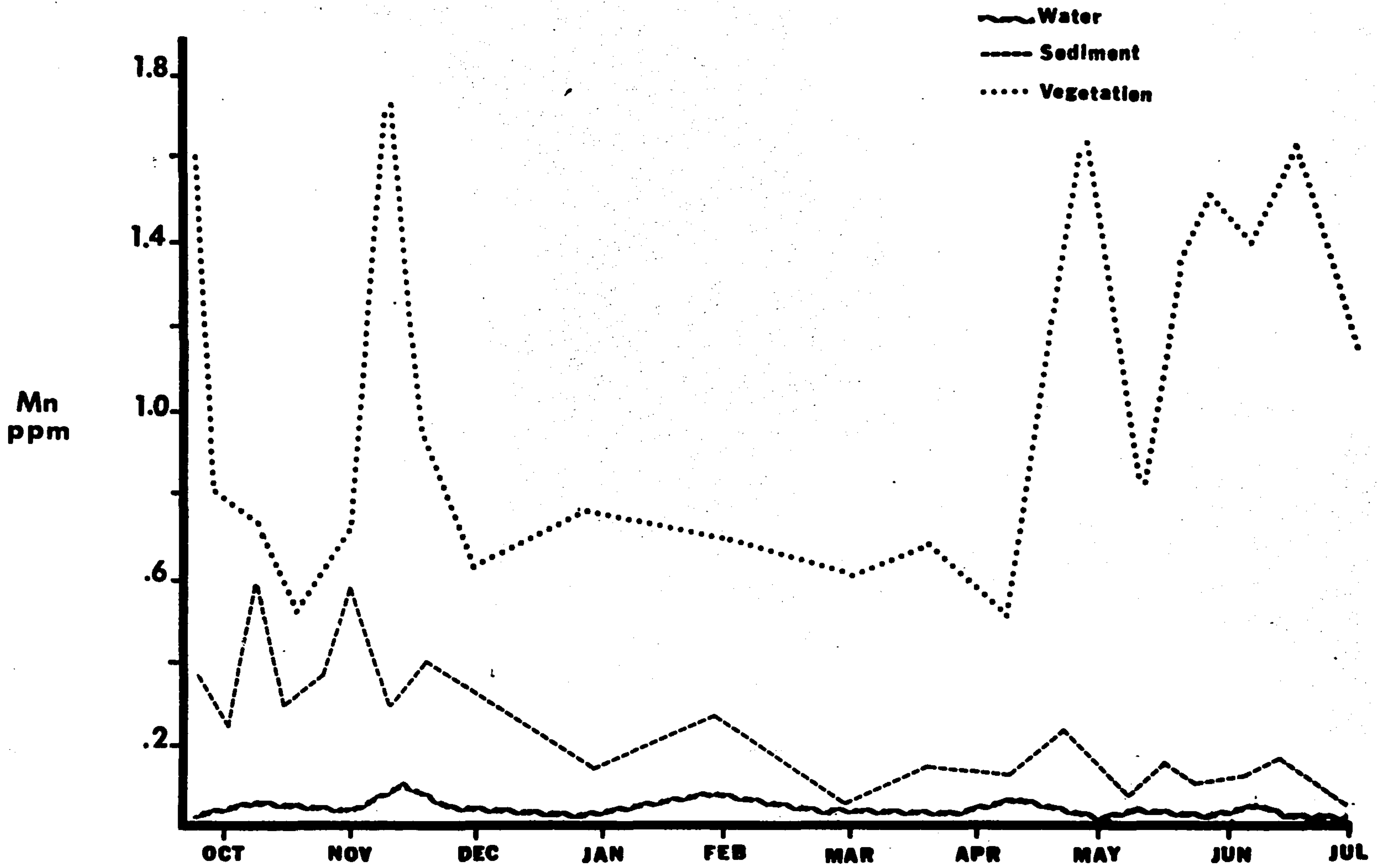

Figure 19. Manganese Concentrations of Bonnie Castle Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

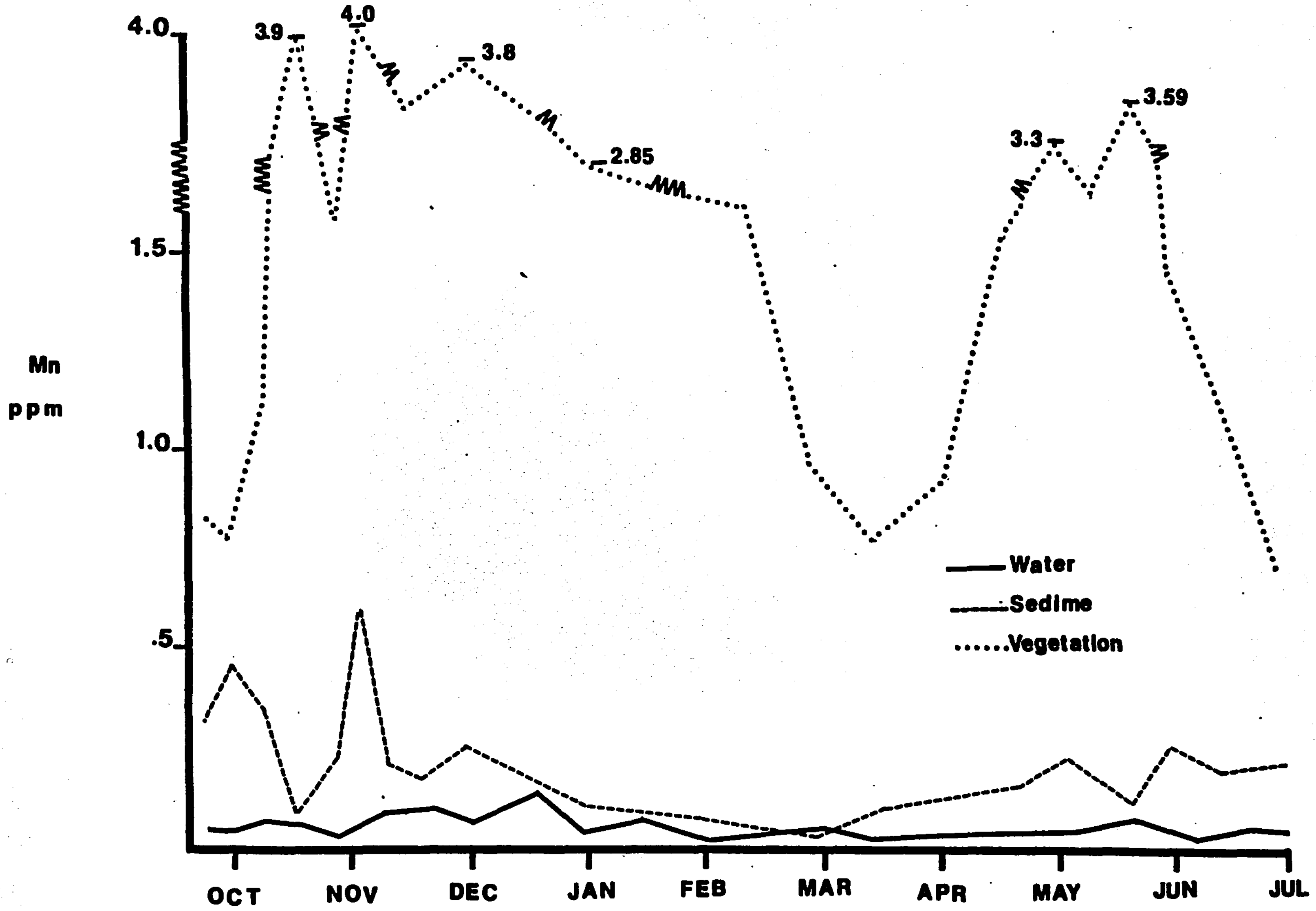

Figure 20. Manganese Concentrations of Asylum Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

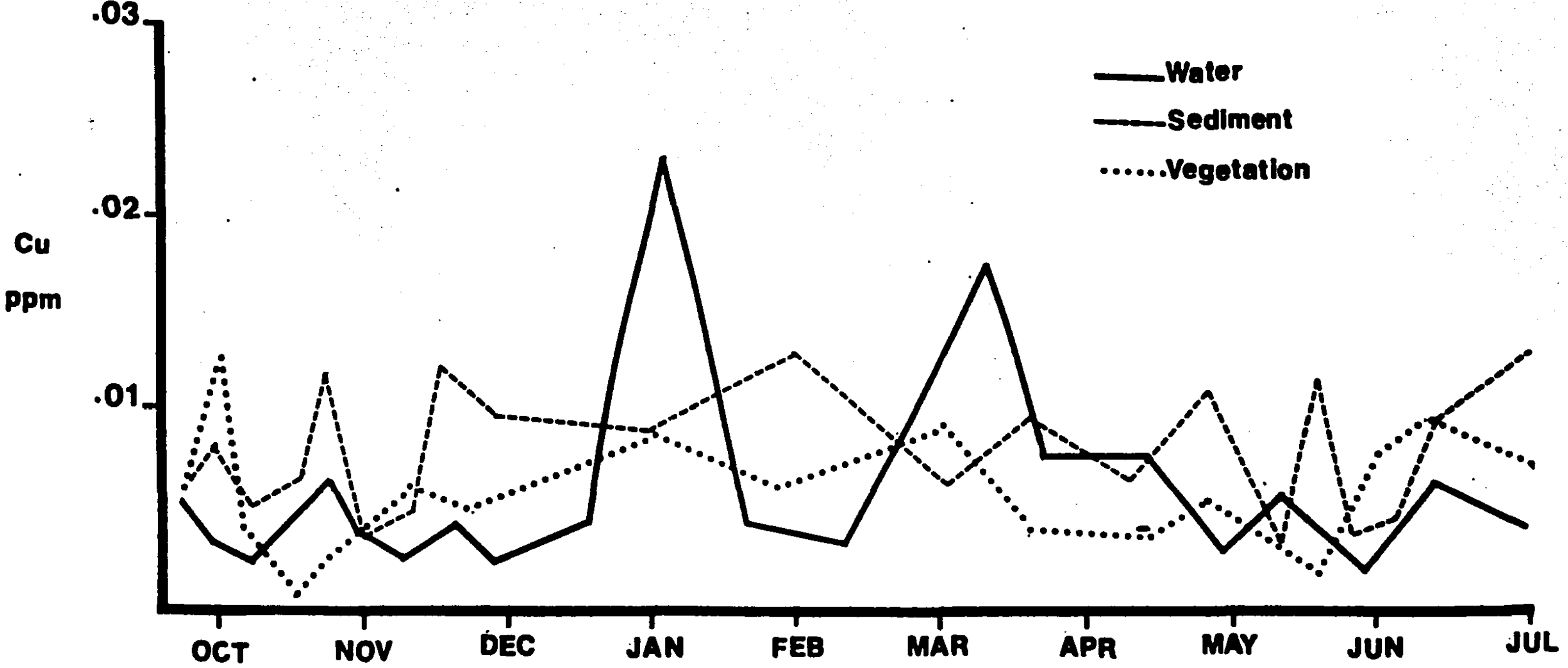

Figure 21. Copper Concentrations of Bonnie Castle Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

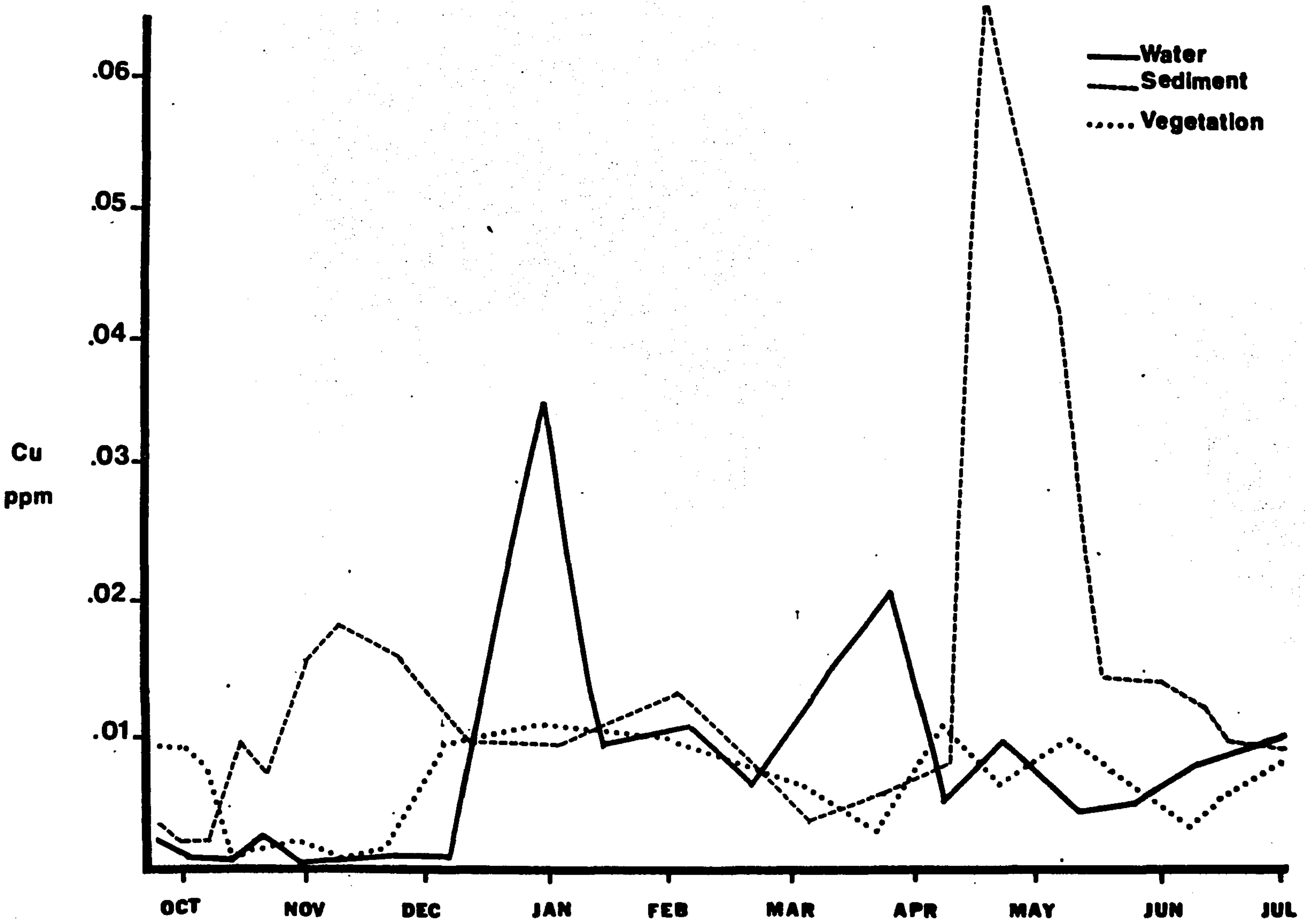

Figure 22. Copper Concentrations of Asylum Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

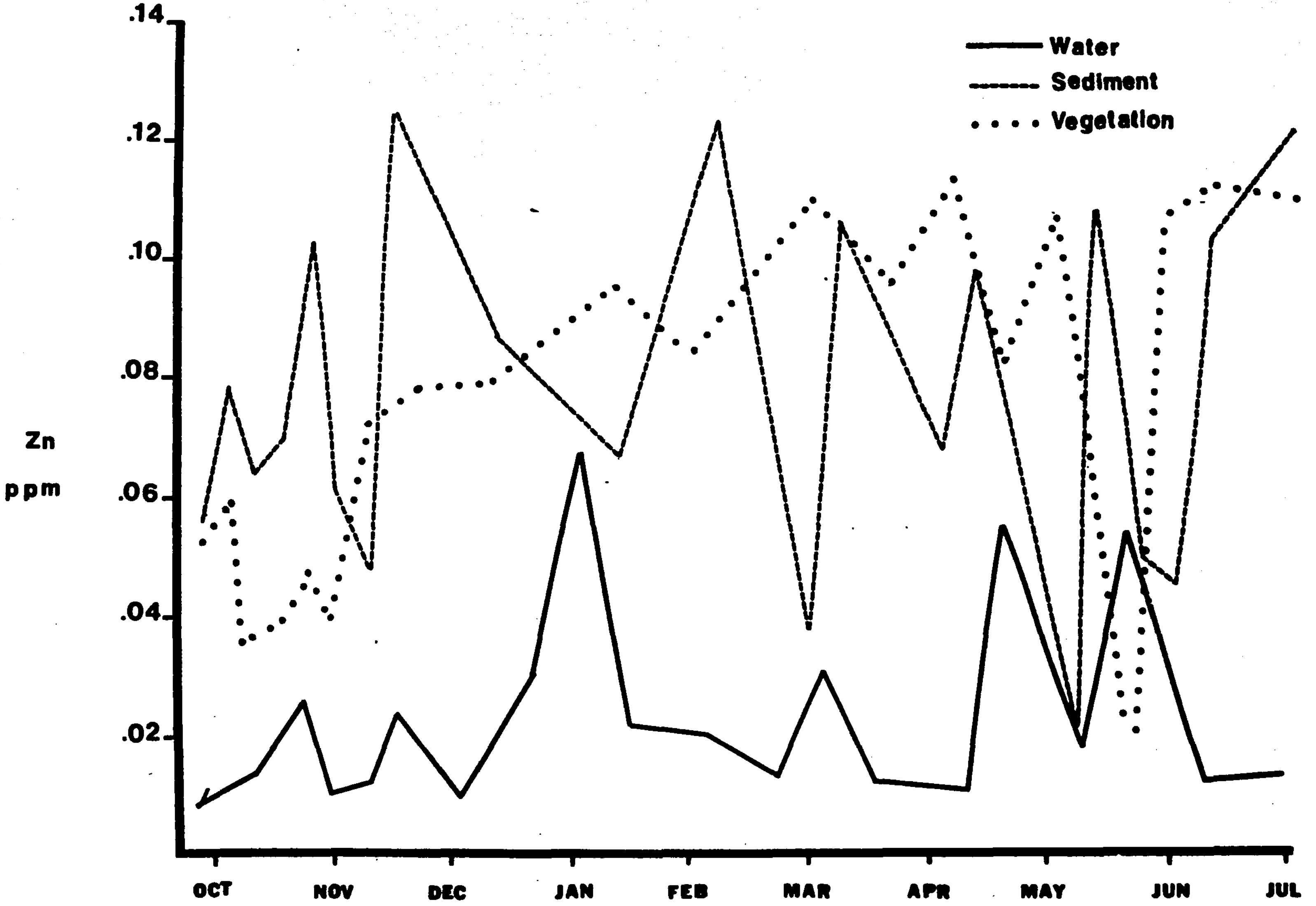

Figure 23. Zinc Concentrations of Bonnie Castle Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

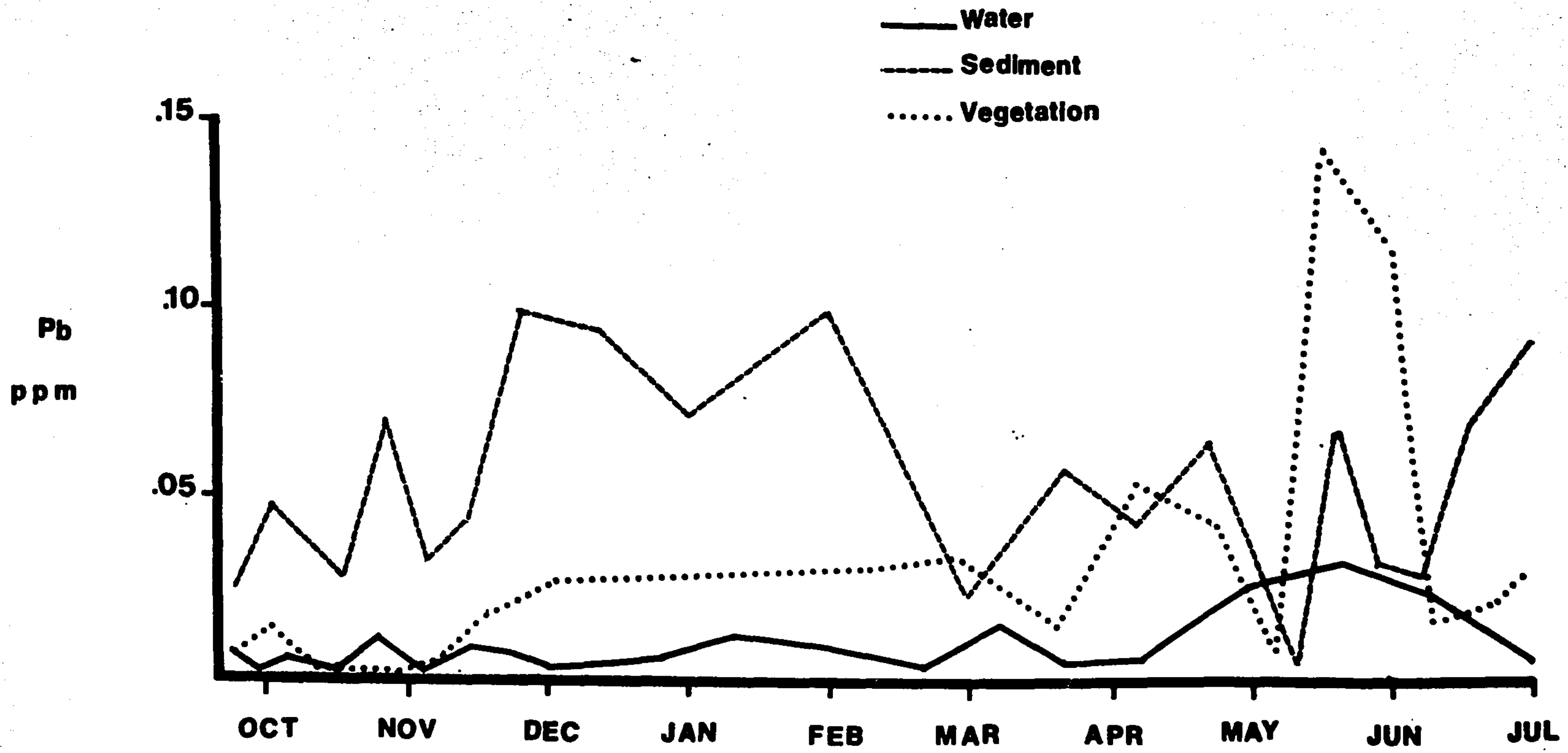

Figure 24. Lead Concentrations of Bonnie Castle Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

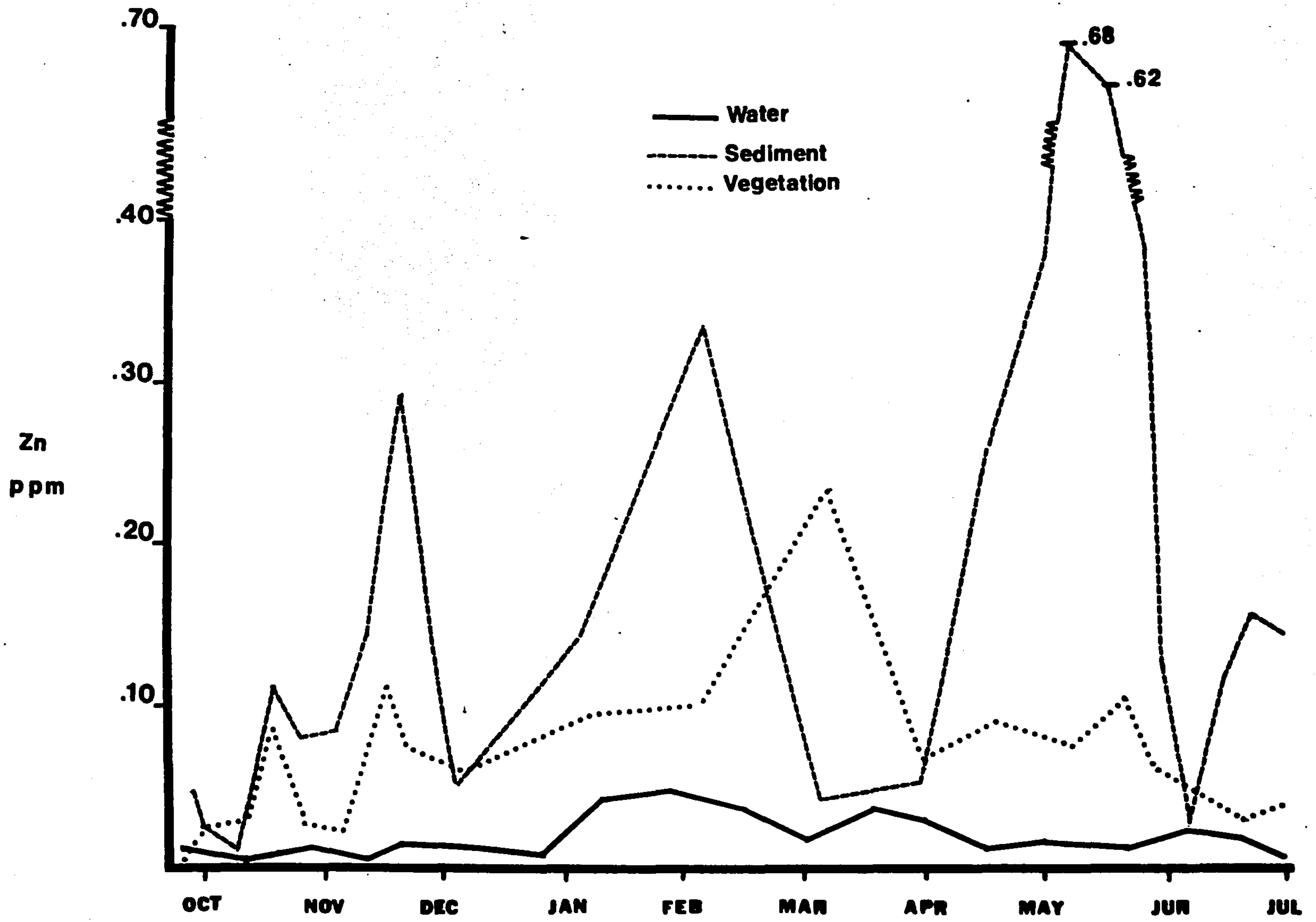

Figure 25. Zinc Concentrations of Asylum Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

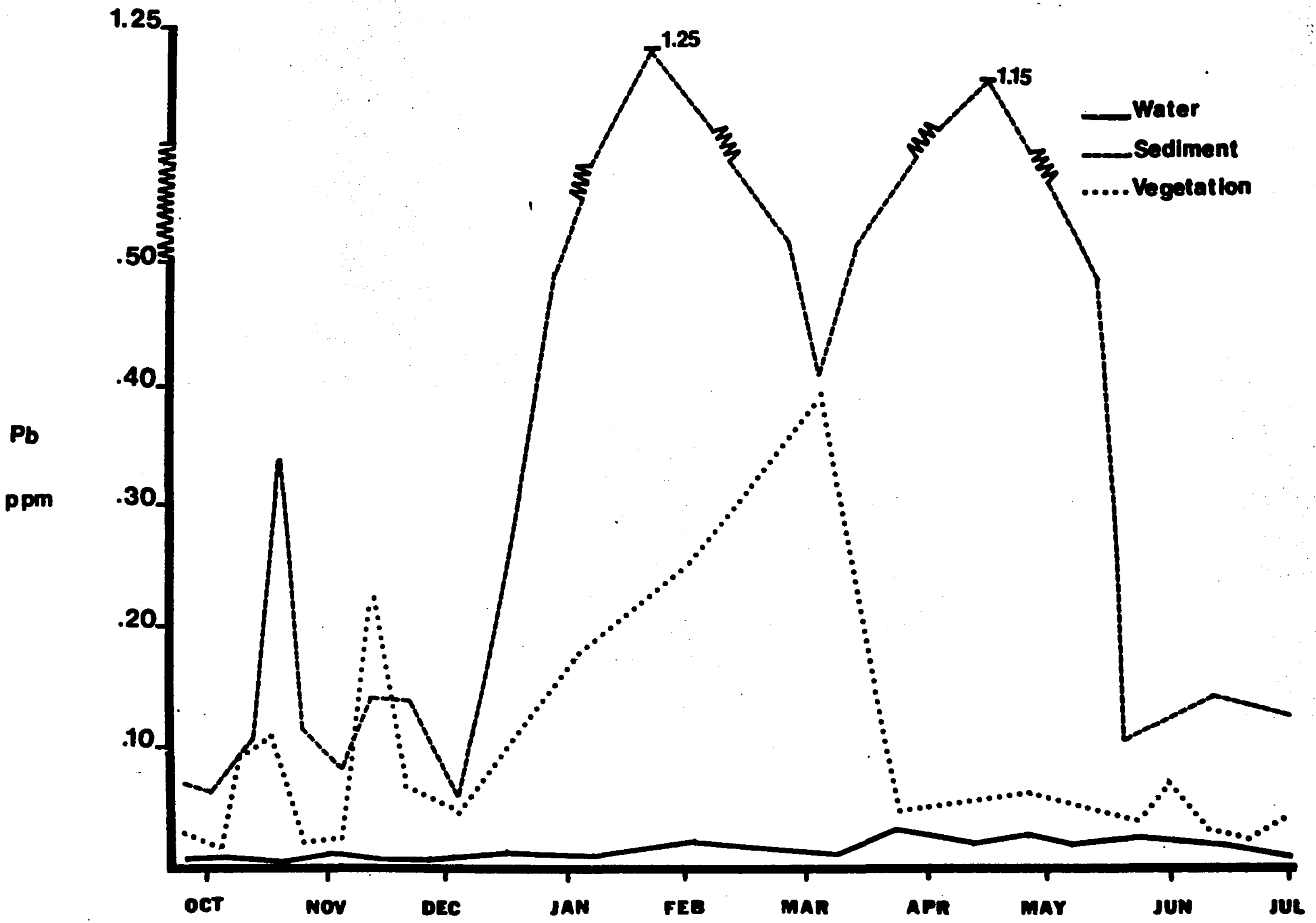

Figure 26. Lead Concentrations of Asylum Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

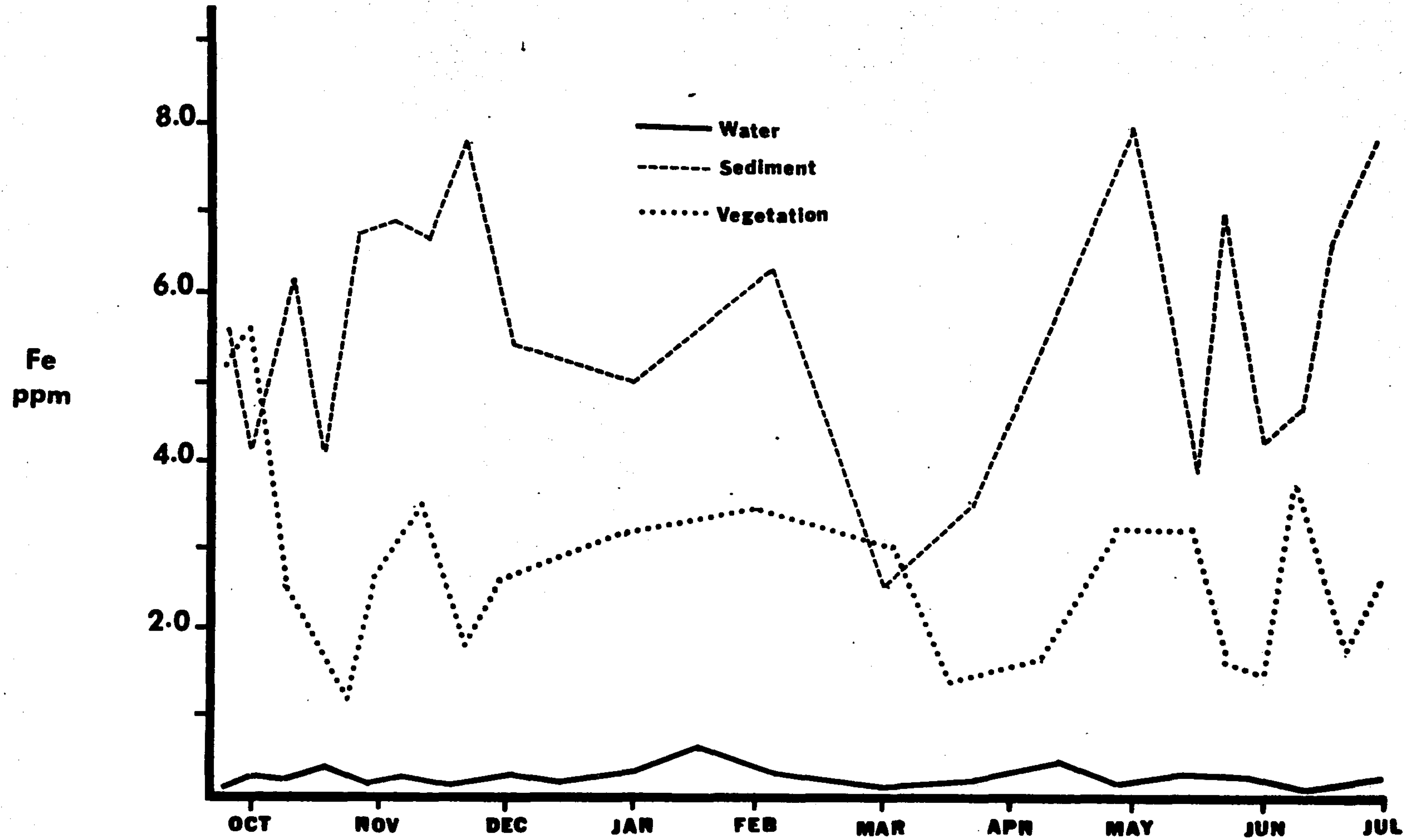

Figure 27. Iron Concentrations of Bonnie Castle Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

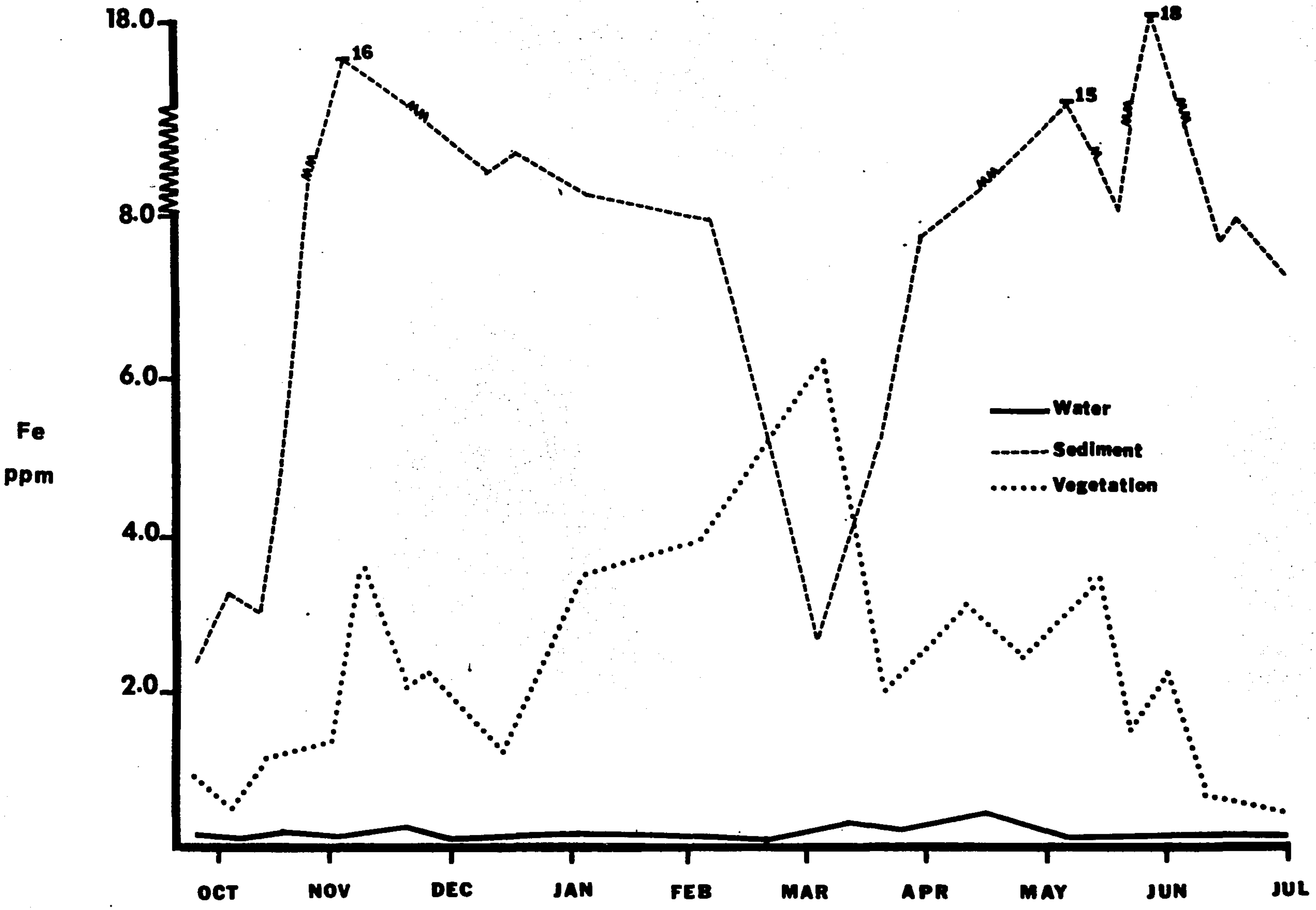

Figure 28. Iron Concentrations of Asylum Lakewaters, Sediment, and Vegetation From October 1983 Through July 1984.

greater affinity for organisms than most heavy metals (Bryan, 1971) and organic matter (Rosen and Williams, 1978). Thus, the end result of the process of adsorption, complexation, and biological accumulation appear to be controlled by the chemistry of copper. Figures 21, 22 (pp. 97-98) illustrate comparable concentrations of this metal in vegetation, sediment, and water for both lakes. According to Bryan (1971), the relatively low ionic potential of copper makes it more susceptible to ion-exchange reactions, particularly with clay material that causes copper to settle at a slower rate.

Chemical studies of sediments revealed that a common phenomenon was the increase in zinc and lead in sediment as far back as 1850 A.D. The coincidence of zinc and lead increases from region to region (and at considerable depth in sediments) and in widely differing lake types (eutrophic to oligotrophic) suggests that zinc and lead and other heavy metals were being deposited by the atmosphere from the polluted air masses (Davis, 1979). Thus, deposition of heavy metals, specifically zinc and lead, is largely responsible for increased levels of these elements.

Figures 23,24 (pp. 99-100) showed more monthly fluctuations for zinc and lead content in sediments than in vegetation in the Bonnie Castle Lake. There is, however, a high positive correlation between zinc and lead in sediment (*r* = .87) and higher correlations between copper and zinc (*r* = .92), and copper and lead (*r* = .91) for the Bonnie Castle sediments. The concentrations of zinc and lead for the solid phases in Asylum Lake (Figs. 25,26, pp. 101-102) were much higher than those for Bonnie Castle. The difference was more pronounced for the lead content of sediment (Asy=.04-.1.25 ppm and BC = .005-.09 ppm). The data are to some extent consistent with those of Hildebrandt and Wood, who studied the nonpoint source pollution affecting Asylum Lake. They suggested that the storm sewer water in Asylum Lake had lead concentrations ranging from 1.3-3.3 ppm. These levels could be a threat to the ecosystem since lead moves through the system in particulate form and accumulates in the organic parts of sediment. Lead could enter the food chain of the lake through organisms that feed in the sediments and are resistant to lead's toxicity.

According to Rosen and Williams (1978) lead and zinc concentrations in the lakes increase monotonically to the sediment-water interface. This can be interpreted to be a result of relative solubility of PbS and ZnS (sediment form) under equivalent condition.

For lakes with a pH > 5.5, the sediments scavenge dissolved zinc and lead. Sedimentation rates for lead are less than for zinc, but increase to levels near those for zinc. This can be seen for Bonnie Castle Lake since its lead concentration is not affected by sewer pollution as is Asylum Lake.

The concentrations of iron in solid phases (sediments and vegetation) are higher than for other metals in the lakes (Figs. 27,28, pp. 103-104).

Iron and manganese concentrations in vegetation and sediment are higher than in the aqueous phase, whereas the iron content of sediment is higher in both lakes (Asylum 10-18 ppm, Bonnie Castle 2.5-8.0 ppm), with the Mn illustrating maximum concentration in vegetation (Asylum = .7-40.0 ppm, Bonnie Castle = .5-1.7 ppm).

The biological effects of all elements in the aquatic environment also depend on their forms and concentrations. The binding of heavy metal ions by organic/inorganic complexing agents may (1) decrease heavy metal toxicity by sequestering the metals in solution, (2) increase heavy metal toxicity by creating dangerous, bioavailable species and, (3) enchance the availability of micronutrients by stabilizing them in solution (Jackson et al, 1980).

The absence of the expected distribution patterns based on a simple atmospheric fallout model, however, suggests that other factors, specifically in Asylum Lake, might also play an important role in controlling the enrichment of certain elements in the study lakes.

The data in this chapter provided an initial understanding of the relationships between acid precipitation and lakewater composition. If the rate of acid precipitation changes, a variety of constituents in both lakes will respond. In order to determine metal concentrations in the precipitation and lakewater samples, a combination of analyses AA and PIXE were used.

Acid precipitation in the study area, however, was associated with the deposition of heavy metals resulting in the elevation of their concentrations in lakewater, sediment, and vegetation.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to verify the extent to which acid precipitation contributes acidity and heavy metals to a lake environment. Asylum and Bonnie Castle Lakes, both of which are located in the western portion of Kalamazoo County, served as the study sites. The chemistry of wet precipitation (rain and snow) was also studied at a site close to both lakes.

All samples were prepared and analyzed by using Hach, AA, and PIXE methods. Metal concentrations were determined for rain/snow water, lakewaters, sediment, and vegetation of the lakes. From the data that were collected, the following conclusions and recommendations were developed:

Conclusions

1. In most of the precipitation events, episodes of acid rain ($pH < 5.6$) were observed. The most acidic of these ($pH = 3.9$) occurred on a stormy day in May 1984.

2. The acid-forming anions in precipitation were sulfate and nitrate. Sulfuric acid, however, contributed more to the total deposition than did nitric acid.

3. The peak of acidity in precipitation also occurred

most frequently during the low ammonium ion concentration. Therefore, the ammonium ion could be at least partly responsible for the reduction in precipitation acidity.

4. The lower acidity of the lakewater may also exist because of neutralization with Ca^{2+} that is four times greater in Michigan's rains than in that of many other states.

In studying the alteration of lakewaters because of acid precipitation, the following conclusions emerged:

1. Asylum and Bonnie Castle Lakes illustrated the complexity of acid-rain effects. The waters of Bonnie Castle remained neutral whereas those of Asylum were alkaline.

2. The pH level of Asylum Lake ranged from 7.0-9.05, and the pH level of Bonnie Castle Lake varied from 5.9-7.9. This indicated that the acidity of precipitation was 800-1000 times greater than the water of Asylum Lake and 200-300 times greater than that of Bonnie Castle Lake.

3. Ca^{2+} was present in significantly higher concentrations in Asylum Lake than in Bonnie Castle Lake. The higher concentrations of Ca^{2+} may be an indication of the groundwater flow characteristics that surround Asylum Lake.

In contrast to Asylum Lake, Bonnie Castle Lake with less basicity, had concentrations of Ca^{2+} that were relatively similar to those in the precipitation.

Therefore, the diluting effects of precipitation, coupled with the absence of any contribution from hardwater sources such as groundwater, may be important in the water chemistry of Bonnie Castle Lake. Asylum Lake, in contrast to Bonnie Castle Lake, did not receive a substantial portion of its total input as direct precipitation.

4. The significantly higher concentrations of sulfate in Asylum Lake than in Bonnie Castle Lake could be again another indication of groundwater flow with its high sulfate concentrations around Asylum Lake. Sulfate is, however, more important than nitrate in promoting acidification of both lakes.

5. Values for metal concentrations obtained using the PIXE process were higher than those obtained by the AA method. This might be expected since the PIXE process is more sensitive to all forms of the elements under investigation than the AA method. Thus the data used for the metal under consideration were those obtained using PIXE.

6. Acidic precipitation was associated with the deposition of heavy metals, resulting in the elevation of their concentrations in both lakes. Among these heavy metals were Zn, Cu, Fe, and Pb.

7. Zn and Fe, with the highest concentrations of heavy metals, were considered to be major elements present in precipitation.

8. The elevated concentrations of heavy metals and

other substances for all samples in precipitation and lakewaters during winter and after snowmelt may occur because of increased weathering of the soil. Thus solubility due to acidification of soils and lakes may be a factor.

9. The concentrations of all metals except Cu were higher in the solid phases, sediment and /or vegetation, than in the lakewater.

Recommendations

1. It is possible that there are factors other then those investigated in this study that might play important roles in controlling the enrichment of certain elements in the study lakes. Therefore, additional research is desirable to try to resolve the uncertainties about the nature, causes, extent, and effects of acid rain in the study area.

2. If the combustion of fossil fuels is assumed to be the primary cause of acid precipitation, emissions of sulfur and nitrogen oxides can be reduced in various ways. Some methods of reducing the level of these emissions include energy conservation which could result in reduced fuel consumption, changing combustion processes to reduce emissions, and substituting alternatives for the production of energy. These latter substitutions could include the construction of nuclear reactors and site development

of renewable energy sources that do not involve combustion as substitutes for our present use of fossil fuels.

3. The most important aspect of the acid precipitation problem is a clear demonstration of the interconnection among air, land, and water. Further study of these vital linkages is needed for the management of environmental problems.

APPENDIX A

Chemical Parameters Measured in the Preliminary Study of Precipitation

Date \ ppm	Nitrate	Nitrite	Ortho-phosphate	Sulfate	Sulfide
Oct. 8	1.70	.012	.18	4.0	.001
12	1.70	.008	.22	3.0	.020
13	.72	.012	.11	4.0	.030
22	1.00	.005	.22	7.0	.002
23	2.10	.022	.21	7.5	0.0
Nov. 2	1.16	.015	.25	.5	.025
11	1.35	.002	.10	2.0	.025
15	1.90	.017	.12	4.0	.010
19	1.10	.007	.26	2.0	0.0
27	1.00	.012	.49	3.0	0.0
28	.90	.012	.26	3.0	.005
Dec. 2	1.80	.012	.20	.5	.010
6	1.00	.033	.25	2.5	.018
8	1.65	.012	.07	6.0	0.0
30	1.50	.019	.09	6.0	.009
Jan. 18	2.80	.010	.07	3.0	.010
19	2.40	.020	.10	4.0	.010
Feb. 7	2.20	.010	.17	2.0	.020
9	1.80	.029	.14	3.0	.010
18	1.90	.018	.12	3.0	.015
27	1.10	.016	.22	11.0	.010
Mar. 6	2.80	.012	.32	11.0	.006
12	1.20	.015	.21	5.0	0.0
16	1.00	.005	.11	2.0	0.0
21	1.25	.006	.10	.75	.040
Apr. 3	2.00	.015	.45	4.0	0.0
4	.90	.045	.29	5.0	.018
12	1.40	.019	.19	0.0	.010
14	1.45	.005	.46	0.0	.005
17	1.20	.010	.10	6.0	0.0
19	2.70	.006	.27	2.0	.020
22	1.00	.005	.12	6.0	.020
May 18	1.45	.007	.43	2.0	.020
19	1.50	.008	.19	2.0	.010
22	.75	.008	.10	1.5	0.0
25	1.40	.012	.36	4.0	.020
28	.80	.008	.12	6.0	.025
June 5	1.20	.012	.25	2.0	.010
23	.90	.008	.22	2.5	.008
July 9	1.20	.008	.19	2.0	.005

Chemical Parameters Measured in the Preliminary Study of Precipitation

Date \ ppm	Ammonia Nitrogen	Iron	Manganese
Oct. 8	1.80	.07	.015
12	1.18	.11	.600
13	.12	.05	.700
22	.48	.04	.005
23	1.99	.11	.300
Nov. 2	1.90	.04	.150
11	.84	.03	.600
15	.10	.08	1.000
19	1.10	.04	.090
27	.46	.04	.250
28	.64	.02	0.0
Dec. 2	1.00	.05	.500
6	.79	.05	.050
8	.58	.01	.200
30	.55	.16	.500
Jan. 18	1.95	.06	.200
19	1.65	.10	.200
Feb. 7	.85	.09	.250
9	2.00	.10	.150
18	1.10	.10	.400
27	1.21	.55	.800
Mar. 6	1.75	.18	.700
12	.50	.12	.100
16	.31	.03	0.0
21	.80	.01	.150
Apr. 3	1.55	.02	.080
4	.85	.04	.130
12	1.20	.10	0.0
14	1.95	.10	.210
17	.50	.06	.050
19	1.30	.10	.010
22	.709	.10	.250
May 18	1.50	.04	.150
19	.50	.04	.100
22	.40	.05	.100
25	1.40	.02	.300
28	.85	.07	.050
June 5	1.40	.05	.050
23	1.12	.07	.050
July 9	2.00	.08	.060

APPENDIX B

Chemical Parameters Measured in the Preliminary Study of Bonnie Castle Lake.

ppm Date	Nitrate	Nitrite	Ortho-phosphate	Sulfate	Sulfide
Oct. 6	1.10	.017	.100	2.5	.015
10	.93	.009	.110	5.5	.001
16	.88	.002	.060	5.8	0.0
23	.82	.010	.100	1.5	.003
Nov. 1	.63	.007	.100	3.0	0.0
6	.60	.010	.100	4.5	.002
13	.75	.006	.100	2.5	.003
20	.75	.011	.120	1.8	.003
Dec. 4	.60	.014	.040	3.0	.004
19	.50	.016	.040	4.0	.006
Jan. 7	2.35	.010	.130	2.0	.006
20	.95	.007	.050	2.0	.006
Feb. 5	1.40	.006	.070	2.0	.020
19	.60	.008	.010	3.0	0.0
Mar. 19	.40	.006	.020	7.5	0.0
24	.45	.002	.120	2.0	.030
Apr. 8	.60	.004	.010	0.0	.010
22	.50	.002	.095	1.5	.005
May 20	.40	.004	.100	0.0	.002
28	.65	.003	.070	0.0	.002
June 5	.50	.002	.030	0.0	.005
13	.50	.003	.060	0.0	.008
20	.45	.003	.035	0.0	0.0
28	.60	.002	.085	0.0	.020
July 9	.75	.007	.030	2.0	.020
20	.85	.008	.010	2.0	.020

Chemical Parameters Measured in the Preliminary Study of Bonnie Castle Lake

Date \ ppm		Ammonia Nitrogen	Iron	Manganese	Carbon Dioxide	Dissolved Oxygen
Oct.	6	.20	.060	0.0	10.0	10.50
	10	.17	.065	.018	10.5	12.75
	16	.37	.030	.430	15.0	8.00
	23	.12	.018	.210	12.0	8.50
Nov.	1	.11	.048	.330	12.0	13.25
	6	.24	.050	.014	13.0	12.75
	13	.11	.015	.260	10.5	13.25
	20	.24	.035	.320	9.5	13.50
Dec.	4	.20	.090	.150	8.0	14.00
	19	.19	.110	.150	10.0	16.00
Jan.	7	.18	.050	.500	9.0	13.50
	20	.22	.050	.150	11.0	13.25
Feb.	5	.40	.020	.350	7.0	11.25
	19	.25	.110	.025	7.5	12.00
Mar.	19	.18	.390	0.0	6.5	14.00
	24	.15	.190	.005	6.0	14.25
Apr.	8	.18	.095	0.0	6.0	12.25
	22	.29	.090	0.0	8.0	13.75
May	20	.05	.100	.060	9.0	7.25
	28	.22	.080	0.0	8.0	10.75
June	5	.22	.090	.050	11.0	9.00
	13	.20	.070	.060	10.0	8.75
	20	.40	.060	.450	11.5	8.75
	28	.20	.050	0.0	11.0	9.75
July	9	.24	.050	0.0	12.0	8.00
	20	.26	.050	.160	12.5	7.50

APPENDIX C

Chemical Parameters Measured in the Preliminary Study of Asylum Lake

ppm Date	Nitrate	Nitrite	Ortho-phosphate	Sulfate	Sulfide
Oct. 6	.85	.007	.016	15.50	.026
10	.80	.005	.009	17.50	.002
16	.73	.010	.063	15.25	0.0
23	.38	.012	.073	13.75	.003
Nov. 1	.58	.014	.083	12.25	0.0
6	.58	.006	.070	12.75	.002
13	.33	.015	.065	15.50	.008
20	.45	.015	.080	15.75	.002
Dec. 4	.55	.016	.190	17.50	.001
19	.65	.019	.210	18.00	.001
Jan. 7	2.25	.021	.310	21.00	.006
20	.65	.021	.080	16.00	.008
Feb. 5	.60	.004	.120	15.00	.020
19	.50	.005	.070	8.00	.020
Mar. 19	.48	.011	.080	12.00	.010
24	.50	.010	.170	12.00	.016
Apr. 8	.40	.010	.010	12.00	.009
22	.40	.007	.050	14.00	.010
May 20	.40	.007	.220	12.00	.005
28	.60	.006	.010	11.00	.020
June 5	.50	.010	.050	12.00	.015
13	.50	.006	.120	12.00	.017
20	.50	.001	.200	14.00	.013
28	.55	.004	.120	12.00	.015
July 9	.65	.002	.055	12.00	.010
20	.55	.002	.065	12.00	.010

Chemical Parameters Measured in the Preliminary Study of Asylum Lake

Date \ ppm	Ammonia Nitrogen	Iron	Manganese	Carbon Dioxide	Dissolved Oxygen
Oct. 6	.195	.050	.150	26	12.25
10	.200	.050	.023	24	14.00
16	.350	.006	.280	24	10.75
23	.225	.075	.150	23	8.50
Nov. 1	.185	.085	.450	23	11.00
6	.275	.008	.045	25	14.75
13	.270	0.0	.128	24	10.25
20	.550	.040	.075	22	9.75
Dec. 4	.750	.009	.150	21	13.25
19	.650	.011	.170	20	12.50
Jan. 7	.300	.012	.250	24	11.75
20	.400	.010	.150	23	11.25
Feb. 5	.900	0.0	.150	21	13.75
19	.350	.080	.010	19	10.75
Mar. 19	.280	.080	.010	14	15.00
24	.180	.200	.030	14	15.00
Apr. 8	.200	.080	0.0	14	14.75
22	.150	.120	.150	15	13.75
May 20	.220	.150	.180	16	13.50
28	.100	.065	.180	14	14.00
June 5	.150	.090	.030	18	11.00
13	.100	.040	.050	14	11.25
20	.120	.020	.150	18	9.00
28	.110	.040	0.0	15	12.25
July 9	.200	.016	.100	17	11.00
20	.180	.014	.100	18	12.00

APPENDIX D

Weekly Concentrations of Metals by PIXE in Precipitation

Date		Metal (mg/L)			
	K	Ca	Mn	Fe	Cu
Oct. 8	17.45	8.66	.012	.108	.009
12	2.71	10.79	.018	.048	.026
13	.83	4.82	.005	.056	.001
22	0.0	5.17	.001	.065	.010
23	.06	7.30	.001	.060	.020
Nov. 2	7.64	17.59	.011	.050	.017
11	18.21	3.76	.004	.014	.005
15	1.85	8.93	.002	.058	.004
19	.11	2.90	.002	.014	.003
27	6.85	7.60	.007	.055	.004
28	6.80	8.20	.013	.050	.005
Dec. 2	3.63	11.10	.018	.062	.006
6	2.52	10.05	.002	.099	.014
8	11.73	10.00	.021	.026	.002
30	5.96	3.87	.002	.056	.004
Jan. 18	3.83	5.83	.004	.041	.012
19	5.56	26.68	.092	.112	.014
Feb. 7	8.94	16.25	.009	.129	.035
9	10.00	37.65	.035	.071	.018
18	5.88	34.45	.016	.136	.018
27	8.27	29.45	.030	.106	.049
Mar. 6	7.80	33.67	.024	.043	.032
12	13.40	58.33	.052	.028	.026
16	5.48	30.14	.007	.100	.045
21	4.86	12.54	.014	.018	.015
Apr. 3	7.47	11.32	.005	.031	.056
4	5.89	26.38	.011	.008	.008
12	7.10	24.37	.018	.038	.036
14	1.95	13.31	.011	.032	.005
17	1.04	3.30	.002	.065	.012
19	7.83	30.11	.031	.060	.016
22	7.00	17.90	.011		
May 18	6.55	33.27	.037	.059	.011
19	1.35	3.51	.004	.030	.010
22	4.10	8.93	.016	.014	.015
25	6.97	12.15	.037	.036	.012
28	4.12	14.12	.016	.030	.010
June 5	4.10	8.93	.016	.014	.015
23	4.90	12.15	.019	.036	.012
July 9	5.10	10.54	.012	.038	.010

Weekly Concentrations of Metals by PIXE in Precipitation

Date	Metal (mg/L)			
	Zn	Pb	Br	Sr
Oct. 8	.016	.002	.004	.002
12	.067	.001	.005	.003
13	.014	.011	.004	.001
22	.023	.010	.010	.008
23	.015	.008	.005	.005
Nov. 2	.032	.021	.008	.004
11	.010	.011	.007	.008
15	.018	.012	.002	.001
19	.008	.001	.003	.002
27	.019	.012	.004	.014
28	.010	.011	.003	.010
Dec. 2	.031	.018	.005	.006
6	.013	.004	.009	.004
8	.022	.024	.007	.019
30	.018	.011	.004	.003
Jan. 18	.037	.014	.006	.001
19	.075	.009	.008	.006
Feb. 7	.100	.019	.014	.004
9	.036	.019	.015	.004
18	.110	.025	.013	.007
27	.135	.018	.012	.010
Mar. 6	.077	.007	.010	.005
12	.100	.005	.019	.014
16	.107	.004	.012	.002
21	.041	.008	.005	.003
Apr. 3	.030	.002	.007	.010
4	.013	.007	.010	.012
12	.135	.002	.008	.006
14	.020	.007	.004	.001
17	.092	.015	.007	.002
19	.052	.022	.010	.010
22				
May 18	.047	.007	.010	.004
19	.033	.006	.003	.006
22	.045	.003	.007	.005
25	.023	.010	.006	.005
28	.030	.006	.005	.004
June 5	.045	.003	.008	.008
23	.029	.007	.008	.006
July 9	.026	.006	.006	.005

APPENDIX E

Weekly Concentration of Metals by PIXE in Bonnie Castle Lakewater.

Date	Metal (mg/L)				
	K	Ca	Mn	Fe	Cu
Oct. 6	3.70	85.96	.003	.065	.005
10	2.48	80.00	.006	.067	.003
16	11.10	131.18	.004	.094	.003
23	7.75	50.12	.030	.140	.004
Nov. 1	15.76	187.15	.007	.104	.006
6	11.27	161.50	.009	.042	.003
13	14.93	166.80	.035	.081	.002
20	12.68	179.78	.060	.071	.004
Dec. 4	16.20	178.40	.007	.100	.003
19	18.27	196.50	.009	.100	.001
Jan. 7	16.21	144.84	.015	.056	.004
20	13.29	126.95	.033	.182	.023
Feb. 5	19.66	192.28	.037	.430	.004
19	11.96	69.55	.025	.194	.003
Mar. 19	16.66	142.91	.006	.120	.009
24	13.04	56.86	.006	.127	.018
Apr. 8	17.54	159.69	.005	.108	.008
22	13.94	103.55	.024	.284	.008
May 20	8.14	38.57	.008	.075	.003
28	10.10	82.69	.014	.184	.006
June 5	8.07	40.11	.014	.156	.002
13	10.10	38.14	.015	.144	.003
20	4.15	84.85	.019	.068	.007
28	4.41	79.36	.022	.064	.006
July 9	4.43	54.44	.010	.091	.004
20	4.40	59.20	.007	.072	.006

Weekly Concentration of Metals by PIXE in Bonnie Castle Lake.

	Metal (mg/L)			
Date	Zn	Pb	Br	Sr
Oct. 6	.005	.001	.002	.016
10	.007	.001	.002	.008
16	.010	.003	.006	.015
23	.014	.003	.004	.005
Nov. 1	.021	.008	.010	.025
6	.007	.002	.010	.022
13	.007	.004	.008	.027
20	.010	.006	.007	.021
Dec. 4	.006	.001	.010	.022
19	.006	.001	.011	.027
Jan. 7	.029	.003	.009	.020
20	.063	.007	.010	.023
Feb. 5	.020	.005	.011	.028
19	.018	.006	.006	.010
Mar. 19	.011	.002	.011	.014
24	.028	.012	.011	.007
Apr. 8	.010	.004	.011	.010
22	.009	.003	.010	.011
May 20	.051	.020	.005	.005
28	.014	.023	.004	.005
			004	
June 5	.047	.030	.003	.006
13	.010	.029	.004	.004
20	.038	.020	.002	.005
28	.012	.019	.008	.004
July 9	.009	.006	.002	.004
20	.011	.003	.003	.004

APPENDIX F

Weekly Concentration of Metals by PIXE in Asylum Lakewater.

Date		Metal (mg/L)			
	K	Ca	Mn	Fe	Cu
Oct. 6	36.91	565.47	.033	.058	.001
10	43.73	504.45	.035	.046	.001
16	42.78	485.15	.051	.045	.001
23	43.38	569.97	.053	.063	0.0
Nov. 1	20.73	556.91	.043	.030	.001
6	46.15	654.73	.065	.041	.001
13	49.13	631.54	.081	.040	0.0
20	32.53	667.95	.085	.055	0.0
Dec. 4	51.18	712.60	.059	.041	.001
19	53.24	752.20	.062	.033	.001
Jan. 7	37.90	793.40	.134	.114	0.0
20	56.92	692.17	.025	.083	.035
Feb. 5	70.40	854.95	.075	.021	.009
19	28.69	253.37	.005	.026	.010
Mar. 19	33.95	224.87	.018	.065	.006
24	20.07	236.19	.028	.193	.014
Apr. 8	26.77	239.78	.013	.125	.021
22	30.83	203.12	.028	.224	.004
May 20	20.78	392.31	.028	.088	.008
28	18.94	201.79	.040	.038	.004
June 5	40.12	422.64	.059	.038	.004
13	40.24	202.15	.060	.032	.004
20	20.96	195.43	.019	.071	.006
28	23.90	201.23	.021	.074	.007
July 9	22.50	341.52	.032	.061	.010
20	23.52	345.15	.036	.066	.009

Weekly Concentration of Metals by PIXE in Asylum Lakewater.

Date		Metal (mg/L)		
	Zn	Pb	Br	Sr
Oct. 6	.010	.003	.001	.187
10	.009	0.0	.085	.167
16	.006	0.0	.110	.106
23	.007	.002	.176	.145
Nov. 1	.008	0.0	.035	.146
6	.007	0.0	.087	.212
13	.004	.004	.045	.169
20	.010	0.0	.064	.143
Dec. 4	.009	0.0	.060	.180
19	.007	.002	.073	.190
Jan. 7	.011	.004	.008	.123
20	.044	.004	.086	.172
Feb. 5	.048	.010	.099	.202
19	.033	.011	.005	.005
Mar. 19	.019	.005	.101	.084
24	.035	.005	.048	.051
Apr. 8	.027	.020	.071	.097
22	.013	.013	.097	.070
May 20	.015	.013	.010	.130
28	.016	.011	.010	.120
June 5	.021	.010	.009	.070
13	.019	.011	.010	.091
20	.018	.010	.010	.120
28	.018	.009	.008	.110
July 9	.021	.009	.008	.100
20	.019	.007	.010	.090

BIBLIOGRAPHY

Allen, W. B., J. B Miller, and W. B. Wood. 1973. Availability of Water in Kalamazoo County, Southwest Michigan. U.S. Geological Survey Water Supply Paper, No. 1973. Washington: Goverment Printing Office.

Almer, B., W. Dickson, C. Ekstrom, E. Hornstone, and U. Miller. 1974. Effects of acidification on Swedish lakes. Ambio. 3:30-36.

Almer, B., W. Dickson, C. Ekstrom, and E. Hornstone. 1978. Sulfur pollution and the aquatic ecosystem. Sulfur in the Environment. Part II. Ecological Impacts. Nriagu, J.O. (ed.). New York: Wiley.

Angyal, J. 1980. Acid rain: The bitter dilemma. Carolina Tips. 43(9): 39-46.

Beamish, R. J. 1976. Acidification of lakes in Canada by acid precipitation and the resulting effects on fishes. Water, Air, and Soil Pollution. 6:501-514.

Beamish, R. J. and H. H. Harvey. 1972. Acidification of the LaCloche Mountain Lakes, Ontario, and resulting fish mortalities. J. Fish. Res. Bd. of Can. 29:1131-1143.

Beamish, R., W. Lockhart, J. VanLoon, and H. Harvey. 1975. Long-term acidification of a Lake and resulting effects on fishes. Ambio. 4:98-102.

Beamish, R. J. and J. C. Van Loon. 1977. Precipitation loading of acid and heavy metals to a small acid lake near Sudbury, Ontario. J. Fish. Res. Bd. Can. 34:649-658.

Born, S. M. and D. A. Stephenson. 1979. Hydrogeology of glacial terrin lakes, with management and planning applications. Journal of Hydrology 43:7-43.

Bryan, G. W. 1971. The effects of heavy metals on marine and estuarine organisms. Proceedings, Royal Society of London, Series B 177:389-410.

Carignan, R. and J. Kalff. 1980. Phosphorus sources for aquatic weeds: Water or sediment? Science 207:987-988.

Conway, H. L., H. L. and G. R. Hendrey. 1982. Ecological effects of acid precipitation on primary producers. Acid Precipitation : Effects on Ecological Systems. Ditri, F. M. (ed.). Ann Arbor: Ann Arbor Science Publishers: Pp. 277-295.

Cowling, E. B. 1980. Acid precipitation and its effects on terrestrial and aquatic ecosystems. Aerosols: Anthropogenic and Natural, Sources and Transport. Kneip, T.J. and P.J. Lioy (eds.). Annals New York Academy of Sciences 338:540-555.

Cronan, C. S. and C. L. Schofield. 1979. Aluminum leaching response to acid precipitation: Effect on high elevation watershed, in the northeast. Science 204:304-305.

Dash, J. M., S. H. Cadle, and Git. Wolff. 1984. Summertime Study of acid deposition in the Detroit area. Water, Air and Soil Pollution 31:51-69.

Davis, A. O. 1979. Lead Accumulation in Lake Sediment. M.S. Thesis, University of Virginia, Charlottesville, Virginia.

Dickson, W. 1975. The acidification of Swedish lakes Inst. Freshw. Res. Drottnigholm Rep. 54:8-20.

Dickson, W. 1980. Properties of acidified water. In International Conf. on Ecological Impacts of Acid Precipitation. Drablos, A. and A. Tollan (eds.). SNSF project. Sandefjord, Norway: Pp. 75-83.

Dillon, P. S., N. D. Yan, W. A. Scheider, and N. Conroy. 1979. Acidic Lakes in Ontario, Canada: Characterization, extent, and response to base and nutrient additions. Arch. Hydrob. Beih. Ergebn. Limnol. 13:317-336.

Douglas, B. E., and D. H. McDaniel. 1965. Concepts and models of inorganic chemistry. Waltham, MA: Wiley.

Eichenlaub, V. L. 1978. Climate. Kalamazoo County, Geology and Environment. Passero, R.N. (ed.). Kalamazoo: Western Michigan University: Pp. 10-16.

Eichenlaub, S. J., G. J. Hollod and S. Langevin. 1978. Precipitation Chemistry and Atmospheric Deposition of Trace Element in Northeastern Minnesota. Minneapolis: Environmental Quality Board.

Eisnereich, S. J., J. D. Thornton, J. W. Munger, and E. Gorham. 1981. Trace metal and strong acid composition of rain and snow in northern Minnesota. Atmospheric Pollutants in Natural Waters. Eisenreich, S. J. (ed.). Ann Arbor: Ann Arbor Science Publishers: Pp. 261-284.

Eisenreich, S. J., G. T. Hollod, and S. Langevien. 1978. Precipitation Chemistry and Atmospheric Deposition of Trace Elements in Northeastern Minnesota. Minneapolis: Envirnomental Quality Board.

Fenner, L. B. 1981. The Hydrologic Factors that Control Carbonate Hardness in Kalamazoo County Lakes, Southwestern Michigan. M.S. Thesis, Western Michigan University, Kalamazoo, Michigan.

Galloway, J. N., G. E. Likens, and E. S. Edgerton. 1976. Acid precipitation in the northern United States: pH and acidity. Science 194:722-724.

Galloway, J. N., S. A. Norton, and M. R. Church. 1983. Freshwater acidification from atmospheric deposition of sulfuric acid: A conceptual model. Environ. Sci. Technol. 17(11):541A-545A.

Giddings, J. C. 1973. Chemistry, Man and Environmental Change: An Integrated Approach. San Francisco: Canfield Press.

Gorham, E. and A. G. Gordon. 1960. Some effects of smelter pollution northeast of Falconbridge, Ontario. Can. J. Bot. 38:307-312.

Gorham, E. 1961. Factors influencing the supply of major ions to inland waters, with special reference to the atmosphere. Bulletin of the Geological Society of America 72:795-840.

Grahn, O., H. Hultberg, and L. Landner. 1974. Oligotrophication--A self-accelerating process in lakes subjected to excessive supply of acid substances. Ambio. 3:93-94.

Grahn, O. 1977. Macrophyte succession in Swedish lakes caused by deposition of airborne acid substances. Water, Air, Soil Pollut. 7:295-306.

Hach DR Colorimeter Methods Manual. 1977. 13 Edition. Loveland, Colorado: Hach Chemical Co.

Hall, R. J., G. E. Likens, S. B. Fiance, and G. R. Hendrey

1980. Experimental acidification of a stream in the Hulbard Brook Experimental Forest, New Hampshire. Ecology 61(4): 976-989.

Hansen, P. 1982. Bitter Rain. Outdoor America 47(1): 6-9.

Harvey, H. H. 1980. Widespread and diverse changes in the biota of North American lakes and rivers coincident with acidification. In International Conf. on Ecology Impact Acid Precipitation. Drablos, D. and A. Tollan (eds.). SNSF project. Sandefjord, Norway: Pp. 93-98.

Harrison, W. B. 1978. Surface Water. Kalamazoo County, Geology and the Environment. Passero, R.N. (ed.). Kalamazoo: Western Michigan University: Pp. 45-52.

Heller, C. F. 1978. Population. Kalamazoo County, Geology and the Environment. Passero, R.N. (ed.). Kalamazoo: Western Michigan University: Pp. 2-4.

Hendrey, G. R. and R. f Wright. 1975. Acid precipitation in Norway: Effects on aquatic fauna. J. Great Lakes Res. 2(1): 192-207.

Hendrey, G. R., K. Baalsrud, T. S. Toraaen, M. Laake, and G. Ruddum. 1976. Acid precipitation: Some hydrobiological changes. Ambio. 5:224-227.

Hendry, C. D. and P. Brezonik. 1980. Chemistry of precipitation at Gainsville, Florida. Environ. Sci. Technol. 14:843-849.

Henriksen, A. and R. Wright. 1977. Effects of acid precipitation on a small acid lake in southern Norway. Nordic Hydrol. 8:1-10.

Henriksen, A. 1982 Changes in Base Cation Concentrations Due to Freshwater Acidification. Report OF-81623. Oslo: Norwegian Institute for Water Research.

Hildebrant, T. A. and J. S. Wood. 1978. Non-Point source pollution affecting Asylum Lake. Kalamazoo County, Geology and Environment. Passero, R.N. (ed.). Kalamazoo: Western Michigan University: Pp. 65-66.

Hultberg, H. 1977. Thermally stratified acid waters in late winter-akey factor inducing self-accelerating process which increase acidification. Water, Air, and Soil Pollut. 7:279-294.

Jackson, T. A., G. Kpphut, R. Hesslein and D. W. Schindler. 1980. Experimental study of trace metal chemistry in soft-water lakes at different pH levels. *Can. J. Fish. Aquat. Sci*. 37:387-402.

Junge, C. E. 1958. The distribution of ammonia and nitrate in rainwater over the United States. *Trans. Am. Geophys. Union* 39:241-248.

Kilham, P. 1982. Acid precipitation: Its role in the alkalization. *Limnol. Oceanogr*. 27(5): 856-867.

Kwiatkowski, R. E. and J. C. Roff. 1976. Effects of acidity on the phytoplankton and primary productivity of selected northern Ontario lakes. *Can. J. Bot*. 54(22): 2546-2561.

Last, T. F., G. E. likens, B. Ulrich, and L. Walloe. 1980. Acid precipitation - Progress and problems. In International Conf. on *Ecological Impact of Acid Precipitation*. Darbolos, D. and A Tollan (eds.). SNSF project, Sandefjord, Norway: Pp. 10-12.

Leupold, M.A. 1985. *Acid Rain*. Rochester, New York: Ward's Natural Science Establishment

Likens, G. E. 1976. Acid precipitation. *Chem. Eng. News* 54(48): 29-44.

Likens, G. E., F. H. Bormann, and N.M. Johnson. 1972. Acid rain. *Environment* 14:33-40.

Likens, G. E. and T. J. Butler. 1981. Recent acidification of precipitation in North America. Atmos. Environ. 15:1103-1109.

Likens, G. E., R. F. Wright, J. N. Galloway, and T. J. Butler. 1979. Acid rain. *Sci. Amer*. 241(4): 43-51.

Loucks, O. L., R. W. Usher, R. W. Millwer, W. Swanson, and D. Rapport. 1981. *Assessment of Sensitivity Measures for Evaluating Resources at risk from Atmospheric Pollutant Deposition*. Final Report to the U.S. Environmental Protection Agency. Indianapolis, Indiana: The Institute of Ecology (TIE).

Messer, J. 1978. *Nitrogen Mass Balance in Florida Ecosystem*. Ph.D. Thesis, University of Florida, Gainsville, Florida.

Moreau, G., C. Barbeau, J. J. Frenette, J. Saint-Onge, and M. Simoneaw. 1983. Zn, Mn, and Sr in opercula and scales of brook trout (*Salvelinus fontinalis*) as indicator of lake acidification. *Can. J. Fish. Aquat. Sci*. 40:1685-1691.

Oden, S. 1976. The acidity problem - An outline of concepts. *Water, Air, Soil, Pollut*. 6:137-166.

Oliver, B. G. and J. R. Kelso. 1983. A role of sediments in retarding the acidification of hardwater lakes. *Water, Air, Soil, Pollut*. 20:379-389.

Overrein, L. N., H. M. Seip, and A. Tollan. 1980. Acid precipitation effects on forest and fish. In *International Conf. on Ecological Impact of Acid Precipitation*. Drablos, A. and A. Tollan (eds.). SNSF project Sandefjord, Norway: Pp. 106-108.

Peterson, I. 1983. Acid lakes and thin soils. *Science News* 123:332-333.

Rosen, W. and P. M. Williams. 1978. Model organo-cupric ion complexes in seawater. *Geochem. J. (Japan)* 12:21.

Rosseland, B. O., I. Sevaldrud, D. Svalastog, and I. P. Muniz. 1980. Studies on freshwater fish population-effects of acidification on reproduction, population structure, growth and food selection. In *International Conf. on Ecological Impact of Acid Precipitation*. Drablos, D. and A. Tollan (eds.). Sandefjord, Norway: Pp. 336-337.

Ryan, P. M. and H. H Haarvey. 1980. Growth responses of yellow perch. *Perca flavescans*, to lake acidification in the Lac loche Mountain Lakes of Ontario. *Environ. Biol. Fish*. 5:97-108.

Schindler, D. W. 1980. Special issue on the experimental lake area. *Can. J. Fish. Auquat. Sci*. 37(3): 313-558.

Schindler, D. W., R. H. Hesslein, R. Wagemann, and W. S. Broecker. 1980. Effects of acidification on mobilization of heavy metals and radionuclides from the sediments of freshwater lake. *Can. J. Fish. Aquat. Sci*. 37(3): 373-377.

Schofield, C. L. 1976. Acid precipitaion: effects on fish. *Ambio*. 5:228-230.

Simms, P. C. and F. A. Rickey. 1978. *The Multielement*

Analysis of Drinking Water Using Proton Induced X-ray Emission (PIXE). EPA-600/1-78-058. Cincinnati, Ohio: Environmental Protection Agency, Office of Research and Development.

Smith, R. A. 1852. On the air and rain of Manchester. Mem. Lit. Phil. Soc. Manchesters (Series 2) 10:207-217.

Smith, R. A. 1872. Air and Rain: The Beginnings of Chemical Climatology. London: Longmans, Greene.

Sparks, D. L. and C. R. Curtis. 1983. An Assessment of Acid Rain on Leaching of Elements from Delaware Soils into Groundwater. U.S. Geological Survey, Water Resources Scientific Information Center, Reston, VA: Water Resource Center Report.

Sutcliffe, D. W. and T. R. Carrick. 1973. Studies on mountain streams in the English Lakes District I. pH, Ca and the distribution of invertebrates in the River Dudden. Freshwater Biology 3:437-462.

Tamm, C. O. 1958. The atmosphere. Handbuch Fur Pflanzen - Physiologie 6:233-242.

U.S. Enviromental Protection Agency. 1979. Methods For Chemical Analysis of Water And Wastes. EPA-600/4-79-020. Cincinnati, Ohio: Environmental Protection Agency.

Wetzel, R. G. 1975. Limnology. Philadelphia: W. B. Saunders Co.

Wiklander, L. 1973. The acidification of soil by acid precipitation. Grund forbattring 26(4): 155-164.

Wright, R. F., T. Dale, E. T. Giessing, G. R. Hendrey, A Henriksen, M. Joannessen, and I. P. Muniz. 1976. Impact of acid precipitation on freshwater ecosystems in Norway. Water. Air. Soil. Pollut. 6:483-499.

Wright, R. F. and E. T. Giessing. 1976. Acid precipitation: Changes in the chemical composition of lakes. Ambio. 5:219-223.

Yan, N., W. Scheider, and P. Dillon. 1977. Chemical and biological changes in Nelson Lake Ontario. Water Pollut. Res. Can. 12:213-231.

Yan, N. and P. M. Stokes. 1978. Phytoplankton of an acid lake and responses to experimental alteration of pH. Environ. Conserv. 5:1-8.