

Seasonal variation of lake water quality: Influence of colloidal suspended solids
and water chemistry in selected Iowa lakes

by

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This is to certify that the Master's thesis of
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Signatures have been redacted for privacy

TO MY FAMILY

This thesis is dedicated to Fanile and my twins Lukani and Zibo. I thank you for giving me all the support and inspiration to face the challenging world of graduate studies. Your love and care helped me sail through and finished what I started.

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GENERAL INTRODUCTION

The State of Iowa is comprised of 145,730 square kilometers, primarily of rolling prairie, located in the middle latitudes between the Upper Mississippi and the Missouri rivers. The climate of the State is marked by seasonal variations, with average seasonal snowfall in the range of 630 – 1100 mm and average annual precipitation around 838 mm (Pesek, 1996). Floods are most frequent in June, maximum rainfall period, but can also occur in March. The growing season extends from early May to early October. Iowa is primarily an agricultural state and the combination of climate, soils, and technology has made it a U.S leader in certain agricultural products.

The rate of soil fertilization in Iowa increased abruptly in the early 1940s from approximately 40,000 tons/year to 450,000 tons/year. Up to 1940, the applied form of nitrogen (N) was Chilean nitrate (NaNO_3) and from 1940 up to early 1950s it was ammonium nitrate (NH_4NO_3). From the early 1950s onwards, anhydrous ammonia became the main source of agricultural N for most farmers in Iowa (personal communication with the Leopold Center, Iowa State University, 2001 and Iowa State University Extension, 2001). The use and chemical composition of manure may also have changed over the years due to the changes in size of animal feed operations as well as changes in animal feed ingredients (personal communication with Iowa State University Extension, Iowa, 2001). It can be hypothesized that the soil-derived sediments from these fertilized and manured fields, deposited into Iowa lakes would exhibit unique chemical compositions depending on fertilizer type, chemical form, quantity, and general land management practices.

In recent years, the development of *hypoxia* in the Gulf of Mexico has been attributed to nutrients derived from agriculturally managed land in the Mississippi River basin, which includes the state of Iowa (Goolsby, 1999; 2001). Hypoxia is a condition of low dissolved oxygen in a water system resulting in change in the trophic status of that system, such as loss of aquatic animals and, release of many materials normally bound to lake-bottom sediments. This often leads to what is termed **eutrophication**. Eutrophication is over-enrichment of receiving waters with mineral nutrients such as phosphorus (P), nitrogen (N) and others resulting in depletion of dissolved oxygen. There are several factors that might lead to this oxygen depletion, a major one being decomposition of organic matter present in the lake-bottom (US EPA, 1996; Correll, 1998; Sharpley, 1998). The US EPA (1996) maintains that eutrophication is a critical problem in most surface waters having impaired water quality, with agriculture being the major source of causative nutrients in 50% of the lakes.

The potential for lakes to become eutrophic appears to depend on the availability of nutrients, sunlight and even the potential of lake-sediments (colloids) to undergo dispersion. Nitrogen and P are two key nutrients that stimulate algal growth with P being the most limiting factor in freshwater systems like lakes (Downing, 1997; Correll, 1998). According to Rabalais et al. (2001), the evidence of increased eutrophication and hypoxia in the Mississippi river delta show a temporal pattern that is paralleled by increased N loads. Marine scientists and geologists have argued that the primary sources of N and P in the Gulf waters are agricultural watersheds in the Midwest (Goolsby et al., 1999). The U.S. Geological Survey estimated that 61% of the nitrogen flux from the Mississippi River basin to the Gulf of Mexico (1980-1996) occurred as nitrate-N, 2% as ammonium-N, 24% as dissolved organic N, and 13 % as particulate organic N (Goolsby et al., 1999). It is assumed that

particulate organic N refers to solid organic particles suspended in water. All these N inputs were attributed to Iowa, Illinois, Indiana, Minnesota and Ohio basins (Goolsby, 2001). It is reasonable to hypothesize that a portion of P and nitrate-N in stream, river water and lakes are the products of in-stream mineralization of dissolved organic P and N, particulate organic matter that is associated with eroded sediments, and nitrification of ammonium-N associated with the charged colloidal particles.

Phosphorus (P) is an important element in plant nutrition, very dynamic and, biologically active. Phosphorus is often not readily available to plants, since added P to soils results in transformation to other less soluble compounds decreasing P bioavailability. Inorganic P can be derived from chemical fertilizers and animal manure (Logan, 1982; Cassell et al., 1998). Initially, the majority of P would be expected to be in the organic form. However, various type of inputs in a receiving body of water the particulates may release inorganic and organic P in the surface water (epilimnion) and various organic P compounds may chemically or enzymatically transform to inorganic P forms through hydrolysis and oxidation. Inorganic P (PO_4) becomes associated chemically with the various soil mineral surfaces and/or precipitates as metal-phosphate (Stumm and Morgan, 1981 pp. 374-382; Correll, 1998; US EPA 1996). Organic and inorganic particulates may be deposited in the bottom sediments, where they are gradually broken down by microbes, ultimately releasing much of the confined P in these sediments into the lake-water as orthophosphate or PO_4 (Logan, 1982; Correll, 1998). Hence any excess P added to a hydro-ecosystem, such as lake-water, will result in pollution that may contribute to eutrophication (Correll, 1998). This project was aimed at elucidating the different forms of N and P in both the lake-water column

and lake-bottom sediments and to determine some of the reactions that might be responsible for N and P release.

Another factor that indirectly may contribute to hypoxia is soil erosion (US EPA 1996 reports). Soil erosion causes sedimentation in ditches, ponds, lakes, and streams and decreases soil fertility due to poorer physical properties of soil that remains at an eroded site (Prato and Wu, 1991; Muller et al., 1998). Fine particles near the soil surface are commonly preferentially eroded (Stumm and Morgan, 1981 p. 669; Meybeck et al., 1989 p. 306). Final destination of these fine particles, are lakes, streams, rivers and finally the Gulf of Mexico (USEPA, 1997; Rabalais et al., 2001; Goolsby et al., 1999). The first step in erosion of soil particles is dispersion and suspension in rainwater that moves across the land-surface during a storm (Stumm and Morgan, 1981 p. 669 & p. 735; Thomas and Meybeck 1997 p. 127; Goolsby et al., 1999). These suspended sediments are then discharged into lakes and rivers. Any seasonal variation in water quality is expected to influence the physical, chemical, and biological properties of sediments in lakes (USEPA, 1997; Meybeck and Helmer, 1989). Variation in water quality parameters would be due to factors like climate, geology, anthropogenic inputs, surface runoff to name a few. Seasonal water quality variation would be controlled by land-fertilization practices, natural and human disturbances of land, and evapotranspiration (Koryak et al. 1998; Neal et al., 1998; Jordan et al., 1997).

Based on the above, it is important that we study the behavior of major constituents in lake-water and lake-sediments, especially $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$. An assessment of these nutrients, quantity and quality, in lake-water and lake-sediments can serve as a tool to enable us to model their stability and dispersability. The nutrients loads would be investigated with respect to their sorption/desorption behavior (Evangelou, 1998 and references therein), which

can ultimately enable us to predict availability to aquatic plants and/or other aquatic organisms (Downing and McCauley, 1992; Downing 1997).

Hypothesis and Objectives

The main purpose of this study was to assess variations in concentration of major nutrient ions in four Iowa lake-waters due to differences in geology, vegetation, and land use and, to determine the influence of lake-water composition on colloidal suspended solids. On the basis of the above, the following hypothesis was formulated: Water quality in some Iowa lakes is influenced by fluctuations in solution components and suspended solids, which would appear to have a natural or anthropogenic source, depending on land-use management practices. In order to test this hypothesis, the following objectives were proposed.

- I. Evaluate seasonal fluctuations in ionic composition of lake water.
- II. Evaluate the relationship between ionic composition of lake water and dispersed solids.
- III. Evaluate sediment composition with respect to mineralogy and extractable nutrients.
- IV. Evaluate the potential epilimnion nutrient-sediment loads with respect to lake eutrophication potential.

Thesis Layout

This thesis is arranged into three major parts. The first part deals with solution (lake-water) and solid (lake-sediments) phase characterization. The second part deals with potential suspended colloidal solids and their potential influence on the chemistry of lake-water. Finally, the third part deals with the relationship(s) between the chemistry of lake-

water and colloidal lake- sediments. Overall the study attempted to demonstrate that lake-water chemistry and lake-sediment dispersion/flocculation behavior are interrelated and that, dispersion/flocculation behavior of lake-sediments are related to chemical forms of some nutrients which contribute to lake eutrophication.

In explaining some physical processes taking place in lakes some information was taken from Dr. V.P. Evangelou's (my major professor) text-book (Evangelou, 1998) with permission.

LITERATURE REVIEW

A lake may be defined as an enclosed body of water (usually freshwater), totally surrounded by land and with no direct access to the sea (Wetzel, 1983). Lakes provide a multitude of uses ranging from municipal water supply, navigation, commercial and recreation to name but a few. Lakes can be natural or man-made and most consist of two major regions, the epilimnion and the hypolimnion. The epilimnion is the upper, less dense and warmer layer whereas the hypolimnion is commonly deeper, denser and cooler. Good water quality in lakes is essential for sustaining the intended uses.

Water quality of natural bodies of water, e.g., lakes, is defined by a set of parameters which include concentration of chemical species, dispersed solids, physical partitioning of inorganic and organic substances or chemical species, biological composition and its variations due to natural and anthropogenic inputs (USEPA, 1997; Meybeck and Helmer, 1989). Therefore, water quality is defined by the condition of the water in a natural system. Technically, water quality encompasses dissolved inorganic ions represented by metals and non-metals or metalloids (e.g., Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , Na^+ , Cl^- , SO_4^{2-} ; NO_3^- , H_2PO_4^- / HPO_4^{2-} which may also be classified as plant nutrients), heavy metals and toxic metalloids (e.g., Zn^+ , Cd^{2+} , Cu^{2+} , HSeO_4^{2-} , HAsO_4^{3-}), man-made organic pollutants (e.g., chlorinated hydrocarbons), colloidal suspended solids and, microbes and viruses (EPA, 1996; WHO, 1984 p. 188 & p. 335).

Anthropogenic inputs due to world industrialization have made it difficult to maintain acceptable natural water quality. Therefore, it has become necessary for government agencies to intervene, hence the US EPA has set up rules and regulations defining and

controlling water quality through the Safe Drinking Water Act (SDWA, 1974, amended in 1986). Furthermore, the Clean Water Act requires that each state should prepare a biennial report on the quality of its water resources as the principal way of relating water quality information to the EPA and the US Congress. Two types of water quality standards have been developed and are referred to as primary and secondary standards. Primary standards refer to those contaminants believed to induce acute or chronic effects, whereas secondary ones deal with aesthetic needs like, odor, taste, color and appearance. The so-called critical contaminant thresholds set by EPA are given in Table 1 and 2 (US EPA, 1996).

Water quality is therefore an overall characterization of the physical, chemical and biological nature of a given water sample. One of the major concerns on water quality in natural systems, e.g., lakes, is the potential of such waters to be ecologically unbalanced and hence fail to maintain an environment where a diversity of organisms sustain normal life cycles. The potential of such waters to maintain an ecologically balanced environment is threatened by agricultural, industrial and urban runoff which may include large inputs of phosphate, nitrogen, pesticides, soap by-products, and de-icing salts like sodium chloride (NaCl), calcium chloride (CaCl₂) and others (Koryak et al., 1998; Neal et al., 1998; Jordan et al., 1997).

Natural water bodies are expected to exhibit a certain buffering capacity with respect to chemical constituents present in water. This study looks at the buffering capacity of four lakes, how it is being generated, and how it influences water quality. Other components that were closely scrutinized in this study were alkalinity, dissolved salts, phosphate, nitrogen, and total suspended solids.

Table 1. National Primary Drinking Water Standards §

Contaminant	Maximum Contaminant Level Goal (MCLG)^a	Maximum Contaminant Level (MCL)^b
Arsenic	none	0.05
Barium	2	2
Cadmium	0.005	0.005
Chromium (total)	0.1	0.1
Copper	1.3	TT ^c action level = 1.3
Lead	Zero	TT action level = 0.015
Nitrate-N	10	10
Nitrite-N	1	1
Selenium	0.05	0.05
Turbidity ^d	5	1
Aluminum	none	none
Nickel	none	none

§ All units are in milligrams per liter unless otherwise stated (EPA website).

^a MCLG is the level of contaminant in drinking water below which there is no known or expected risk to health.

MCLGs allow for a margin of safety and are non-enforceable public health goals.

^b MCL is the highest level of a contaminant that is allowed in drinking water.

MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable.

^c TT = Treatment Technique is a required process intended to reduce the level of a contaminant in drinking water.

^d Units are nephelometric turbidity units (NTU); In Iowa, systems that filter must ensure that the turbidity (cloudiness of water) go no higher than 1 NTU in at least 95% of the daily samples in any month. As of January 1, 2002, turbidity may never exceed 1 NTU, and must not exceed 0.3 NTU in 95% of the daily samples in any month.

Table 2. National Secondary Drinking Water Standards §

Contaminant	Maximum Contaminant Level (MCL) ^a
pH	Range 6.5 – 8.5
Color	10 colorimetric units
Taste ^b	Aesthetic need
Aluminum	0.05 – 0.2 mg L ⁻¹
Chloride	250 mg L ⁻¹
Color	15 (color units)
Copper	1.0 mg L ⁻¹
Iron	0.3 mg L ⁻¹
Manganese	0.05 mg L ⁻¹
Silver	0.10 mg L ⁻¹
Sodium	50 mg L ⁻¹
Sulfate	250 mg L ⁻¹
Suspended Solids	35 mg L ⁻¹
Odor	3 threshold odor number
Total dissolved Solids	500 mg L ⁻¹
Zinc	5.0 mg L ⁻¹

§ All units are in milligrams per liter unless otherwise stated.

(EPA website: www.epa.gov/OGWDW/wot/appa and Evangelou, 1998 pp. 488-491).

^a MCL is the highest level of a contaminant that is allowed in drinking water.

MCLs are enforceable standards.

^b Taste depends on an individual.

Relationship(s) between some of these components were established and the influence of temperature due to seasonal changes was examined. Below, an outline illustrating how temperature can influence processes like microbial growth and mineral solubility (precipitation/dissolution) were presented.

Temperature Effects

In Iowa as the season progresses towards summer an elevation in temperature is observed which affects microbial processes as well as chemical processes. Commonly, the latter are affected less than the former. Rate constant of a homogeneous reaction on temperature, can be expressed by the Arrhenius equation developed by Arrhenius in 1889 (Stumm and Morgan, 1981 pp 95-96). In the case of microbial processes, the Arrhenius equation can be used as an index of microbial activity and is given as:

$$k = A e^{-E_a/RT} \quad [1]$$

where 'k' is defined as the rate constant of a particular microbial reaction representing a particular catabolic process, R the gas constant (8.314 kJ/mol) and T the absolute temperature (K). The rate constant, 'k' is related to the Arrhenius constant A which is defined as the maximum k attained as temperature approaches infinity, and E_a (kJ/mol) is the activation energy, unique to a particular reaction and independent of temperature (Stumm and Morgan, 1981 p. 96). The Arrhenius equation becomes more useful when linearized by taking the natural logarithm on both sides of the equation (Evangelou, 1998 p. 313), thus yielding

$$\ln k = \ln A - E_a/RT \quad [2]$$

However, the most commonly used equation is obtained by converting equation [2] to base 10, yielding

$$\text{Log } k = (-E_a/2.303 R) (1/T) + \text{log } A \quad [3]$$

which is equivalent to $y = (m) (x) + c$. Thus a plot of $\log k$ versus $1/T$ gives a straight line, the slope of which would be $-E_a/2.303 R$, from which the activation energy for a particular reaction can be calculated. Activation energies less than 42 kJ/mol suggest diffusion controlled reactions (entropy driven) whereas reactions with activation energies higher than 42 kJ/mol suggest chemical reactions (ΔH driven) or surface controlled reactions (Evangelou, 1998 p. 314). The y-intercept would be $\log A$. Equation [1] points out that under constant microbial population, as temperature increases, the rate constant k of the reaction increases. Furthermore as temperature reaches an optimum level microbial population growth also increases, which also influences the rate of reaction. Commonly, microbial reactions experience a doubling of the reaction rate for each 10-degree increase in temperature, up to a given temperature maximum.

In the case of dissolution/precipitation reactions, e.g., Ca^{2+} and HPO_4^{2-} temperature also has an influence. Ion concentration is controlled by the so-called solubility product constant K_{sp} , of the particular mineral, e.g., CaHPO_4^{2-} . The latter's magnitude depends on two factors. One factor is temperature, and the second factor is ionic strength (Stumm and Morgan, 1996 pp. 355-357). The temperature's influence on solubility can be demonstrated as follows:

$$\Delta G^\circ = -RT \ln K_{sp} \quad [4]$$

and

$$K_{sp} = \exp (-\Delta G^\circ /RT) \quad [5]$$

where ΔG° is Gibbs free energy at the standard state, R is the universal gas constant and T is temperature in Kelvin. Equation [5] reveals that if the ΔG° of a solubility reaction increases at a lower rate than that of temperature, then Ksp increases and as temperature increases and Ca^{2+} and HPO_4^{2-} in solution increase as well. On the other hand, if ΔG° increases at a higher rate than that of temperature, then Ksp decreases as temperature increases and Ca^{2+} and HPO_4^{2-} in solution decrease as well. The second factor's influence on solubility of a particular mineral in freshwater systems, e.g., CaHPO_4 , can be demonstrated by combining the Debye Huckle limiting law with the solubility equation:

$$\text{Log } \gamma_i = A Z^2 \sqrt{I} \quad [6]$$

where γ_i denotes the activity coefficient of an ion in solution and is dependent on A which also depends on temperature (at 25°C is approximately 0.5), Z denotes valence of the cation, and I is the ionic strength of the solution. The latter is related to the electrical conductivity (EC) of the solution (Evangelou and Garyotis, 1985) by the equation

$$I = 0.014 (\text{EC}) \quad [7]$$

where EC is in mmhos cm^{-1} or mS cm^{-1} or dS m^{-1} . Equations [7] and [8] suggest that as EC of the solution, e.g., lake-water increases, γ_i decreases. Incorporating γ_i into the Ksp gives

$$[\text{Ca}^{2+}] = [\text{HPO}_4^{2-}] = [\text{Ksp}]^{1/2} [\gamma_{\text{Ca}}^{1/2} \gamma_{\text{HPO}_4}^{1/2}] \quad [8]$$

As an example, if EC of natural systems increases due to chemical, physical (runoff) or microbial processes, γ_i decreases, and the concentration of Ca^{2+} and HPO_4^{2-} increases (Evangelou, 1998 and references therein). Therefore, solubility of a particular mineral may decrease or increase depending on the overall change in Gibbs free energy (ΔG°) (Stumm

and Morgan, 1996 p. 357). Note however, in the real world a multitude of reactions control concentrations of chemical constituents, not just K_{sp} alone.

Based on the above, temperature influences a number of reactions in lake systems, some of which are dissolution, precipitation, and colloid dispersion. Hence, this project deals with chemistry of lake-sediments (e.g., the sediment's potential to carry inorganic and organic phosphate and ammoniacal nitrogen) and its dispersion potential perhaps due to seasonal fluctuation in lake-water chemistry.

If one starts to describe processes controlling water quality of impoundments or lakes, the spring-flush effect would be an appropriate point to start. The spring flush-effect describes mainly release of various microbial products in soil due to the increase in microbial activity, e.g., increase in plant residue decomposition as temperature increases. This results in the production of dissolved metals, inorganic nitrogen species, phosphate, and sulfate (Goolsby, 2001). Rainfall events carry these products to lakes and/or water impoundments (Stumm and Morgan, 1981 p. 65; Goolsby et al. 1999; US EPA, 1996). As these products accumulate in lakes or water impoundments a number of reactions, e.g., microbiological, chemical, continue to take effect and thus influence water chemistry. Specifically, these reactions may include microbial mineralization/immobilization reactions, sorption/desorption processes and cation exchange reactions. In addition to these reactions/processes, direct contribution of various soluble constituents to lake water or water impoundments may also have effect, e.g., land application of bio-solids, agrochemicals, road winter de-icing salts etc (Koryak et al., 1998).

Some research on influences of catchment area and landscape on the quality of water and sediments in the receiving lakes has been carried out. Mueller et al. (1998) demonstrated

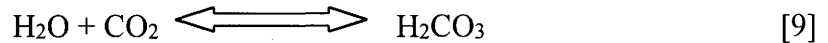
influences of geographic location, vegetation and land use in the catchments with respect to sediment and water quality of small lakes in Central Europe. Furthermore, these researchers established that nutrient loads, e.g., nitrogen and phosphorus increased with increasing agricultural land use and showed that monovalent cations like Na^+ and K^+ in lake-water increased as urban development within the catchment area increased. This suggested that different land-uses exhibited different impacts on lake-water quality.

In another study, involving Mid-western US streams, landscape characteristics that encompassed land-use, land cover and, elevation with respect to their influence on water chemistry were investigated. The stream's major catchment area was dominated by row-crop agriculture (Johnson et.al., 1997). They observed strong seasonal differences in nitrogen loads but not in phosphorus loads or suspended solids, especially during summer time. They further established that all nutrient concentrations were higher in summer than autumn. Johnson et al. (1997) also showed that during summer phosphorus load and suspended solids were influenced by land use within the stream ecotone (riparian zone) compared to nitrogen loads.

Mechanisms of Lake-Water pH Buffering

Alkalinity is a key parameter in all water processes. There are two potential inorganic alkalinity sources in natural systems. One alkalinity source is phosphate (H_2PO_4^- / HPO_4^{2-}), the concentration of which is quite minimal in natural water systems and hence its influence as a pH buffer is negligible. The other alkalinity source is bicarbonate (HCO_3^-), which is the most predominant species regulating alkalinity and serves as a carbon source for primary production (Surapata, 1993). There are a number of sources of inorganic carbon

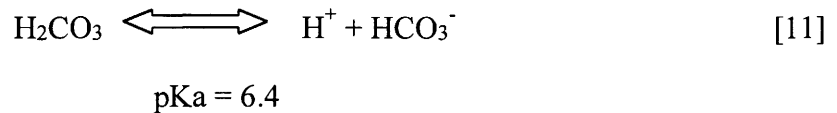
contributing to the initial carbonate/bicarbonate system cycle. These sources include carbon-dioxide (CO_2) from the atmosphere and CO_2 from organic decay. The following depicts the role of CO_2 in regulating pH in natural water systems: Carbon-dioxide (CO_2) absorbed by rain forms carbonic acid (H_2CO_3), a weak acid, as follows:



and

$$\text{H}_2\text{CO}_3 = K_H \cdot p\text{CO}_2 \quad K_H = 10^{-1.47} \quad [10]$$

where K_H denotes Henry's constant and $p\text{CO}_2$ is the partial pressure of CO_2 in the atmosphere. This weak carbonic acid undergoes dissociation thus,



Reaction [11] if expressed as the Henderson-Hasselbalch equation gives

$$\text{pH} = \text{pKa} + \log [\text{HCO}_3^- / \text{H}_2\text{CO}_3] \quad [12]$$

The balance between HCO_3^- and H_2CO_3 in nature is controlled by biological as well as chemical processes. For example, during processes where CO_2 is produced more H_2CO_3 results (Eq. [10]) and pH is driven downwards, assuming no secondary products would override the CO_2 influence. On the other hand, production of organic material in lakes via photosynthesis may consume CO_2 and pH would be driven upwards.

In the case where a solid source of carbonate (CO_3^{2-}) is present, e.g., CaCO_3 , pH would be controlled by the chemistry of CO_2 as well as the solubility of CaCO_3 . For example,



and



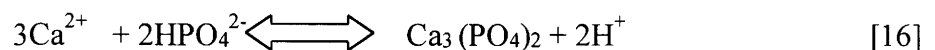
Considering that under $p\text{CO}_2$ of 0.00032 (0.032%) for a normal atmosphere, the CO_3^{2-} species in water is negligible in comparison to the HCO_3^- species and therefore pH would be around 8.3 (see Eq. [12]). As $p\text{CO}_2$ increases, pH would decrease. This is also demonstrated by Eq. [12]. However, upon increasing $p\text{CO}_2$, HCO_3^- would also increase (Jackson, 1975). It turns out that in the presence of CaCO_3 and under an equilibrium state any increase in H_2CO_3 due to increasing $p\text{CO}_2$ would be greater than the corresponding HCO_3^- increase. Therefore, upon increasing $p\text{CO}_2$ and in the presence/absence of CaCO_3 pH decreases (Jackson, 1975). It can reach a minimum of around 6 under very high $p\text{CO}_2$ ($p\text{CO}_2 = 1$), a medium pH of around 8.3 under $p\text{CO}_2$ of 0.00032 (0.032%) and a high of 9.9 under $p\text{CO}_2$ of approximately 10^{-6} . Surapata (1993) and other researchers illustrated that when bicarbonate is present in sufficient quantities some of the pH-dependent processes such as flocculation, waste-water digestion, etc. proceed continuously due to HCO_3^- pH buffering capacity.

Mineral Solubility

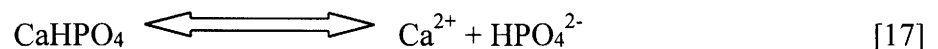
Solubility of minerals also plays an important role in controlling dissolved components within a lake system. For example, Ca^{2+} may react with phosphate to precipitate Ca-phosphate as follows:



or



Considering the rule of solubility equilibrium, CaHPO_4 may undergo dissociation as follows



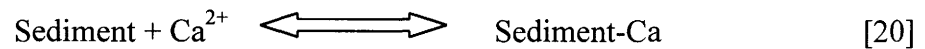
According to the reaction's stoichiometry equal molar quantities of Ca^{2+} and HPO_4^{2-} are produced hence the K_{sp} can be expressed as:

$$K_{sp} = (\text{Ca}^{2+}) (\text{HPO}_4^{2-}) \quad [18]$$

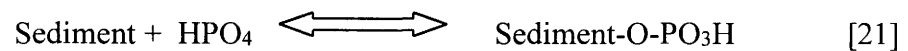
therefore,

$$(\text{Ca}^{2+}) = (\text{HPO}_4^{2-}) = (K_{sp})^{1/2} \quad [19]$$

Equation [19] points out that the magnitude of K_{sp} controls the concentration of Ca^{2+} and HPO_4^{2-} . It can therefore be drawn from this that, any component controlling the K_{sp} will also control the solubility of CaHPO_4 (Evangelou, 1998 and references therein). Reactions [18] and [19] also demonstrate that dissolved phosphate in water could be suppressed due to precipitation. Adsorption reactions in clay minerals and/or mineral surface precipitation reactions may also control concentrations of Ca^{2+} or $\text{PO}_4\text{-P}$ (Evangelou, 1998 and references therein). For example, adsorption of Ca^{2+} can be expressed as:



or in the case of HPO_4^{2-}



The above point out that removal of cations and anions from the solution phase may take place simultaneously or independently of each other.

Exchange Reactions / Quantity Intensity (Q/I) Relationships

Replacement of a given cation by another cation on a mineral surface is defined as an exchange reaction. Exchange reactions control ion availability and/or release of metals to lake-water. Availability of essential ion nutrients in lake-water or lake-water/sediment to aquatic organisms is expected to be related to the quantity (Q) of nutrients adsorbed by the

solid phase and the intensity at which they are released into the solution phase (I), hence Q/I . Woodruff (1955a and b) showed that the availability of an ion or nutrient in soil systems, hence lake-sediments could be thermodynamically defined as the difference between the electro-chemical potential of that particular ion in the solid-sediment phase and that of any competing ion (expressed as the change in ion's free energy, ΔG). Thus, the chemical potential of the replacing ion can be expressed as the ratio of the two ions involved. Beckett (1964a,b) expanded Woodruff's (1955a,b) work by relating the activity ratio (AR) of a give ion to some quantity of the exchangeable form of this ion (potassium) in the soil, hence lake-sediment also. However, any ion can be used instead of potassium. The present study deals with ammonium and phosphate Q/I behavior.

Availability of a certain nutrient in soil, hence lake-water/sediment suspension, was expanded by Khasawneh (1971) to include a replenishment factor. The replenishment factor describes the interaction of the quantity of the nutrient in reserve (Q) and the intensity (I), known also as the buffering capacity (BC) of the lake-sediment for that nutrient. These availability nutrient factors are obtained from a Q/I plot. An example of a typical Q/I plot is illustrated in Fig. 1 (Evangelou et al. 1994, p. 183). Chappell and Evangelou, (2000a,b) showed that N in the form of soluble NH_4^+ or NO_3^- is readily bioavailable. They further showed that exchangeable $\text{NH}_4\text{-N}$ is slightly less bioavailable, and that confined or 'fixed' or non-exchangeable (fixed) NH_4^+ is practically non-bioavailable, but not always. Q/I curves can be used for K^+ or NH_4^+ or $\text{H}_n\text{PO}_4^{3-n}$ to estimate, for any intensity level, the ability of the bottom-lake sediment to buffer these ions in solution (Beckett, 1964, Barbayiannis et al. 1996, Holford, 1997).

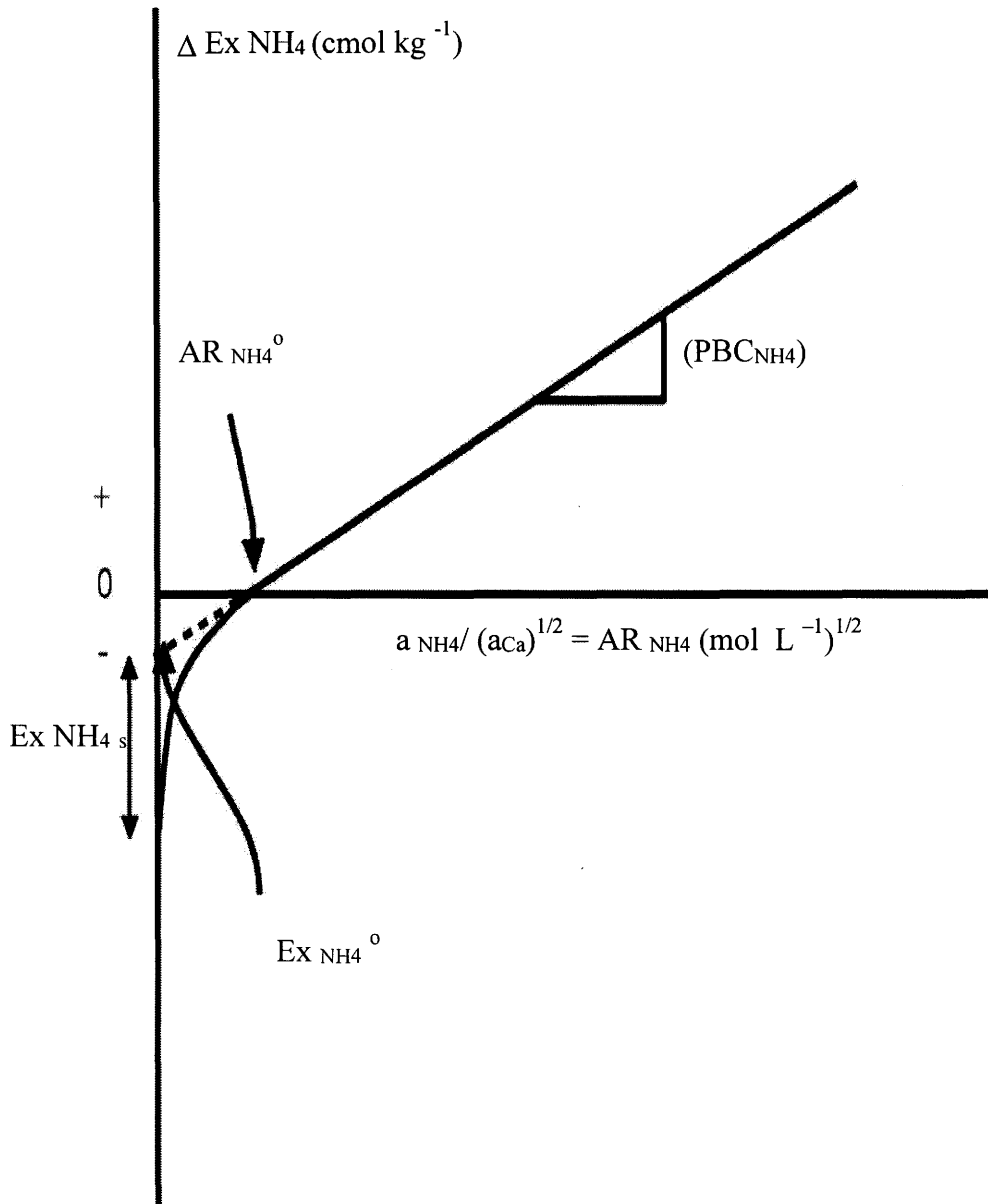
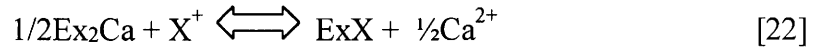


Figure 1. Typical Quantity-Intensity plot for NH_4 . $\Delta \text{Ex NH}_4$ is the Quantity factor (Q) and represents changes (gains or losses of exchangeable NH_4). AR_{NH_4} or CR_{NH_4} is the intensity factor (I) or concentration ratio for NH_4 ; Ex NH_4^0 is the labile or exchangeable NH_4 ; $\text{Ex NH}_4 \text{ s}$ represents the specific sites for NH_4 , and PBC_{NH_4} is the linear potential buffering capacity for NH_4 . The same plot applies to PO_4 .

As pointed out above, P bioavailability would also depend on chemical species or major forms. For example epilimnetic P may exist in two major forms: organic and inorganic. The inorganic form (orthophosphate) in lake-sediments may exist in various chemical forms. These are oxide-phosphate complexes (e.g., clay-mineral-edge-phosphate complexes), minerals of apatite (e.g., Ca-apatite), Fe(III)-phosphates, Mn-phosphates, Al-phosphates, and to a lesser extent pyrophosphate (e.g., $\text{Ca}_2\text{P}_2\text{O}_7(\text{s})$) (Evangelou, 1998 and references therein). It is hypothesized that the forms of bioavailable P (organic and/or inorganic) have to exist as colloidal phases in a dispersed mode, and/or dissolved in the epilimnion in order to cause eutrophication. Commonly, the dissolved concentration of inorganic P in lake systems is very small (range of 0.03 mg/l) (US EPA, 1996). However, most of the mobilized inorganic P in soils or sediments is in the form of small mineral or colloidal particles (Evangelou, 1998). Jordan et al. (1997) reported that in all regions of the Coastal plains under investigation in the Chesapeake Bay watersheds, P concentrations correlated with the concentration of suspended solids. Large amounts of P (organic and/or inorganic) in lakes are attributed to eroding soil colloids during rainstorm events. (Sharpley et al., 1994, Gburek and Sharpley, 1998). Therefore, bioavailability due to dispersion potential of these forms of P would depend on the nature of the colloids (Stumm and Morgan, 1981), and their potential to maintain certain intensity and the intensity's magnitude.

The potential of bottom-lake sediments to disperse in the epilimnion would depend on surface composition and lake-water chemistry. Let's consider a lake-sediment binary cation exchange reaction at equilibrium involving for example X^+ (X^+ denotes any monovalent cation, e.g., Na^+ , K^+ or NH_4^+) and Ca^{2+}



where, Ex denotes an exchanger phase taken to have a charge of negative one (-1), X^+ and Ca^{2+} denote cations X and Ca in solution, respectively. For reaction [22] an equilibrium exchange expression is given by

$$K_v = (\text{M}_x)(\text{Ca})^{1/2} / (\text{M}_{ca})^{1/2}(\text{X}^+) \quad [23]$$

where $(\text{X}^+)/(\text{Ca}^{2+})^{1/2}$ is known as the X^+ adsorption ratio (XAR), and K_v is the Vanselow exchange selectivity coefficient. The magnitude of K_v is taken to represent relative affinity of X^+ with respect to Ca^{2+} by a charged surface (Sposito, 1981a). Rearranging Eq. [23] and solving for the fraction of the colloid surface covered by X (EXP) by considering

$$\text{M}_x = \text{ExX}/(\text{ExX} + \text{Ex}_2\text{Ca}) \quad [24]$$

and

$$\text{M}_{ca} = \text{Ex}_2\text{Ca}/(\text{ExX} + \text{Ex}_2\text{Ca}) \quad [25]$$

where M_x , and M_{ca} denote mole fraction of X^+ and Ca^{2+} , respectively, and Ex denotes exchange phase with a valence of 1, and equivalent fractions for the X^+ and Ca^{2+} are given by:

$$\text{Ex} = \text{ExX}/(\text{ExX} + 2\text{Ex}_2\text{Ca}) \quad [26]$$

and

$$\text{Eca} = 2\text{Ex}_2\text{Ca}/(\text{ExX} + 2\text{Ex}_2\text{Ca}) \quad [27]$$

(note, Eq. [26] is used to estimate exchangeable X^+ percentage (EXP) by multiplying Ex by 100), gives (Evangelou and Phillips, 1987)

$$\text{EXP} = \text{ExX}/\text{CEC} = (\text{K}_v)(\text{XAR})/[4 + (\text{K}_v \text{XAR})^2]^{1/2} \quad [28]$$

Taking limits of Eq. [28] as XAR approaches zero (0) and XAR approaches infinity (∞) gives

$$\text{Limit}_{\text{XAR} \rightarrow 0} \quad \text{EXP} = 0 \quad \text{and} \quad \text{Limit}_{\text{XAR} \rightarrow \infty} \quad \text{EXP} = 100 \quad [29]$$

In Eq. [28] it is assumed, generally justifiably, that CEC and K_v are constant for the entire X^+ - Ca^{2+} exchange isotherm. According to Eq. [28], a plot in terms of XAR versus EXP will give a curvilinear function asymptotically approaching 100.

However, sodium (Na^+), K^+ , NH_4^+ , and Ca^{2+} plus Mg^{2+} exhibit different soil dispersive properties due to their difference in preference by sediment-colloid surfaces and because of differences in osmotic potential (Arora and Coleman, 1979; Oster et al., 1980; U.S. Salinity Lab Staff, 1954). For example, at a certain XAR (where X is any monovalent cation in water and $\text{XAR} = X^+ / (\text{Ca} + \text{Mg})^{1/2}$), a specific portion of the CEC, depending on the magnitude of preference of X^+ over Ca^{2+} plus Mg^{2+} or vice versa, is occupied by X^+ (Evangelou 1998 and references therein). When X^+ represents Na^+ , the U.S. Soil Salinity Laboratory Staff (1954) reported that XAR, or in this case SAR ($\text{SAR} = \text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})^{1/2}$) values of 10 to 15 usually correspond to ESP (exchangeable sodium percentage) values in the range of 10 to 15 at which 2:1 clays (common to Iowa soils) undergo dispersion. This relationship may vary among clays with different mineralogy (Oster et al., 1980) and/or mixtures of clays of different mineralogies (Arora and Coleman, 1979) and presence or absence of organic matter (Salmon, 1964). Consequently, the force by which given types of lake-sediment colloids attract or repulse each other in a X^+ - Ca^{2+} solution is a function of the total concentration of salt, type of X^+ , e.g., Na^+ , K^+ , or NH_4^+ , as well as lake-water ionic strength and pH.

Suspended Solid Effects

Suspended solid (SS) concentrations in natural bodies of water are a water quality-determining factor (US EPA. 1996, WHO. 1993). Commonly, natural waters with concentrations of suspended solids greater than 35 mg/l are considered undesirable (US EPA, 1996 public law 95-87 (see also Table 1 and 2). Suspended solids inhibit light penetration, which adversely affects aquatic life. Furthermore, suspended solids often carry adsorbed constituents, e.g., phosphates, ammonium, heavy metals, pesticides and their presence in water can be detrimental to aquatic life (Goolsby, 2001; Thomas and Meybeck 1997 pp 140-141; Stumm and Morgan, 1981 p. 736). These suspended solids represent turbidity in lake system and are products of colloid dispersion.

Double Layer Phenomena

Soil colloid dispersion/flocculation processes are controlled by double layer swelling, adsorbed hydrolyzed Fe or Al, and chemical bridging (Stumm & O'Melia, 1968). The classical theory of colloidal stability developed by Derjaguin and Landau (1941) and Verwey and Overbeek (1948) (DLVO) generally accounts for the influences of ion valence and concentration of suspended colloid interactions (Hesterberg and Page, 1990). According to the DLVO theory the particle surface and the 'swarm' of cations around it form an electrostatic double layer. Cations are adsorbed by colloidal particle surfaces, whereas anions are generally repelled. It is postulated that once colloids are dispersed they stay dispersed due to the long-range repulsive potential force between these like-charge colloids (Sposito, 1984; Stumm and Morgan, 1981). This force of repulsion is related to the thickness

of the double layer and is usually represented by ions concentrated near the oppositely charged colloid surface (Stumm and Morgan, 1981 pp. 610-623).

The diffuse double layer theory further stipulates that, as the distance increases from the particle surface to the bulk solution, the concentration of counter-ions decreases at some exponential rate. There exists a net interaction between the two forces one pulling cations towards the negative surface and one pulling them away towards the bulk solution. This long-range repulsive potential between like-charge colloids shows that colloid stability (maximum dispersion) depends on the repulsive energy between the two colloidal surfaces (Sposito, 1984). It also appears that the maximum repulsive potential is controlled by the surface electrical potential (ψ_o) and ionic solution composition (C_o). The component ψ_o on the other hand is controlled by the pH of the colloidal suspension (Stumm and Morgan, 1981 p. 669).

The influence of pH on ψ_o of a clay-organo colloid, e.g., colloid sediments, can be demonstrated by quantifying the increase in cation exchange capacity (CEC) as a function of pH. Generally, in clay-organo colloids upon increasing pH, under constant I, ψ_o becomes more negative and thus repulsive energy increases. Conversely, upon decreasing pH, ψ_o decreases and, repulsive energy decreases. The point or pH at which repulsion energy approaches zero is known as the point of zero charge (PZC) and leads to colloid flocculation (Singh and Uehara, 1986; Emerson, 1964; Tama and EL-Swaify, 1978; and Keren et al., 1988). In the case of C_o (ionic strength), increasing C_o in a colloidal suspension under any given ψ_o decreases the thickness of the double layer and therefore decreases the repulsive energy, which enables colloid flocculation to take effect. The opposite happens at low ionic

strength, where the double layer swells and increases the repulsive energy, which enables colloids to disperse.

Surface Charge, pH and Ionic Composition

The relationship between pH and surface charge of soils or lake-sediments with variable charge surfaces (constant electrical potential), e.g., clay-organo surfaces, is rather difficult to predict. This is especially true in systems where colloids represent a mixture of constant (variable electrical potential) and variable charge surfaces, e.g., smectites and humic substances, respectively. Surface charge is also affected by specific adsorption commonly associated with H^+ and OH^- , which are known as potential determining ions (PDI's). However, other ions capable of chemically coordinating on surfaces and acting as PDI's include HPO_4^{2-} , Fe^{3+} , Al^{3+} , heavy metals etc., which may also specifically or strongly adsorb and ultimately influence the surface charge of soils (Wann and Uehara, 1978; Uehara and Gillman, 1981; Sposito, 1984a; Singh and Uehara, 1986). Ions forming outer-sphere complexes, e.g., Ca^{2+} , shift the PZC to lower pH values. This is analogous to coordinating anions forming inner-sphere complexes, e.g., HPO_3^{2-} , which may also shift the PZC to lower pH values (Sposito, 1981; Singh and Uehara, 1986). On the other hand, cations forming inner-sphere complexes, e.g., Al, shift the PZC to higher pH values (Singh and Uehara, 1986). This is analogous to anions forming outer-sphere complexes, e.g., SO_4^{2-} , which shift the PZC to higher pH values. Therefore high pH of lake-water coupled with the presence of PDIs such as PO_4 , have the potential to increase surface charge and may contribute to lake-sediment dispersion. Thus, sediment-surface charge, ionic composition and pH may play an important role on dispersion/flocculation processes in lakes.

Wann and Uehara (1978) and Singh and Uehara (1986) presented evidence of weak specific adsorption having an influence on variable charge surfaces. Therefore, factors that control the magnitude of lake-sediment colloid electrical potential include: temperature, electrical conductivity, chemisorbed-phosphate, -silicate and -humic substances to name but a few. Dispersion of clay-size soil colloid particles or lake-sediment colloids under constant proportion of solution cationic species but varying dissolved solids is related to the repulsive index (RI) (Evangelou 1990). The RI represents relative thickness of the electric double layer, which is inversely related to ionic strength. As previously stated, surface electrical potential of colloids is related to cation exchange capacity (CEC). The greater the CEC, the greater the electrical potential assuming all other variables are fixed, and the greater the tendency of colloids to disperse e.g., increase water turbidity.

Generally, upon increasing temperature, the double layer theory predicts that turbidity is expected to increase whereas upon increasing EC, turbidity is expected to decrease. On the other hand, upon increasing chemi-sorbed-phosphate, -silicate, and -humic substances, under constant temperature and EC turbidity is expected to increase. On the basis of this statement, two suspension systems with similar colloids and ionic strength should exhibit identical dispersion/flocculation behavior, irrespective of whether the suspension-solution consists of monovalent cations, e.g., NaCl, or divalent cations, e.g., CaCl₂ (Evangelou, 1998 and references therein). However, because studies have shown that Na⁺ and Ca²⁺ exhibit different clay dispersive properties due to differences in preference by colloid surfaces and because of differences in limiting ionic osmotic potential, the above statement is not valid (Arora and Coleman, 1979; Oster et al., 1980; US Salinity Lab Staff, 1954). Therefore, cation exchange behavior of monovalent and divalent cations on colloids has to be

considered in order to predict dispersion in heterogeneous cationic suspension systems. Smectites, also known as 2:1 expanding clays, are common to Iowa soils, possess an external surface as well as an internal surface. These clays are capable of controlling dispersion/flocculation processes through shrinking/swelling influenced by type and concentration of cations present in the system.

**PART 1: THE SOLUTION (SURFACE WATER) AND SOLID PHASES
(SEDIMENT)**

INTRODUCTION

Lake-water concentration of phosphate, inorganic nitrogen species as well as inorganic salts, is affected by a number of variables which influence a lake-system's overall buffering capacity. These variables include agricultural and municipal run-off, biological processes and chemical equilibria (US EPA, 1996 report). The established relationship(s) between lake-sediment suspension and lake-water chemistry for the lakes under study could help build a model to predict Iowa lake dispersed-solids sensitivity to management practices within catchment areas.

MATERIALS AND METHODS

Site Description

Lake-water samples were collected from four Iowa lakes, namely Big Creek, Laverne, Little Wall, and Saylorville. Big Creek and Saylorville are located south-west of Ames, in Polk County. Big Creek is used for recreation, while Saylorville is used for recreation and serves as back-up reservoir for Des Moines's drinking water supply. Little Wall lake, which is situated approximately 18 miles north of Ames, in Hamilton County is mainly used for recreational purposes. Lake Laverne, on the other hand, is on the Iowa State University campus which is located in the city of Ames, in Story County. This lake receives runoff from the urban storm-water drainage, which includes parking lots, university and city streets as well as runoff from the greens around campus. The lake also serves as university attraction facility and acts as drain to most of the university's runoff. The other three lakes receive runoff from fields in the catchments area including agricultural runoff, e.g., corn and soybean fields.

Soils of the surrounding area of all four lakes belong to clarion and storden series except Saylorville, which belongs to storden, hayden, orthents and psammaquents series. Taxonomic description of the soils around the four lakes, are as follows:

- I) Big Creek: Fine loamy, mixed, superactive, mesic Typic Hapludolls ; Fine-loamy, mixed, superactive, mesic Typic Eutrudepts
- II) Laverne: Fine loamy, mixed, superactive, mesic Typic Hapludolls
- III) Little Wall: Fine loamy, mixed, superactive, mesic Typic Hapludolls

- IV) Saylorville: Fine-loamy, mixed, superactive, mesic Glossic Hapludalfs; Fine-loamy, mixed, superactive, mesic Typic Eutrudepts¹

These different soils and potential different sources of lake-runoff inputs served as selection criteria of the four lakes for this study.

Sampling and Sample-Preservation Techniques

Sample selection sites represented an area of approximately 100 m² near the lake-edge (approximately 15-m from lake shore). Composite lake-water samples were collected from a depth of approximately zero to 30-cm for all four lakes. Like-wise, composite lake-sediment samples were obtained at the same locations, from the zero to 15-cm depth of the lake-bottom sediments. The procedures were as follows: Several grab samples representing lake-water or bottom-lake sediments were obtained from the 100-m² area, mixed and split into duplicate samples. The lake-water samples were collected in 1 L acid rinsed narrow-mouthed plastic bottles and the bottom-lake sediment samples were placed in 1 L acid rinsed wide-mouthed plastic bottles. The lake-water and bottom-lake sediment samples were transported from the field to the laboratory in cooler boxes packed in ice. Upon arrival in the laboratory, the lake-water samples were filtered through a 0.45 µm filter paper (Gelman Sciences, Ann Arbor, Michigan), while the lake-sediments were air-dried and crushed to pass through a 0.5 mm sieve. The storage temperature for both lake-water and bottom-lake sediments was at constant 4° C.

¹ Source: USDA (NRCS) – Soil survey book series and website

Field measurements of electrical conductivity (EC), pH and redox (Eh) were carried out in the field by placing the appropriate sensors in the lake-water and at the lake-bottom sediments of the selected lakes.

Analytical Techniques

Physical Properties

Electrical Conductivity (EC), pH, Alkalinity, Redox (Eh), Dissolved Oxygen (DO) and, Temperature measurements

Field measurements were carried out on lake-water (solution phase) and lake-bottom sediments (solid phase). They included electrical conductivity (EC), temperature, pH, redox (Eh) and dissolved oxygen (DO). Field EC, pH and Eh were measured using a dual EC and pH voltmeter (Denver Instruments, model AP50, Arvada, Colorado, USA). Dissolved oxygen was measured using an oxygen meter (Hanna Instruments, model 9143, Ronchi di Villafranca (PD), Italy).

Laboratory measurements of EC and pH were carried out using a dual pH/Ion/Conductivity meter (Accumet Fischer, AR50 model, Pennsylvania, USA). Potentiometric titrations were carried out on a 25-ml aliquot of lake-water sample by employing an automatic titrimeter (Radiometer ABU Auto burette, model 901 and, TIM 900 used as a titration manager (Radiometer Copengagen) to pH 4.0 with standardized 0.1069 M hydrochloric acid (HCl). Potentiometric titrations were also carried out on the lake-sediments. Two air-dried lake-bottom sediment sub-samples of approximately 0.2-g were equilibrated with 25-ml deionised water. The titrations were carried out using a stop-and-go technique at 300-second delay period under constant stirring. The amount of acid consumed

was used to calculate total alkalinity and estimate apparent experimental pK_as. Duplicate samples were run for both lake-water and lake-bottom sediments.

Major Cations and Anions in Lake-Water

The selected major cations and anions were determined using an Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES) (Thermo Jarrell Ash Corporation, model 61E, Franklin, MA, USA) equipped with a computer for data acquisition. From the results of a qualitative scan performed on the lake-water samples an analytical method (WATER-3/4) was developed to analyze the elements of interest. Three different standards were prepared according to the results from the qualitative scan. The first standard, referred to as 'standard 1', contained the following elements: Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Pb, Sr, and Zn. The second standard, referred to as 'standard 2', contained P, Si, S, and B. The third standard, referred to as 'standard 3', contained doubly distilled water. As means of quality control, scandium (Sc) was used as an internal standard and an equal amount was added to all standards and samples. Duplicate samples were prepared for each analysis and four replicate readings were taken for each of the elements analyzed. Background correction was enabled during the sample readings, yielding direct analyte concentrations.

Inorganic nitrogen forms in lake-water samples were also quantified. Nitrate was determined by ion specific electrode (Lachat Instruments, QuickChem Automatic Ion Analyzer model, Milwaukee, WI USA), whereas ammonium (NH_4^+) was determined using a universal microplate reader (Bio-TEK Instruments Inc, Model ELx 800, Winooski, VT USA) and employing the modified Berthelot reaction (Ngo et al., 1982). In the latter procedure, 20- μl lake-water sample was added to the microplate wells along with 100- μl of phenol-

nitroprusside reagent (I) and 100- μ l of sodium hydroxide-hypochlorite reagent (II). After 30-min shaking colorimetric readings were taken at 630 nm by the universal microplate autoreader.

Orthophosphate was determined by the 'Ascorbic Acid Method' (Murphy and Riley, 1962.) In this method, ascorbic acid acts as a reducing agent and antimony produces a molybdenum blue color in approximately 10 min. Absorbance measurements were made at a wavelength of 880 nm by a UV/VIS spectrophotometer (Varian Instruments, Cary50 Bio model, Walnut Creek, CA, USA).

Sediment Characterization: Physical Properties

Sediment Composition: Carbon and Nitrogen

The air-dried lake-sediment samples were analyzed for total carbon (TC) and total nitrogen (TN) by dry combustion at 950°C using a CHN-600 analyzer (LECO Corporation, St. Joseph, MI USA). In addition to total carbon, inorganic carbon (IC) forms were determined by use of Chittick apparatus (Dreimanis, 1962). The procedure is often referred to as volumetric, manometric, or gasometric. In the procedure, 6 M HCl was added to approximately 1.7-g of sediment sample plus few drops of FeSO₄ to limit the oxidation of organic matter. Evolution of CO₂ from the sediment sample was then measured. The total quantity and the rate at which the CO₂ was evolved allowed total quantification of metal carbonates and distinction between calcite and dolomite. Organic carbon (OC) of the sediments was determined by subtracting the inorganic form from the total carbon concentration (OC = TC – IC).

X-ray Analysis

The clay fraction of lake-sediments was separated as follows: approximately 30-g of air-dried lake-sediment sample was placed in a 250-ml plastic bottle, and 200-ml of deionized water was added and thoroughly mixed in a reciprocal shaker (Eberbach Corporation, Ann Arbor, Michigan USA) at a speed of 180 min/cycle for 5-minutes. These suspensions were sonicated for 5-min using Branson sonicator (Branson Ultrasonic Corp, 2210R-MT model, Danbury, CT USA). The suspensions were then transferred to a tall 1000-ml measuring cylinder, and filled to the appropriate mark with deionised water. Time for settling was 3 hours, 36 minutes and 45 seconds (USDA, 2000). After this time, the first 5-cm which contained the clay fraction ($\leq 2\text{-}\mu\text{m}$) was siphoned out, centrifuged at $2859 \times g$ for 5-min and left to dry at room temperature (USDA, 2000). Sub-samples of these isolated clays were placed in 50-ml Teflon centrifuge tubes and the following three treatments were introduced: 1) suspension in 20-ml of deionised water, 2) saturation with 1 M MgCl_2 and 3) saturation with 1 M KCl . The salt wash was repeated twice. The suspensions were then shaken in a reciprocal shaker (Eberbach Corporation, Ann Arbor, Michigan USA) at a speed of 180 min/cycle for 1 hour and were further sonicated in a cell disruptor (Heat Systems–Ultrasonics Inc., model W-225R, Plainview, NY) for an additional 3-min. The desired clay oriented samples (mounting) were obtained by adding small increments of these suspensions, using a pasteur pipette, to a rectangular (33mm x 15mm x 4 mm) bisque ceramic tile (National Tile & Manufacturing Co., Anderson, Indiana). Dry clay films representing each treatment listed above were obtained under vacuum. The prepared clay tiles were stored in a dessicator, containing saturated MgNO_3 solution, prior to X-Ray diffraction analysis. In addition to the control and cation saturated films, treatment of 50% glycerol was applied to

the surface of the 1 M MgCl₂ saturated-tile. This was achieved by adding two drops of 50% glycerol solution to the surface of the Mg-saturated tile using a pasteur pipette and, tilting the tile to spread the glycerol over the surface evenly. These tiles were stored in a dessicator at 54% relative humidity and saturated with free glycerol until analyzed by X-ray diffraction.

Mineralogical characterization of these clay samples were carried out using a Siemens D500 diffractometer equipped with a copper anode X-ray tube, operated at 50 kV and 27 mA. It was also equipped with a diffracted beam graphite monochromator that tuned to Cu K-alpha 1,2 radiation. The scintillation counter and a pulse height analyses (PHA) circuit were used to collect and process the intensity information. The diffractometer was controlled via a MDI databox and the diffractograms were processed using MDI JADE software.

Thermal Analysis

Thermal analyses of clays from the lake-sediments were carried out in a thermo analyzer (Seiko Instruments Inc SSC\5200, TG/DTA model 320, Manhattan Place, Torrance CA, USA). The temperature ranged from room to 1500°C.

Sediment Characterization – Chemical Properties

Extractable Cations and Anions

Different techniques were used to extract the different major ions from the lake-sediment samples. These techniques included sodium carbonate fusion, Mehlich III extraction, nitric acid digestion, 1N HF-1N HCL extraction, ignition and extraction with NH₄⁺ and PO₄ solution reagents. Below, the methods are described in some detail.

Sodium carbonate fusion technique

This technique has been extensively used for determining total P in soil or sediment samples (Jackson, 1958; Mattingley, 1965; Sherrel and Saunders, 1966; Syers et al., 1967, 1969). However, the extract can also be used for determining other ions in soils or sediments (Dick and Tabatabai, 1977). The procedure was as follows: two air-dried 1.0 g sediment samples were weighed and 4-g of anhydrous sodium carbonate was added to each sample, and mixed uniformly with the sediment. This mixture was then heated with a full flame of the Meeker burner on a 30-ml platinum crucible until the mixture formed a melt. This melt was then extracted with 30-ml of 4.5 M sulfuric acid (H_2SO_4) into a 250-ml volumetric flask. The crucible was further boiled using 25-ml of 1 M H_2SO_4 , and was quantitatively transferred to the same 250-ml volumetric flask made up to volume with distilled-deionized water. Prior to analysis, five drops of 0.25% *p*-nitrophenol indicator were added and the solution pH adjusted to alkaline conditions by 1 M NaOH. Total P was determined, by the 'Ascorbic Acid Method' (Murphy and Riley, 1962) and all other ions by ICP-AES as previously described.

Mehlich III

Mehlich III extraction solution is a mixture of NH_4F -EDTA and nitric acid (HNO_3). The method has been developed for determining Ca, Mg, Na, Fe, Mn, Fe, Cu, Zn, B and P (Mehlich, 1984). Two air-dried sediment sub-samples of 2.0 g were placed in 50-ml centrifuge tubes. To each centrifuge tube, 20-ml of mehlich III solution was added and the mixtures were shaken for 5-min in a reciprocal shaker (Eberbach Corporation, Ann Arbor, Michigan USA), at 180 cycles per minute. The mixture was then filtered, using a Whatman

no. 42 filter and the filtrate analyzed by ICP-AES for elements of interest as previously outlined.

Boiling nitric acid

Boiling nitric acid is one of the most commonly used methods for extracting non-exchangeable K^+ (Helmke and Sparks, p. 560). The procedure was as follows: two 2.5 g duplicate samples of air-dried lake-bottom sediment were weighed, placed in 50-ml Erlenmeyer flasks and 25-ml of 0.1 M HNO_3 was added. The sediment- HNO_3 mixture was then placed on a hot plate and heated. After boiling was initiated heat was adjusted and boiling continued for an additional 15-min. The flasks were then removed from the heat and cooled. The resultant slurry was then filtered through a Whatman no. 42 filter and the leachate was collected in a 100-ml volumetric flask. This filtrate was then analyzed for non-exchangeable potassium (K) by atomic absorption spectrophotometry (Perkin Elmer Corp., Analyst-100 model, Norwalk, CT, USA) and other ions, e.g., most hard metals (Al, Ba, Ca, Fe, K, Mg, Mn, Na, S, Si, and Sr, plus some heavy metals (Cu, Pb, Zn) using an ICP-AES (Thermo Jarrell Ash Corporation, model 61E, Franklin, MA, USA).

1 N HF-1 N HCL extraction

Fixed or non-exchangeable NH_4^+ determination was carried out by the procedure of Bremner and Mulvaney (1982). To 5.0 g of duplicate air-dried lake-bottom sediment samples in a 50-ml centrifuge tubes, 35-ml of 1 N HF-1 N HCl solution was added and shaken for 24 hours in a reciprocal shaker (Eberbach Corporation, Ann Arbor, Michigan, USA) at a speed of 180 cycles/min. After shaking, the sediment-solution suspension were quantitatively transferred to a 125-ml teflon flask and 1.0-ml concentrated H_2SO_4 (18 N) was added. The

suspensions were then digested to about 1-5 ml using a hot plate equipped with a sand bath. The contents in the flasks were allowed to cool and carefully transferred to a 100-ml volumetric flask and made to volume using distilled-deionized water. The contents were then transferred to 250-ml polyethylene bottles and neutralized by titration to approximately pH 5.0 using 8.0 N NaOH and volume correction due to added NaOH was introduced. Finally, the solution was filtered with a Whatman no. 42 filter and analyzed for fixed NH_4^+ using the modified Berthlot reaction (Ngo et al. 1982).

Ignition method

Several methods are available for determining total organic P in soils or sediments. In this study, the ignition method (Saunders and Williams, 1955; Walker & Adams, 1958) was employed. In the procedure organic P was converted to inorganic P by high temperature oxidation. Organic P was then determined by difference between the amount of P in the ignited and non-ignited air-dried sediment samples. Quantitative $\text{PO}_4\text{-P}$ determination was carried out using the ascorbic acid technique (Murphy and Riley, 1962).

1 N KCl extraction

Determination of exchangeable ammonium (NH_4^+) was carried out on sediment samples using 1 N KCl. Duplicates of 1.0 g air-dried sediment samples were weighed and placed in 50-ml centrifuge tubes. Thirty-five ml of 1 N KCl (Keeney and Nelson, 1982) was added to the tubes and, the suspension was shaken for 1 hour at a speed of 180 cycles per minute using a reciprocal shaker (Eberbach Corporation, Ann Arbor, Michigan USA). After shaking, the samples were centrifuged at $2859 \times g$ for 10-min using a Sorvall centrifuge

(Sorvall Corp, model RC 5B, Wilmington, DE). The tubes were left to equilibrate for 10-min, then the supernatant (filtrate) was carefully collected with one 'continuous' pour. The collected filtrate was then analyzed for exchangeable ammonium (NH_4^+) following the microplate reader method as detailed previously.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) method

The filtrates from the above techniques (sodium carbonate fusion, Mehlich III and boiling nitric acid) were analyzed using an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES) (Thermo Jarrell Ash Corporation, model 61E, Franklin, MA, USA) equipped with computer for data acquisition as previously detailed. However, a different analytical method was developed to run the samples, selecting those elements of interest from a qualitative scan performed on the samples. As a way of quality control, cadmium at a concentration of 30 ppm was used as an internal standard; an equal amount was added to all standards and samples. Duplicate samples were prepared for each run and three replicate readings were taken at the time of analysis.

Analytical results from the samples were expected to have higher concentrations than their 'true' concentrations due to interfering ions in the extracted solutions. Because of this interfering element ion correction (IEC) was introduced. The IEC factor involved the analysis of a solution with known concentration of the interfering element, which does not contain that element of interest hence, pure standards of the interfering element was used. From the resultant concentration of this pure element, a ratio was established between the apparent concentration of the element of interest relative to the concentration of the interfering ion. The 'true' element concentration in samples was then determined by

correcting the apparent analytical values using the established ratio. For all the samples analyzed, IEC calculations were performed manually.

Quantity/ Intensity (Q/I) Relationships

Quantity/Intensity (Q/I) relationships for $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ in lake sediment samples were obtained using a slightly modified procedure of that proposed by Beckett (1964a) and described by Lumbanraja and Evangelou (1990). Solutions were made up of 1.5 mmol/L CaCl_2 containing $\text{NH}_4\text{-N}$ plus $\text{PO}_4\text{-P}$ concentrations in the range zero to 2.78 mmol/L and zero to 1.58×10^{-2} mmol/L respectively. Two sets of duplicates, one containing lake-water only (control), while the other containing 2-g of air-dried lake-bottom sediment sample and 0.02 L lake-water were placed in 50-ml centrifuge test-tubes. The samples were shaken for 24 hrs in a reciprocal shaker (Eberbach Corporation, Ann Arbor, Michigan USA) at a speed of 180 cycles/min. The test-tubes were then centrifuged at $1,572 \times g$ for 5-min. After centrifuging, the supernatant solutions were analyzed for $\text{NH}_4\text{-N}$ using a modified Berthlot reaction (Ngo et al., 1982) and for $\text{PO}_4\text{-P}$ using the Murphy and Riley method (1962). Other ions like Ca, Mg, K and Na were analyzed by atomic absorption spectrophotometry (Perkin Elmer Corp., AAnalyst-100 model, Norwalk, CT, USA). The quantity (Q) of $\text{NH}_4\text{-N}$ or $\text{PO}_4\text{-P}$ that the sediment gained or lost ($\pm \Delta \text{Ex NH}_4\text{-N}$ or $\pm \Delta \text{S-PO}_4\text{-P}$; S denotes sorbed $\text{PO}_4\text{-P}$) upon reaching equilibrium was calculated from the difference between the $\text{NH}_4\text{-N}$ or $\text{PO}_4\text{-P}$ concentration in the initial solutions and final or equilibrated solutions. The experimental data for $\pm \Delta \text{Ex NH}_4\text{-N}$ or $\pm \Delta \text{S-PO}_4\text{-P}$ and final solution concentrations of $\text{NH}_4\text{-N}$ or $\text{PO}_4\text{-P}$ were used to construct the Q/I plots. The PBC_{NH_4} or PBC_{PO_4} of the lake-sediment was

estimated by linear regression (Barbayiannis et al., 1996; Lumbanraja and Evangelou, 1990; Chappell and Evangelou, 2000).

RESULTS AND DISCUSSION

Lake-Water – Physical Characteristics

Water quality standards in Iowa, are regulated by Federal and State regulations (IDNR, 2001). Iowa lake-waters are classified as class 'B' waters. The latter are those that need some protection to safeguard them from toxins. The lakes are thus protected as a raw water source of potable water (IDNR, 2001). The studied lakes were expected to experience, as previously stated, different types and sources of inputs due to differences in geomorphology, geology or soil parent material, management of the surrounding watersheds and seasonal variation.

Table 3 shows variation in pH, EC, redox potential (Eh) and dissolved oxygen in the lake-water and sediments of the four lakes studied. The lake-water pH varied from 8.2 to as high as 9.4 whereas the lake-sediments showed slightly lower pH (7.2- 7.9). According to IDNR, pH shall not be less than 6.5 nor greater than 9.0, with a maximum change permitted due to any waste discharges not exceeding 0.5 pH units (Environmental Protection Rule 567, Chapter 61, "Water Quality Standards"). Therefore, according to the data in Table 3 all lake-waters and -sediments fall within this permissible pH limit. Electrical conductivity (EC) for surface water ranged from 382 to 722 $\mu\text{S}/\text{cm}$ and was within the minimum acceptable levels as set by USEPA (1996) and IDNR (IDNR, 2001). Field measurements of EC at the lake-bottom sediment-associated water varied from 234 to 840 $\mu\text{S}/\text{cm}$, well within the acceptable limit. Measurements of Eh, representing lake-water, suggested reduction processes at Little Wall, Big Creek and Saylorville lakes, and oxidation process at Lake Laverne.

Table 3. Variation in pH, electrical conductivity (EC), redox potential (Eh), and dissolved oxygen for lake-water and sediments of the four lakes studied.

Sample Location	Sample ID [§]	Temperature (°C)	pH ^a	Electrical Conductivity ^a (µS/cm)	Redox Potential ^a (mV)	Dissolved Oxygen ^b (mg/L)
Big Creek	SW - 1	26.6	8.8	382	+214	9.7
	SW - 2	19.6	8.6	401	+200	10.2
	SW - 3	3.2	8.2	413	+234	13.1
	SED - 1	24.9	7.2	382	+120	- ^c
	SED - 2	1.4	7.3	264	-40	-
Laverne	SW - 1	21.4	8.3	575	+203	8.5
	SW - 2	17.8	8.7	605	+212	12.6
	SW - 3	2.1	8.3	651	+171	13.1
	SED - 1	20.1	7.6	466	-214	-
	SED - 2	-0.1	7.9	840	-89	-

[§] SW = surface water; SED = sediments 1,2,3 is August, September and October samplings, respectively.

^a pH, Electrical conductivity and redox measurements were carried out using a dual voltmeter (Denver Instruments, model AP50, Arvada, Colorado).

^b Dissolved Oxygen was measured using a dissolved oxygen meter (Hanna, model 9143, Ronchi di Villafranca (PD) Italy).

^c not determined.

Table 3. (continued)

Sample Location	Sample ID^s	Temperature (°C)	pH	Electrical Conductivity (µS/cm)	Redox Potential (mV)	Dissolved Oxygen (mg/L)
Little Wall	SW - 1	26.1	9.4	445	+221	8.7
	SW - 2	17.0	9.2	464	+149	10.7
	SW - 3	0.6	8.7	517	-88	15.7
	SED - 1	22.8	7.5	304	-	-
	SED - 2	0.3	7.3	320	-93	-
Saylorville-	SW - 1	27.5	8.5	598	+244	8.8
	SW - 2	19.9	8.8	613	+192	10.4
	SW - 3	1.3	8.5	722	+183	15.6
	SED - 1	26.4	7.6	616	+221	-
	SED - 2	-0.2	8.3	234	+215	-

The data also showed a negative potential for Laverne lake-bottom sediments suggesting reduction processes.

Dissolved oxygen (DO) concentration for the four lake-waters showed a stepwise increase, ranging from 8.5 to 15.7 mg/l as temperature in the lakes decreased with time (Table 3). This was expected since the ideal gas law predicts that the solubility of a gas that is not reacting chemically with water (an ideal gas) increases as temperature decreases (Atkins, 1998 p. 13). This is consistent with the ideal gas law equation, $n = PV/RT$ where n = moles of dissolved gas, PV = pressure times volume, and RT is the universal gas constant times temperature. This equation, $n=PV/RT$, shows that as temperature increases PV is held relatively constant, gas molecules number (n) increases. This is due to the open structural arrangement of water. As temperature decreases, gas molecules in the void spaces of water decreases, consequently gas solubility increases. This solubility increase can also be linked to Henry's law, $n = K_h P_{gas}$ where K_h is Henry's constant and P_{gas} is the partial pressure of the ideal gas. It appears that as P_{gas} increases, the solubility of an ideal gas increases. Moreover, Henry's constant, according to the ideal gas law, is temperature dependent. As temperature decreases, K_h increases and therefore under the same P_{gas} , when temperature decreases, solubility increases.

Dissolved oxygen in freshwater at sea level, ranges from 15 mg/l at 0°C to 8 mg/l at 25°C (Meybeck and Helmer, 1997). According to Class 'B' waters in Iowa, as designated in sub rule 61.3(5) (Environmental Protection Rule 567), dissolved oxygen is not expected to be less than 5.0 mg/L as either a minimum value for at least 16 hours of each 24-hour period or a minimum value at any time during each 24-hour period. However this rule applies only to the upper layer of stratification in lakes. Concentration of dissolved oxygen below 5 mg/L

may adversely affect functioning and survival of biological organisms in aquatic systems and may result in fish-kill. Thus, all the lake-waters studied showed dissolved oxygen levels within limits.

Temperature of lake-waters can be influenced by a number of factors, some of which include, weather, latitude or altitude, season and, even depth of the water body (Meybeck and Helmer, 1997). Iowa water quality standards chapter 61.3 (3) (IDNR, 2001 website) states that no heat shall be added to lakes resulting in an increase of more than 2°C, and the rate of increase is not allowed to exceed 1°C per hour. Furthermore, the maximum temperature a lake or stream can reach is 32°C (Environmental Protection Rule 567, 61.3 (3)). This is critical information since temperature affects physical, chemical and biological processes of aquatic systems.

Alkalinity and carbonate speciation for the four lake-waters and lake-bottom sediments are given in Table 4. It can be concluded from these data that the carbonate is mainly bicarbonate (HCO_3^-). Typical examples of titration curves of lake-waters and sediments are shown in Fig. 2 and Fig. 3. The curves show that for all lakes initial pH was greater or equal to pH 8.3 suggesting alkaline waters with high levels of dissolved bicarbonate and most likely presence of alkaline earth carbonates. Potentiometric titration curves showed three pKa's for all four lake-systems. One pKa, owed to the solution (lake-water) alone, was around 6.4 (Fig. 2), which suggested presence of HCO_3^- . The lake-sediment system titration curves provided two pKa's. One pKa was approximately 5.75 and, a second pKa was approximately 4.75. These two pKa values could be due to carboxylic groups of humic substances and/or in the case of 4.75 ~Al-OH clay surfaces as well. The

Table 4. Alkalinity content and speciation of lake water.

Sample Location	Sample ID§	Total Alkalinity	CO ₃ ²⁻	HCO ₃ ⁻	Estimated pCO ₂ (atm)	Solution apparent pKa	Sediment apparent pKa
			----- (meq/L) -----				
Big Creek	SW - 1	4.02 ± 0.001	0.14 ± 0.005	3.88 ± 0.007	3.69E-04	6.4	5.7
	SW - 2	3.40 ± 0.002	0.00	3.40 ± 0.002	1.20E-03		
	SW - 3	3.37 ± 0.023	0.00	3.37 ± 0.023	2.21E-03		
Laverne	SW - 1	4.63	0.09 ± 0.065	4.54	1.19E-03	6.3	5.7
	SW - 2	5.71 ± 0.12	0.03 ± 0.048	5.68 ± 0.076	1.58E-03		
	SW - 3	6.23 ± 0.02	0.00	6.23 ± 0.002	2.34E-03		
Little Wall	SW - 1	4.57 ± 0.19	0.41 ± 0.130	4.17 ± 0.059	2.51E-04	6.3	5.7
	SW - 2	4.20 ± 0.02	0.42 ± 0.007	3.77 ± 0.021	1.21E-04		
	SW - 3	4.30 ± 0.11	0.03 ± 0.004	2.62	6.67E-04		
Saylorville	SW - 1	3.67 ± 0.010	0.12 ± 0.001	3.55 ± 0.011	4.83E-04	6.4	5.6
	SW - 2	3.79 ± 0.001	0.10 ± 0.007	3.69 ± 0.006	6.58E-04		
	SW - 3	4.62 ± 0.012	0.06 ± 0.019	4.57 ± 0.031	1.08E-03		

§ SW = Surface Water

1,2,3 = August, September, October samplings, respectively.

pCO₂ estimated using the Henderson-Hasselbalch equation (pH = pKa + log Base/Acid)

Apparent pKa was established from experimental titration data.

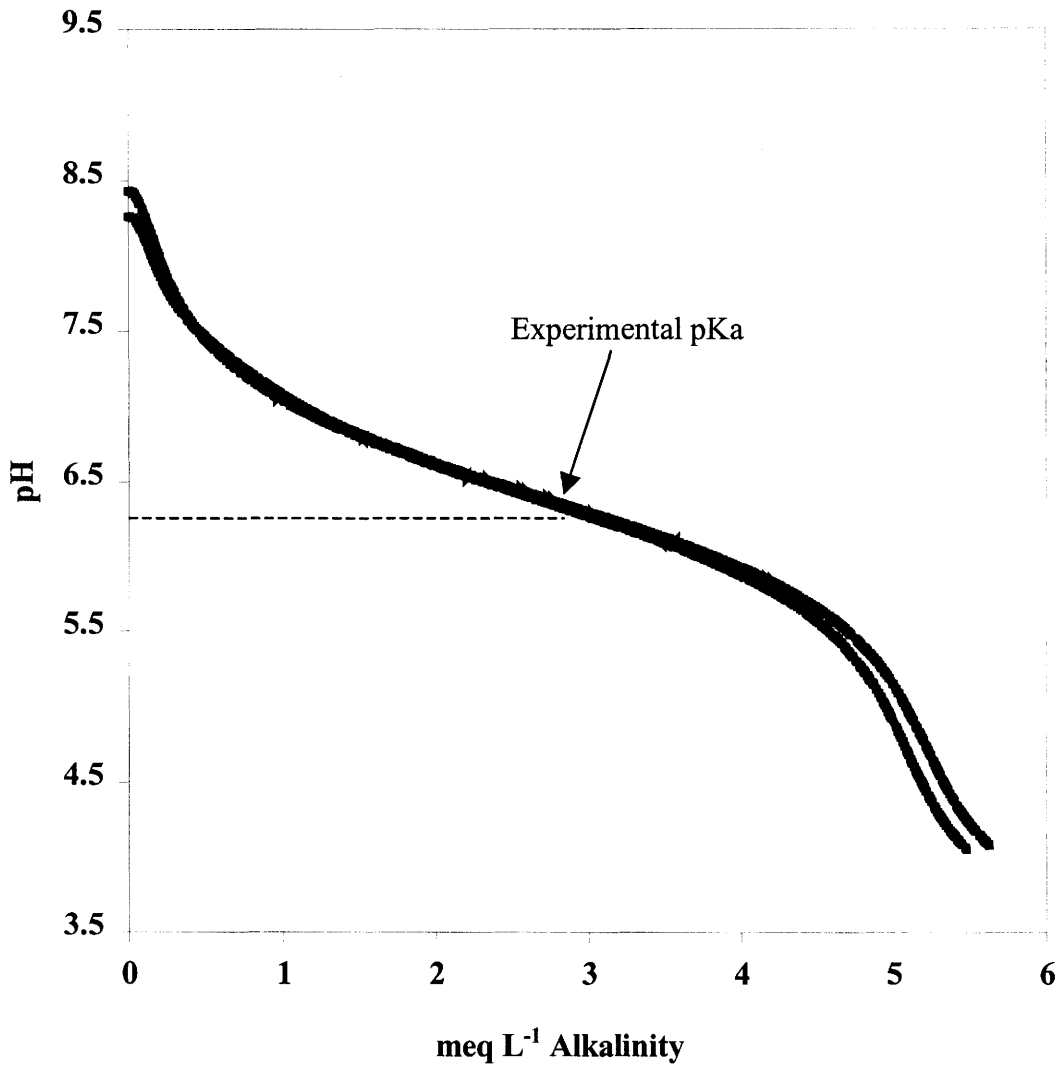


Figure 2. Typical alkalinity titration curve for lake-water. Potentiometric titrations were carried out on duplicate 25-ml aliquot of filtered and unfiltered water samples titrated to pH 4.0 with standardized 0.1069 M HCl using a continuous end-point technique under constant stirring. The titrations were accomplished by using autotitrimetry (Radiometer ABU Autoburette, model 910, Copenhagen) using TIM 900 (Radiometer, Copenhagen) as a

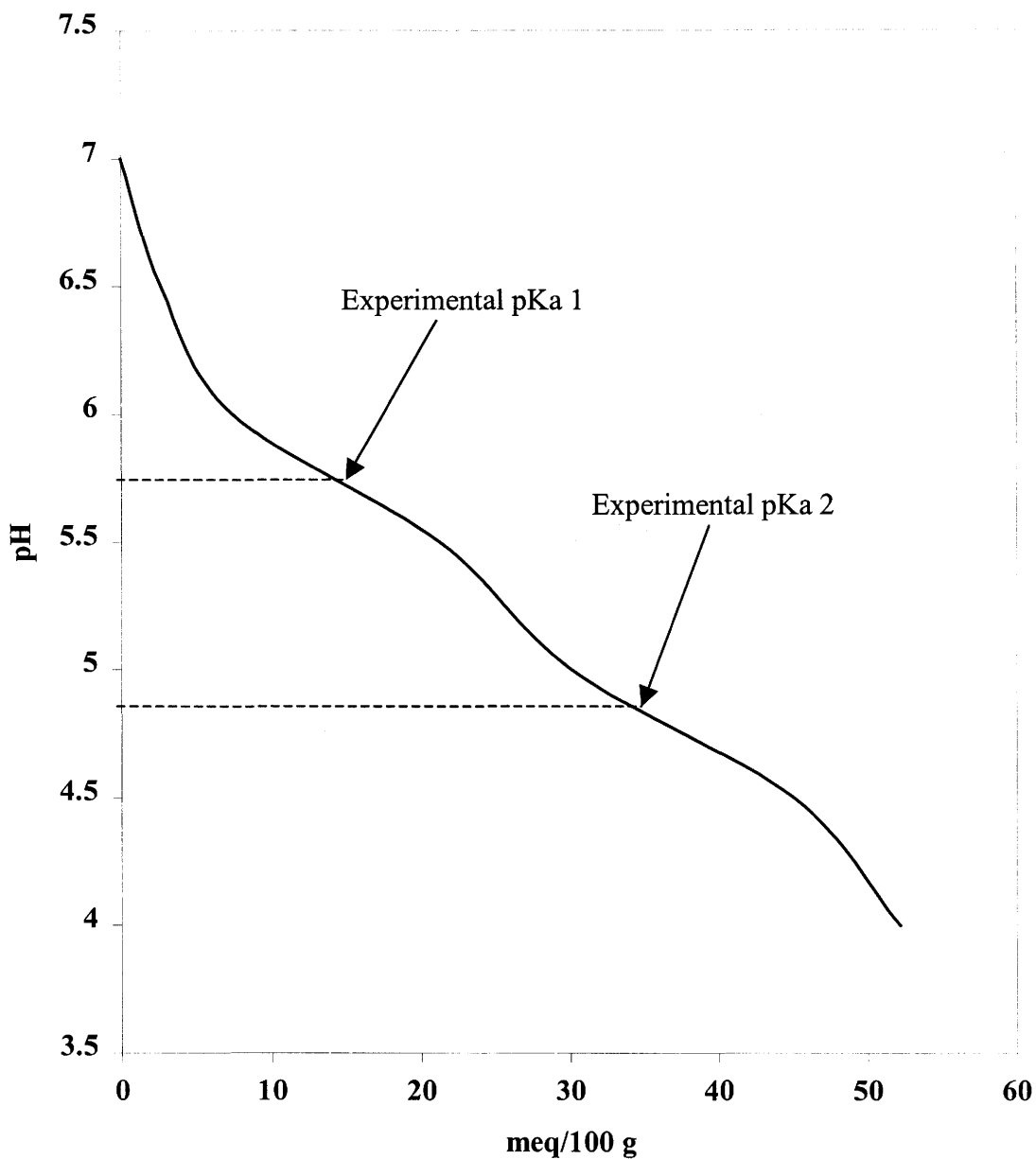


Figure 3. Typical alkalinity titration curve for lake-bottom sediments. Potentiometric titrations were carried out on two sub-samples of 0.2-g sediment suspended in 25-ml deionised water and titrated to pH 4.0 with standardized 0.1069 M HCl using stop and go technique at 300 second delay period under constant stirring. The titrations were accomplished by using autotitrimetry (Radiometer ABU Autoburette, model 910, Copenhagen) using TIM 900 (Radiometer, Copenhagen) as a titration manager.

pKa measures the relative tendency of a weak acid to dissociate. Typical pKa values of Bronsted-Lowry acids range from 1-14 (Evangelou, 1998 and references therein). Apparent pKa's can be used for approximating the pH of any water system through the Henderson-Hasselbalch equation (Evangelou, 1998 p. 27).

Estimation of pCO₂ in the four lake-systems indicated levels supported by less than but close to the partial pressure of CO₂ in the atmosphere (0.0003 or 0.03%), suggesting that the systems were not actively respiring, but most likely were actively photosynthesizing, thus a net consumption of CO₂ was taking place.

Lake-Water – Chemical Characterization

Water quality in freshwater bodies such as lakes, are prone to degradation. This may be due to land use management practices (Ceballos et al., 1995), population growth, and increased nutrient inputs. As previously discussed, agriculture is a potential major contributor of nutrients to surface waters in Iowa (Goolsby, 2001). Iowa, a leading state in agricultural production, uses plant nutrients like nitrogen, potassium, and phosphorus to improve fertility and enhance plant growth. Leaching of these nutrients to Iowa's natural bodies of water may contribute to hypoxia as far away as the Gulf of Mexico (Rabailas et al., 1996).

Table 5 and 6 show composition of the four lake-water samples with respect to hard and soft cations. The latter are also known as heavy metals. Furthermore, Fig. 4 is a graphical illustration of the data in Table 5. The overall data in Table 5 show that in general the four lake-water samples differed in ionic composition and some trends were observed with respect to time or seasons. In general, as temperature decreased total cation

Table 5. Water composition showing hard cations of four Iowa lakes studied^a.

	Na	K	Mg	Ca	Sr	Ba	Mn	Fe	Si	Al
Sample§										
BC 1	2.9E-01	6.2E-02	9.7E-01	7.1E-01	1.2E-03	3.3E-04	5.4E-05	1.3E-05	1.3E-01	1.7E-04
BC 2	4.8E-01	1.3E-01	1.2E+00	6.1E-01	1.3E-03	6.0E-04	2.5E-04	5.1E-04	9.8E-02	8.7E-04
BC 3	3.3E-01	1.5E+0	1.0E+00	8.6E-01	1.4E-03	4.8E-04	6.0E-05	5.0E-04	1.1E-01	4.1E-01
Lav 1	8.4E-01	2.0E-01	1.2E+00	1.1E+0	6.6E-03	2.0E-04	2.8E-05	2.5E-05	1.1E-01	3.8E-04
Lav 2	8.5E-01	1.7E-01	1.2E+00	1.3E+0	7.0E-03	2.1E-04	1.2E-04	7.9E-04	8.9E-02	6.2E-04
Lav 3	8.5E-01	2.1E-01	1.3E+00	1.7E+0	8.0E-03	2.3E-04	6.1E-05	1.8E-04	1.5E-01	4.6E-02
LW 1	6.0E-01	1.9E-01	1.3E+00	4.3E-01	1.2E-03	5.3E-04	6.0E-05	6.6E-05	4.7E-02	3.7E-04
LW 2	6.8E-01	2.1E-01	1.5E+00	5.0E-01	1.3E-03	6.2E-04	8.6E-04	1.7E-03	9.1E-02	1.8E-03
LW 3	6.9E-01	3.8E+0	1.5E+00	7.4E-01	1.5E-03	4.4E-04	4.1E-04	8.4E-04	9.4E-02	1.2E-01
S 1	6.6E-01	9.2E-02	1.1E+00	1.3E+0	2.4E-03	5.3E-04	2.2E-05	nd	1.9E-01	1.6E-05
S 2	7.4E-01	7.6E-02	1.2E+00	1.4E+0	2.4E-03	1.1E-04	1.2E-04	4.2E-04	1.9E-01	1.4E-03
S 3	8.6E-01	4.3E-01	1.2E+00	1.7E+0	2.8E-03	5.0E-04	4.9E-05	4.9E-04	2.0E-01	3.7E-01

§ BC = Big Creek, Lav = Laverne, LW = Little Wall, and S = Saylorville.

1, 2, 3 = August, September and, October samplings, respectively.

^a Analyzed by Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES Thermo Jarrel Ash Model 61E).

Table 6. Composition of lake water with respect to heavy metals and soft bases for the four lakes studied.

Sample ID §	Soft Cations / Heavy Metals ^a			Hard Bases ^a
	Cu	Pb	Zn	SO ₄ -S
-----mmol/L-----				
Big Creek 1	2.71E-05	nd ^b	5.76E-05	1.36E-01
Big Creek 2	2.64E-05	nd	8.52E-05	9.77E-02
Big Creek 3	nd	nd	1.45E-05	1.45E-01
Laverne 1	6.44E-05	nd	7.15E-05	1.81E-01
Laverne 2	6.12E-05	nd	1.57E-04	1.90E-01
Laverne 3	4.30E-05	nd	3.13E-04	1.64E-01
Little Wall 1	3.87E-05	nd	1.21E-04	4.51E-02
Little Wall 2	1.94E-05	nd	1.30E-04	6.12E-02
Little Wall 3	nd	nd	2.15E-04	1.82E-01
Saylorville 1	4.35E-05	nd	7.90E-05	6.25E-01
Saylorville 2	6.35E-05	nd	9.54E-04	6.58E-01
Saylorville 3	nd	nd	1.41E-04	6.16E-01

§ 1,2,3 = August, September and, October samplings, respectively.

^a - classification according to Sullivan, 1977. Other hard bases such as CO₃⁻, NH₃, NO₃⁻, and PO₄-P can be found in Tables 12, 22 and 23 respectively.

^b - non-detectable

All analysis were carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

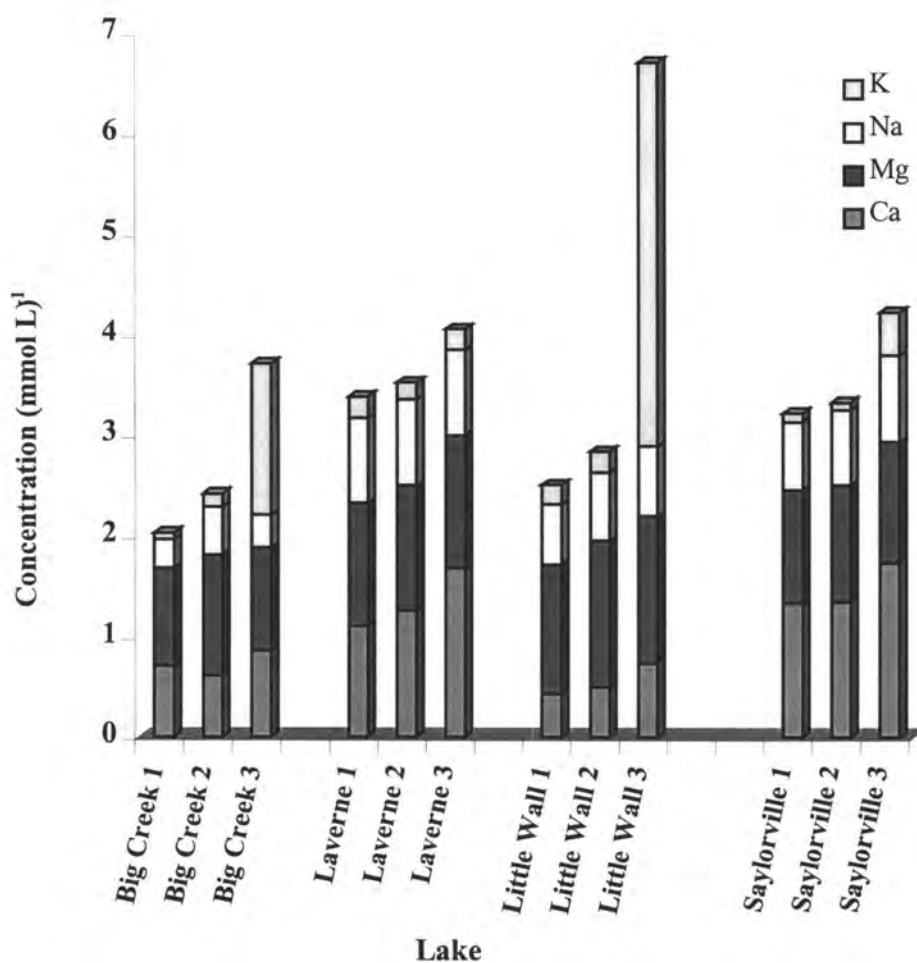


Figure 4. Graphic illustration of major cations for four Iowa lakes studied. 1,2 and 3 = August, September and October sampling dates. Note the proportional increase in K content in three lakes namely, Big Creek, Little Wall and Saylorville compared to Lake Laverne. These three lakes receive their input mainly from agricultural runoff as compared to Lake Laverne which receives runoff from urban center.

concentration increased (for example compare August data vs. October data). A possible explanation for this observation is algal bloom decomposition and/or agricultural runoff.

The data in Table 5 further show that there was a significant increase in K^+ concentration as the seasons progressed from summer to fall for Little Wall, Big Creek and Saylorville lake-water. All three lakes receive agricultural runoff. Lake Laverne, which does not receive agricultural runoff, did not show this trend. The time-period that this significant increase in potassium concentration was observed was during fertilization (October sampling), and it can therefore be speculated that this increase might be due to runoff from fertilized fields. More data are needed to confirm this observation. Monovalent cations are associated with elevated osmotic pressures on colloidal surfaces causing dispersion (Stumm and Morgan, 1997).

In the case of heavy metals (Table 6), there was no definite trends due to temperature. In some cases, e.g. that of Zn, there appeared to be an increase in heavy metal concentration as temperatures in lake decreased, whereas, Cu showed decrease as temperatures decreased in two of the lakes (Big Creek and Saylorville) compared to the other two lakes (Laverne and Little Wall), which showed a decrease in heavy metal concentration. A number of mechanisms may account for this observation and a most likely one is that the K_{sp} of minerals containing heavy metals is most likely temperature dependent.

GEOCHEM - Chemical speciation and saturation indices

Ion-association models such as the GEOCHEM-PC (Sposito and Mattigod, 1979; Parker et al., 1995), MINTEQ (Allison et al., 1991), and SOILCHEM, (Sposito and Coves, 1988) can be used for speciation of natural waters. In this study, the GEOCHEM-PC model,

version 1.24 (Sposito and Mattigod, 1979; Parker et al., 1995), was used. This model is capable of simulating solution speciation at standard pressure and temperature, hence, only experimental data representative of standard pressure and temperature was processed. The model was allowed to compute ionic strength (Table 7) at fixed pH and, no solids were allowed to precipitate.

The output from the GEOCHEM-PC, representing the four lake-waters, is shown in Tables 8-10. Table 8 shows the relative distribution of free metals and ligands whereas Table 9 and Table 10 show the relative distribution of metal complexes and complexed ligands, respectively. These data revealed that most of the metals were complexed as phosphates, carbonates and sulphates as well as hydroxides. For example more than 8 percent of the Fe^{2+} was in the form of an OH complex whereas in the case of aluminum almost all (100%) was associated with OH. In the case of manganese, more than 46% was associated with the CO_3^{2-} ligand. The latter ligand also formed significant number of complexes with Ca^{2+} and Mg^{2+} (see Table 10). There are two important implications with respect to formation of these complexes. One implication is that complexes play an important role in maintaining high dissolved concentration of the metals and ligands forming the complexes. The higher the complexation potential, the higher the impact on the solubility potential of the elements involved in the complexes. The second implication is the role of complexes on toxicity. Elements in a particular complex may be less or more toxic than in their pure ionic form.

Experimental data show that free CaCO_3 is available in all four lakes and because of this CaCO_3 occurrence, stability lines of CaCO_3 as a function of pH at three different pCO_2 values that might be encountered in the environment were established. These stability lines were generated by the Eq. $\log \text{Ca} = 9.9 - 2 \text{pH} + \log 1/\text{pCO}_2$ (Evangelou, 1998 and

Table 7. Chemical speciation of the four lakes studied showing computed ionic strength, alkalinity and pCO₂.

Sample ID	pH	Computed Ionic Strength	Computed alkalinity	Computed pCO ₂
			(eq/l)	(atm)
Big Creek	8.67	5.40 E-03	4.78 E-03	4.17E-04
Laverne	8.52	3.45 E-03	5.23 E-03	- ^a
Little Wall	9.10	5.64 E-03	4.78 E-03	1.74 E-04
Saylorville	8.57	7.76 E-03	3.43 E-03	4.90 E-04

^a not computed
 GEOCHEM (Sposito and Mattigod, 1979; Parker et al., 1995). The model considered fixed pH and no solids were allowed to precipitate.

Table 8. GEOCHEM output showing primary distribution of free metals and ligands for the four studied Iowa lakes.

Sample ID	Free Metal						Free Ligand				
	Ca	Mg	K	Na	Fe ²⁺	Mn ²⁺	Al	CO ₃	SO ₄	PO ₄	NO ₃
Big Creek	90.2	89.6	99.9	99.3	88.5	37.4	-	-	87.4	-	100
Laverne	94.1	94.0	99.9	99.4	93.5	53.4	-	-	57.8	-	100
Little Wall	81.9	79.3	99.9	99.0	75.7	17.7	-	5.76	88.8	23.9	100
Saylorville	89.0	89.4	99.7	99.3	88.3	- ^a	-	-	83.7	-	100

^a not computed

GEOCHEM version 1.24 is an equilibrium or ion association model (Sposito and Mattigod, 1979; Parker et al., 1995).

Data input included fixed pH and allowed no solids to precipitate.

Table 9. GEOCHEM output showing primary distribution of complexed metals for the four studied Iowa lakes.

Sample ID	Complexed Metals						
	Ca	Mg	K	Na	Fe ²⁺	Mn ²⁺	Al
Big Creek	8.7 with CO ₃	9.3 with CO ₃	- ^a	-	10.3 with OH	62.0 with CO ₃	100 with OH
Laverne	5.4 with CO ₃	5.6 with CO ₃	-	-	-	46.2 with CO ₃	100 with OH
Little Wall	17.7 with CO ₃	20.2 with CO ₃	-	-	23.4 with OH	82.0 with CO ₃	100 with OH
Saylorville	6.5 with CO ₃	6.9 with CO ₃	-	-	7.9 with OH	-	100 with OH

^a not given

Data obtained from GEOCHEM (Sposito and Mattigod, 1979; Parker et al., 1995).

Data input included fixed pH and allowed no solids to precipitate.

Table 10. GEOCHEM output showing primary distribution of complexed ligands for the four studied Iowa lakes.

Sample ID	Complexed Ligand		
		------(%)-----	
	CO ₃	SO ₄	PO ₄
Big Creek	- ^a	5.98 with Ca 6.52 with Mg	23.3 with Ca 22.2 with Mg 54.5 with H
Laverne	17.1 with Ca 78.8 with H	39.6 with Ca	74.2 with Ca 6.32 with Mg 19.5 with H
Little Wall	5.56 with Mg 76.9 with H	7.6 with Mg	23.9 with Ca 24.4 with Mg 51.6 with H
Saylorville	83.6 with H	9.59 with Ca 6.5 with Mg	30.8 with Ca 20.6 with Mg 48.6 with H

^a not given

GEOCHEM-PC version 1.24, is an equilibrium or ion association model (Sposito and Mattigod, 1979; Parker et al., 1995)

Data input included fixed pH and no solids were allowed to precipitate.

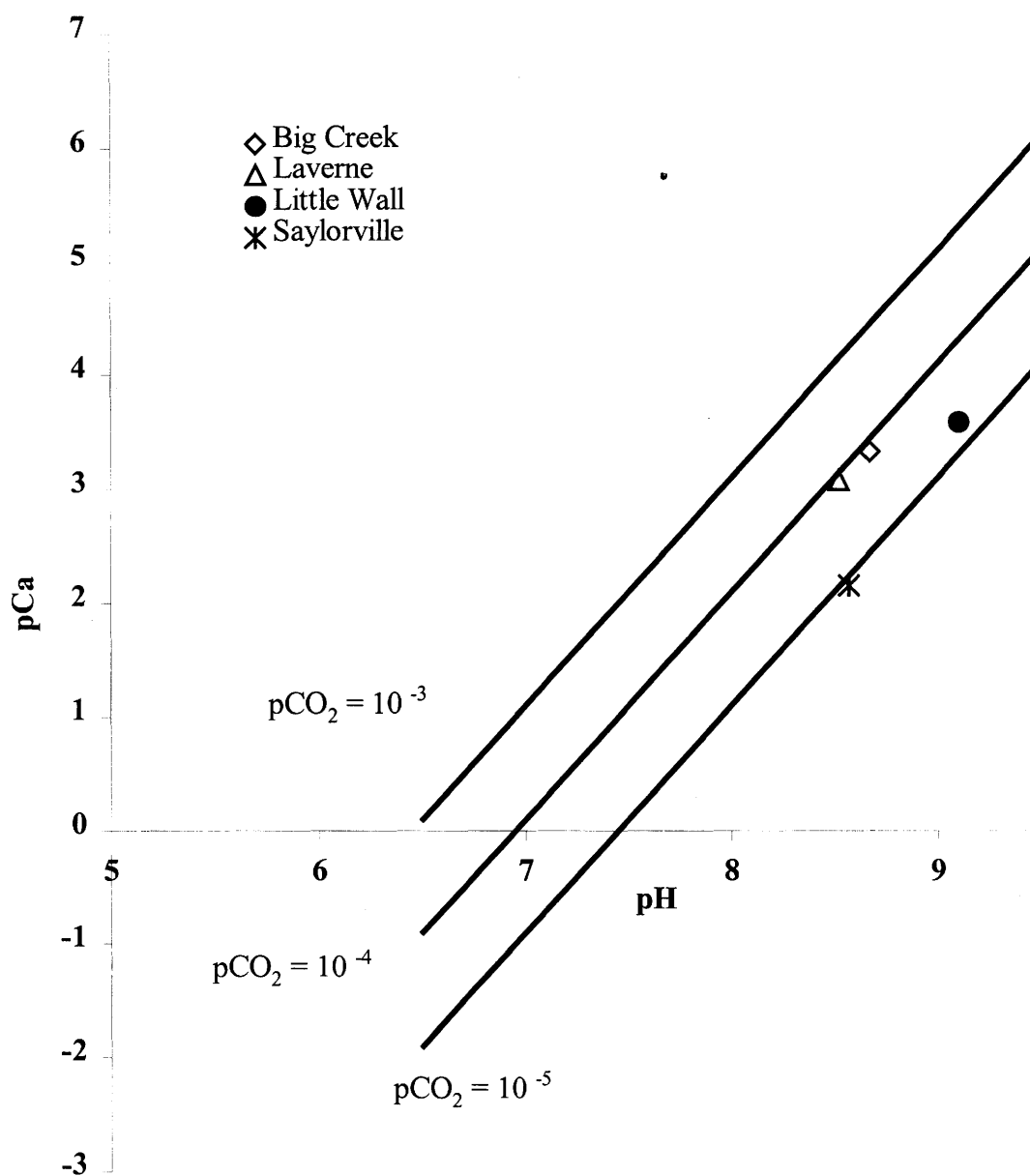


Figure 5. Stability diagram for calcium carbonate as a function of pH for the three pCO_2 levels and experimental data points representing the four lakes studied.

references therein). Experimental data points from the four lakes were fitted into this stability diagram to demonstrate the $p\text{CO}_2$ boundaries that govern solubility of CaCO_3 (Fig.5). From these stability lines, lake Laverne and Big Creek appear to be in equilibrium with $p\text{CO}_2$ at 10^{-4} atmospheres whereas Little Wall and Saylorville appear to be in equilibrium with $p\text{CO}_2$ at 10^{-5} atmospheres. These data suggested that, all lake-systems were low in $p\text{CO}_2$, which may imply that the systems were biologically inactive or strongly photosynthesizing.

Single ion activity data produced by the GEOCHEM-PC were used to compute for ion-activity products (IAP) for various hypothetical solids. Ion activity products were used to estimate saturation indices (SI) where $\text{SI}=\text{IAP}/\text{K}_{\text{sp}}$ for various solids that may potentially form or have formed based on the ionic composition of the lake-water. If SI was less than 1 then the system was considered to be undersaturated with respect to the specified solid, but if SI was greater than 1, then the system was considered to be supersaturated with respect to that particular solid, and/or the particular solid may be in the process of forming by precipitation. Therefore, based on the data in Table 11, all lake-waters under study were supersaturated with respect to CaCO_3 , MgCO_3 and Fe-OH-PO_4 and in the case of Laverne $\text{Ca}_3(\text{PO}_4)_2$. However, these data did not in any way prove that any or all of these solids were present. The data gave an indication that these solids might be formed or they are in the process of being formed.

Lake-Sediments – Physical Characterization

Some chemical characterization of the lake sediments used in this study is included in Table 12. The table shows composition of lake-sediments with respect to nitrogen and

Table 11. Table showing saturation indices of the potential solids that may form in the lakes upon any anthropogenic inputs.

Lake ID	Complex	IAP*	Ksp**	Saturation Index	Undersaturated Supersaturated
Big Creek	CaCO ₃	3.04E-08	3.98E-09	7.64E+00	Supersaturated
	CaSO ₄	4.10E-08	2.50E-05	1.64E-03	Undersaturated
	CaHPO ₄	1.35E-23	1.26E-19	1.07E-04	Undersaturated
	Ca ₄ H(PO ₄) ₃	2.50E-55	1.26E-47	1.99E-08	Undersaturated
	Ca ₃ (PO ₄) ₂	1.85E-32	1.26E-29	1.47E-03	Undersaturated
	Mg ₃ (PO ₄) ₂	4.81E-32	1.00E-25	4.81E-07	Undersaturated
	MgHPO ₄	1.85E-23	6.31E-19	2.94E-05	Undersaturated
	MgCO ₃	4.18E-08	7.90E-09	5.29E+00	Supersaturated
	Fe-OH-PO ₄	7.62E-25	1.00E-36	7.62E+11	Supersaturated
	Fe ₃ (PO ₄) ₂	3.19E-46	1.00E-36	3.19E-10	Undersaturated
	AlPO ₄	2.04E-30	7.94E-20	2.57E-11	Undersaturated
	MnHPO ₄	4.45E-28	1.58E-20	2.81E-08	Undersaturated
	Mn ₃ (PO ₄) ₂	6.64E-46	1.00E-30	6.64E-16	Undersaturated
Laverne	CaCO ₃	3.34E-07	3.98E-09	8.40E+01	Supersaturated
	CaSO ₄	3.62E-07	2.50E-05	1.45E-02	Undersaturated
	CaHPO ₄	2.06E-22	1.26E-19	1.63E-03	Undersaturated
	Ca ₄ H(PO ₄) ₃	6.65E-51	1.26E-47	5.28E-04	Undersaturated
	Ca ₃ (PO ₄) ₂	3.24E-29	1.26E-29	2.57E+00	Supersaturated
	Mg ₃ (PO ₄) ₂	3.98E-32	1.00E-25	3.98E-07	Undersaturated
	MgHPO ₄	2.20E-23	6.31E-19	3.49E-05	Undersaturated
	MgCO ₃	3.58E-08	7.90E-09	4.53E+00	Supersaturated
	Fe-OH-PO ₄	8.51E-25	1.00E-36	8.51E+11	Supersaturated
	Fe ₃ (PO ₄) ₂	1.74E-45	1.00E-36	1.74E-09	Undersaturated
	AlPO ₄	1.39E-29	7.94E-20	1.75E-10	Undersaturated
	MnHPO ₄	3.00E-28	1.58E-20	1.89E-08	Undersaturated
	Mn ₃ (PO ₄) ₂	1.00E-46	1.00E-30	1.00E-16	Undersaturated

* IAP = Ion Activity Product

** Solubility products (Ksp) of selected species at 25°C (298K) and 1.01 bar total pressure obtained from GEOCHEM (Sposito and Mattigod, 1979)

Table 11 (continued)

Lake ID	Complex	IAP*	Ksp**	Saturation Index	Undersaturated Supersaturated
Little Wall	CaCO ₃	5.07E-08	3.98E-09	1.27E+01	Supersaturated
	CaSO ₄	7.64E-09	2.50E-05	3.06E-04	Undersaturated
	CaHPO ₄	2.31E-23	1.26E-19	1.84E-04	Undersaturated
	Ca ₄ H(PO ₄) ₃	5.08E-54	1.26E-47	4.04E-07	Undersaturated
	Ca ₃ (PO ₄) ₂	2.20E-31	1.26E-29	1.75E-02	Undersaturated
	Mg ₃ (PO ₄) ₂	5.13E-30	1.00E-25	5.13E-05	Undersaturated
	MgHPO ₄	6.61E-23	6.31E-19	1.05E-04	Undersaturated
	MgCO ₃	1.45E-07	7.90E-09	1.83E+01	Supersaturated
	Fe-OH-PO ₄	4.36E-23	1.00E-36	4.36E+13	Supersaturated
	Fe ₃ (PO ₄) ₂	3.69E-43	1.00E-36	3.69E-07	Undersaturated
	AlPO ₄	9.23E-31	7.94E-20	1.16E-11	Undersaturated
	MnHPO ₄	6.44E-28	1.58E-20	4.06E-08	Undersaturated
	Mn ₃ (PO ₄) ₂	4.75E-45	1.00E-30	4.75E-15	Undersaturated
Saylorville	CaCO ₃	3.96E-08	3.98E-09	9.96E+00	Supersaturated
	CaSO ₄	3.03E-07	2.50E-05	1.21E-02	Undersaturated
	CaHPO ₄	6.30E-23	1.26E-19	5.00E-04	Undersaturated
	Ca ₄ H(PO ₄) ₃	4.53E-53	1.26E-47	3.60E-06	Undersaturated
	Ca ₃ (PO ₄) ₂	7.19E-31	1.26E-29	5.71E-02	Undersaturated
	Mg ₃ (PO ₄) ₂	4.50E-31	1.00E-25	4.50E-06	Undersaturated
	MgHPO ₄	5.38E-23	6.31E-19	8.53E-05	Undersaturated
	MgCO ₃	3.39E-08	7.90E-09	4.29E+00	Supersaturated
	Fe-OH-PO ₄	1.50E-24	1.00E-36	1.50E+12	Supersaturated
	Fe ₃ (HPO ₄) ₂	1.84E-45	1.00E-36	1.84E-09	Undersaturated
	AlPO ₄	8.67E-31	7.94E-20	1.09E-11	Undersaturated
	MnHPO ₄	4.39E-28	1.58E-20	2.77E-08	Undersaturated
	Mn ₃ (HPO ₄) ₂	2.43E-46	1.00E-30	2.43E-16	Undersaturated

Table 12. Sediment Composition for the four studied Iowa lakes^a.

Sample Location	Sample ID §	Total C	Total N	Calcite	Dolomite	Inorganic C	Estimated Organic C	CaCO ₃ (equiv)
		-----mg/kg-----						
Big Creek	SED - 1	1200	1800	9.15	0.10	1.11	0.09	9.26
	SED - 2	1530	2800	0.49	2.45	0.38	1.15	3.16
Laverne	SED - 1	2600	2200	3.27	11.24	1.86	0.74	15.5
	SED - 2	2240	2300	2.28	8.13	1.33	0.91	11.1
Little Wall	SED - 1	1840	2300	1.41	1.83	0.41	1.43	3.40
	SED - 2	1290	1800	1.45	6.39	1.01	0.28	8.39
Saylorville	SED - 1	1350	1300	4.10	7.91	1.52	nd ^a	12.7
	SED - 2	630	1200	2.13	6.14	1.06	nd	8.80

^aDry combustion at 950 °C using LECO CHN 600 analyzer.

§ SED = Sediment

1,2 = August and October samplings, respectively

nd^a = non-detectable.

carbon. It can be deduced from these data that the sediments are alkaline earth carbonate-rich and also contain considerable amounts of nitrogen (N).

X-Ray Analysis

The mineralogy of soil or geologic material e.g., lake-sediments controls many of the physical and chemical properties of the sample material. The chemical properties of soils surrounding the studied lakes were described in the introduction section of the Thesis. X-ray diffractograms from the lake-sediment samples are as shown in Figs. 6-9. They indicate that the sediment samples obtained from the bottom of the four lakes are of mixed mineralogy but mostly smectitic in nature. Smectites are responsible for a large portion of a sample's CEC.

The basal diffraction peaks obtained from the untreated lake-sediment samples and identified at 14, 10, 7.1, 5.0 and, 3.57 angstroms (Å) suggest presence of smectites, mica, kaolinite and gibbsite respectively. Smectites are responsible for the shrink-swell properties of clay minerals (Whittig, L.D and W.R Allardice, 1986). These shrink-swell properties are responsible for the potential fixation of ions like K^+ and NH_4^+ (Liu et al. 1997; Evangelou, 1998 and references therein), and/or clay flocculation/dispersion processes in nature. Smectites yield x-ray diffraction patterns that vary with exchangeable cation, relative humidity, association with certain organic molecules and heat treatment. There are quite a number of different smectites (Whittig, L.D and W.R Allardice, 1986 p. 351) with the most common being montmorillonite. When saturated with magnesium ions, smectites with whatever layer charge yield a strong basal reflection at 14 - 15 Å (Wilson, 1987).

A near 14 Å diffraction peak from Mg-saturated air-dried sample shown in all four lake diffractograms (Figs. 6-9) indicated the presence of either smectite, vermiculite,

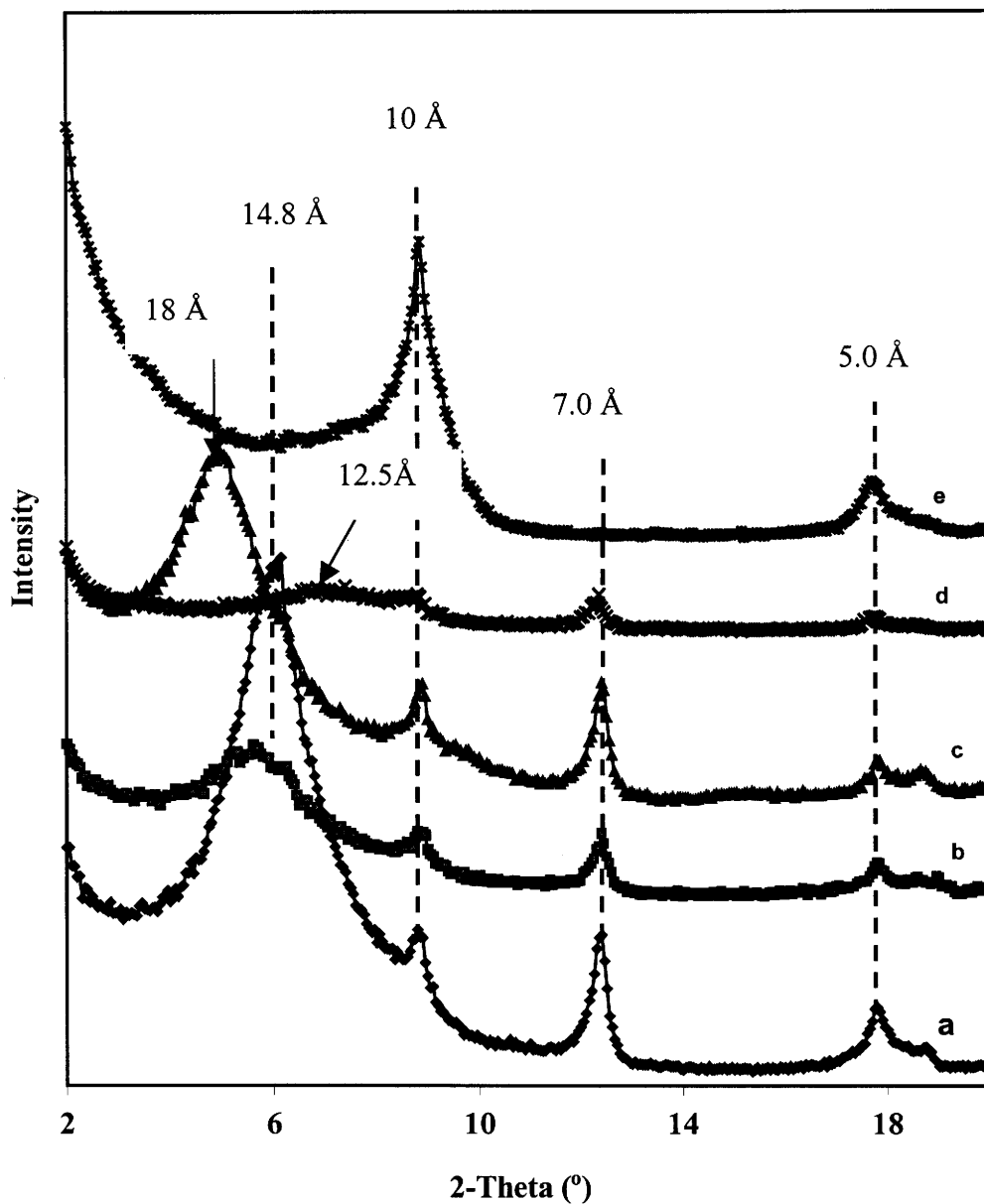


Figure 6. X-Ray diffractogram for Big Creek Lake under different treatments. a = untreated, b = Mg treated, c = Mg+Glycerol treated, d = K treated, and e = K + 550 C° treated. The test was conducted on Siemens D 500 Diffractometer equipped with a copper anode X-ray tube that was operated at 50KV and 27mA.

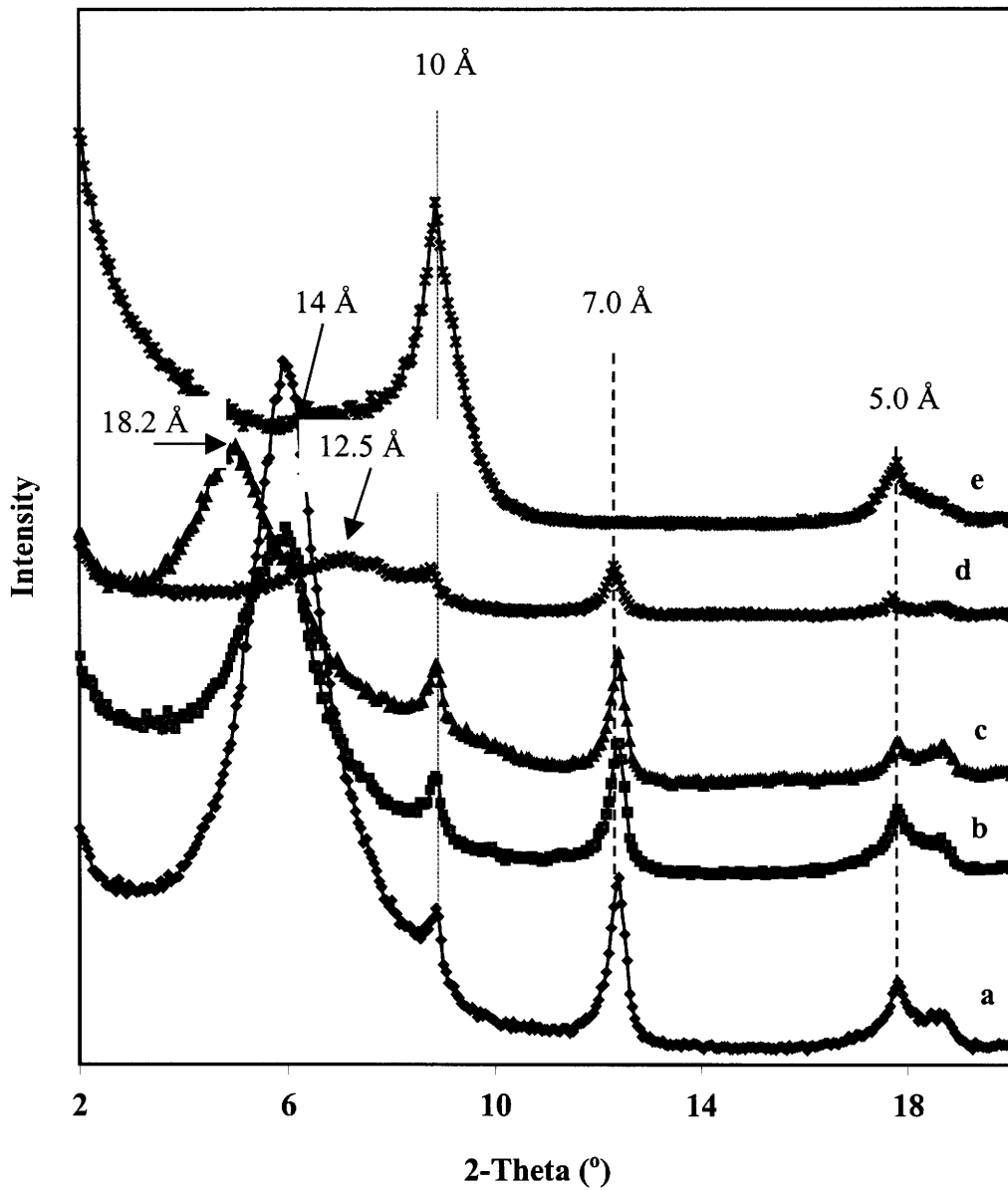


Figure 7. X-Ray diffractogram for Lake Laverne sediments under different treatments. a = untreated, b = Mg treated, c = Mg+Glycerol treated, d = K treated, and e = K + 550 °C treated. The test was conducted on Siemens D 500 Diffractometer equipped with a copper anode X-ray tube that was operated at 50 KV and 27 mA.

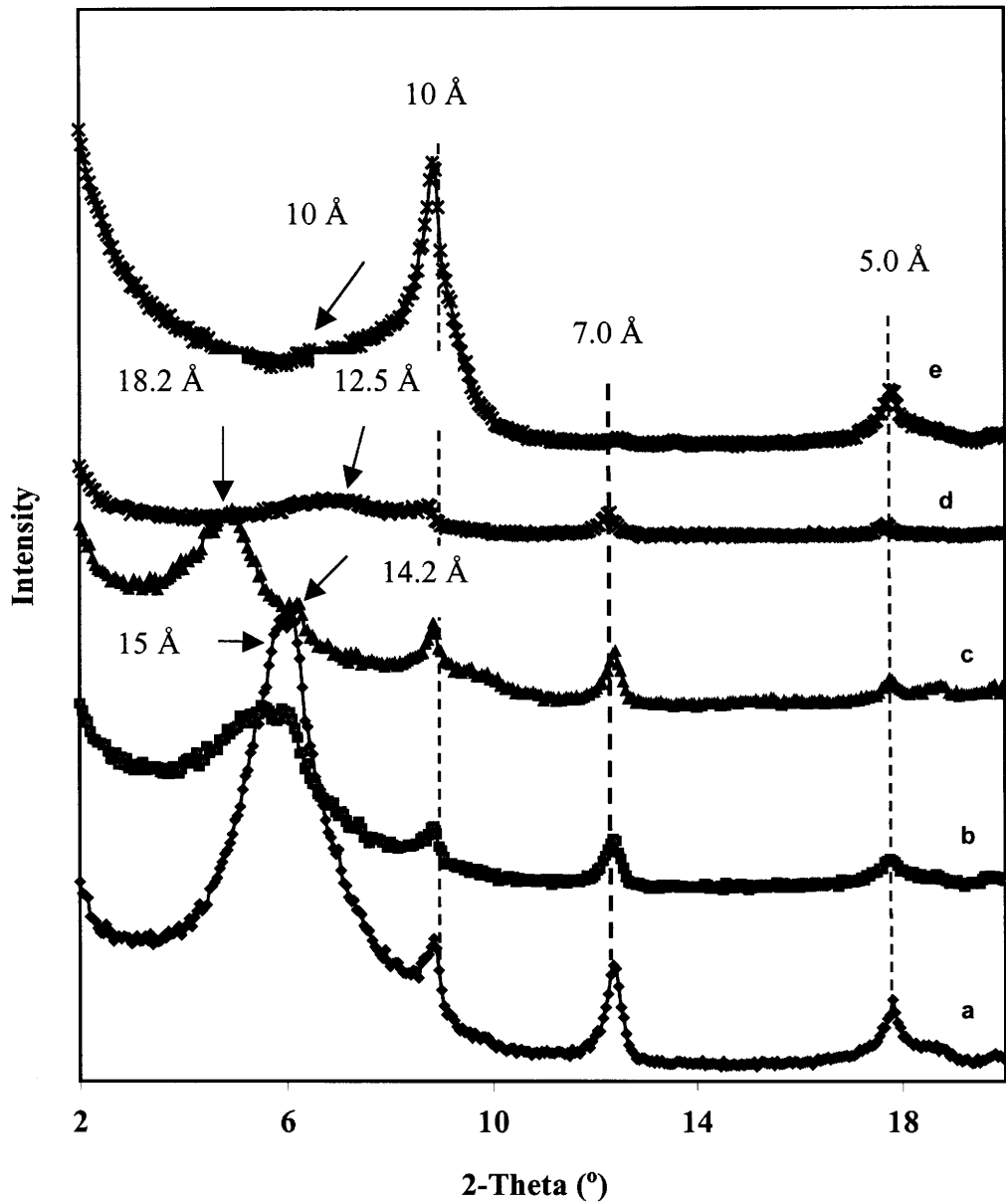


Figure 8. X-Ray diffractogram for Little Wall lake sediments under different treatments. a = untreated, b = Mg treated, c = Mg+Glycerol treated, d = K treated, and e = K + 550 °C treated. The test was conducted on Siemens D 500 Diffractometer, equipped with a copper anode X-ray tube that was operated at 50 KV and 27 mA.

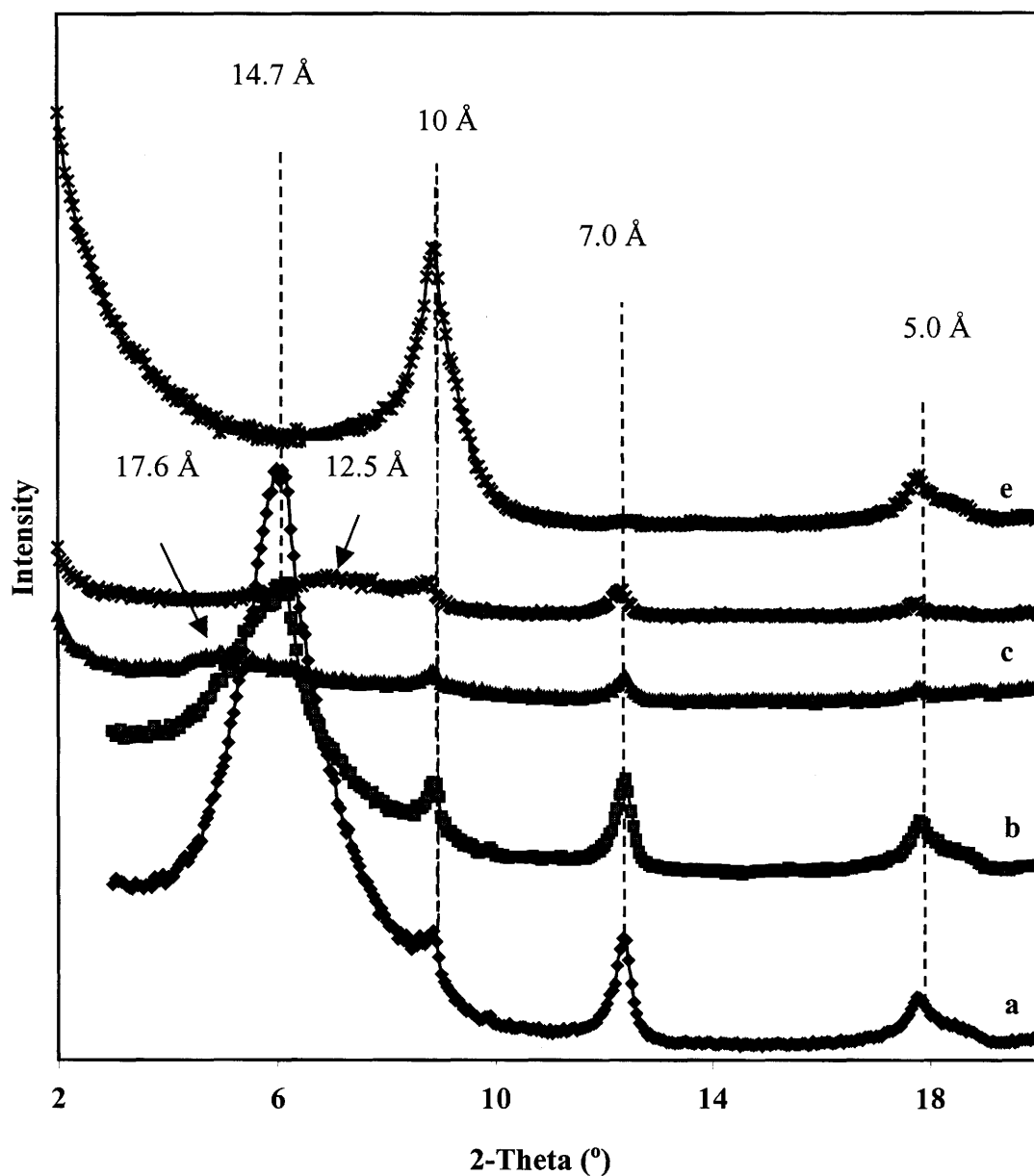


Figure 9. X-Ray diffractogram for Saylorville lake sediments under different treatments. a = untreated, b = Mg treated, c = Mg+Glycerol treated, d = K treated, and e = K + 550 °C treated. The test was conducted on Siemens D 500 Diffractometer, equipped with a copper anode X-ray tube that was operated at 50 KV and 27 mA.

solvated sample in all four lakes (Figs. 6-9) indicated the presence of montmorillonite. The 18 Å spacing is due to the expansion of the 2:1 layers, and allows their distinction from non-expanding 2:1 minerals. Solvation in glycerol simply expands the clay mineral. Testing for non-expandable 2:2 clays required treatment with K^+ . All K-saturated clay samples showed collapse from 14 Å peak to 12.5 Å signifying loss of water of hydration and thus presence of vermiculite. Heating of the K-saturated clays samples at 550°C allowed for distinction between smectite and chlorite, verifying presence/absence of hydroxy-aluminum inter-layered clays. Amongst all the sediment samples, lake Laverne and Little Wall showed traces of chlorite since the 14 Å peak did not disappear despite heat treatment at 550 °C (Fig. 7, 8).

The x-ray data was run up to 30 2-theta and did not allow us to identify carbonates. However, quantification and identification of total carbonates and distinction between calcite and dolomite in lake-sediments was carried out using the Chittick apparatus as outlined in the sediment composition part. In summary, clays from all four lakes indicated that they were smectitic in nature. Generally, smectites are not expected to be associated with fixed quantities of K^+ or NH_4^+ . However, on-going work in Dr. V.P Evangelou's laboratory and others at Iowa State university has revealed that the particular smectite associated with Iowa soils does fix considerable quantities of K^+ and NH_4^+ .

Thermal Analysis

Thermo-analytical techniques complement the principal investigation tools like X-ray diffraction, hence thermal analysis can be of importance in determining and quantifying mineralogy of lake-sediment samples. Differential thermal analysis (DTA) gives basic

mineralogy of lake-sediment samples. Differential thermal analysis (DTA) gives basic differences in temperature between the sample and reference material while both are subjected to a controlled temperature regime. The resultant plot is change in temperature (ΔT) in the y-axis and time or temperature in the x-axis, with the identified peaks either being endothermic or exothermic (Paterson and Swaffield, 1987). From the results obtained for all lake sediment samples, the DTA curves (Figs. 10-11) showed two main peaks, an endothermic peak in the temperature range of 500-600°C and an exothermic one at around 900°C, suggesting presence of the kaolin group. The main endothermic peak at 600°C in all lake-sediments was attributed to dehydroxylation of the mineral (Paterson and Swaffield, 1987). Furthermore, all four lake-sediments showed a low endothermic peak in the DTA curves, which is the most significant peak for the smectite group. This peak was attributed to loss of sorbed water in the interlayers of the clay mineral (Paterson and Swaffield, 1987).

Sediment Composition – Chemical Characterization

Extractable Cations and Nutrients

In the sediment-water systems complexes are formed by cations with some central species. Stable complexes are also formed when the cations become adsorbed to soil exchange surfaces (Sullivan, 1977 and references therein). Upon reacting with a surface, a chemical species may form either an inner sphere or an outer sphere complex (Evangelou, 1998 p.167 and references therein). However, stability of a given complex depends on further reactions with all other cations introduced to the system. This brings about the

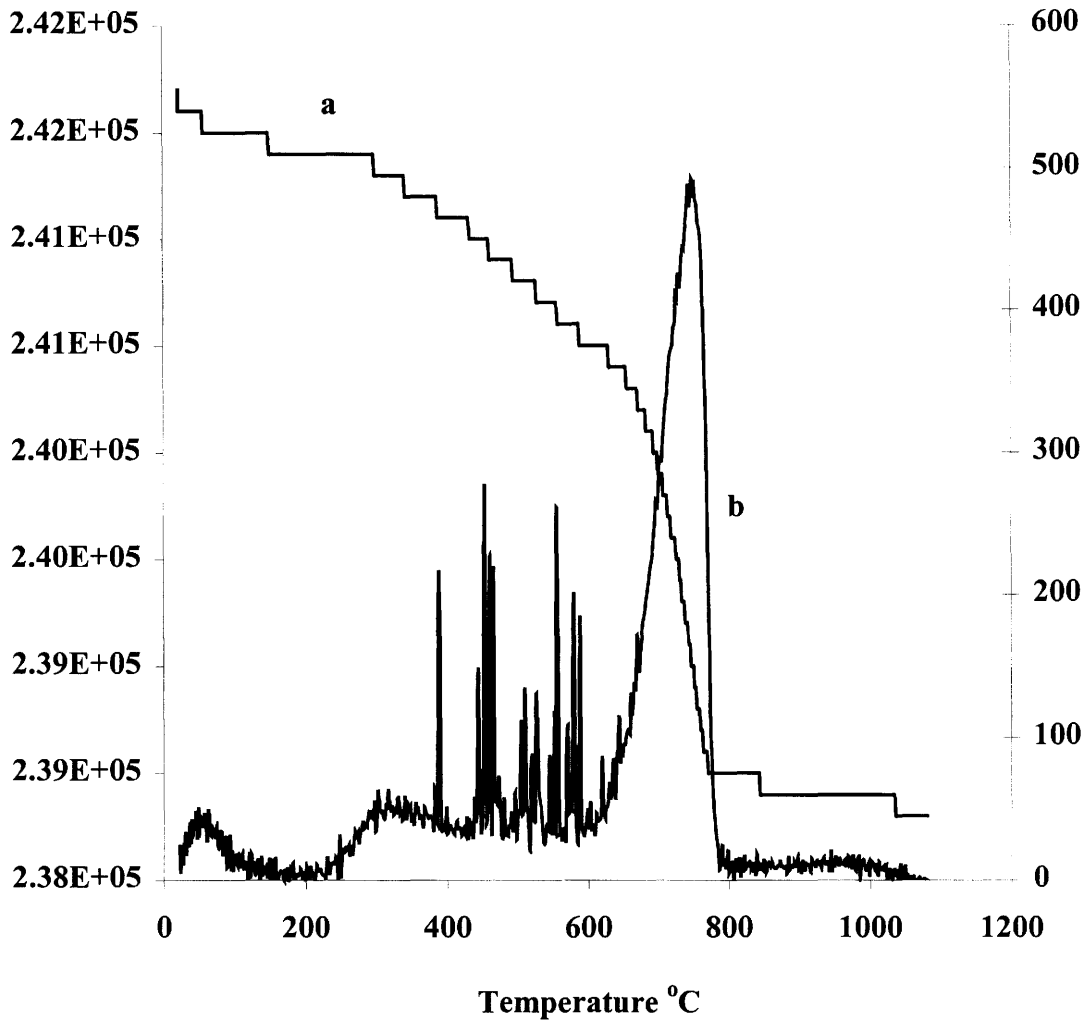


Figure 10. Typical example of a Thermogravimetric (TG)^a [ug] and Derivative Thermogravimetric (DTG)^b [ug/min] curves for Little Wall Lake bottom-sediments. Thermal analysis was obtained by using approximately 0.2-g sediment of <2- μ m pore size. The TG measures the change in mass of the sample as it is heated on a controlled temperature program setting and the DTG curve is obtained through differentiation of the TG curve.

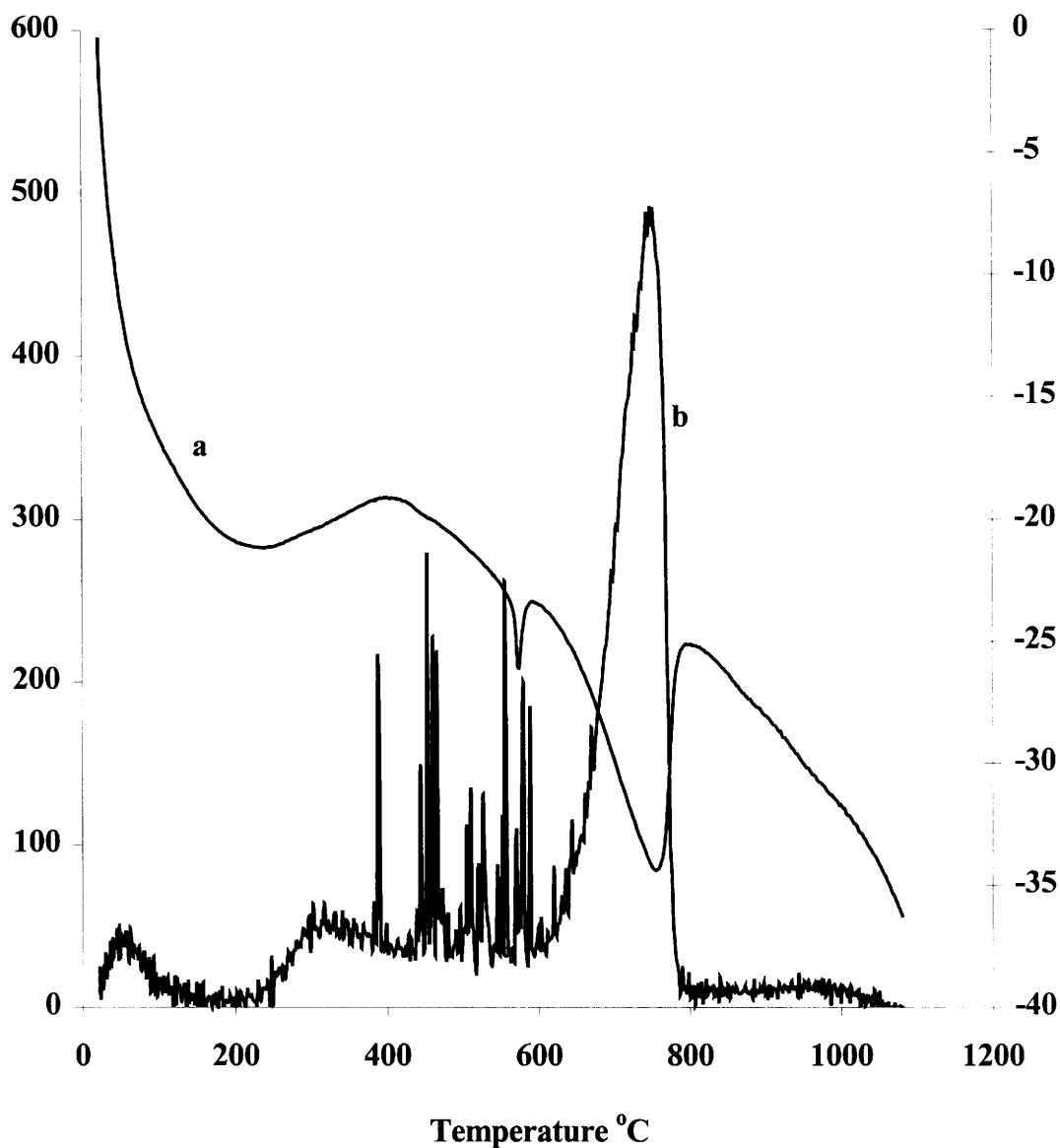


Figure 11. Typical example of a Differential Thermal Analysis (DTA) in [uV]^a and Derivative Thermographic (DTG)^b [ug/min] curves for Little Wall bottom-lake sediments. Thermal analysis was obtained by using approximately 0.2-g sediment of <2 μm pore size. The TG measures the change in mass of the sample as it is heated on a controlled temperature program setting and the DTA measures the change in temperature. This change in temperature is plotted on the ordinate, with endothermic peaks pointing downwards and temperature of the sample is plotted on the x-axis.

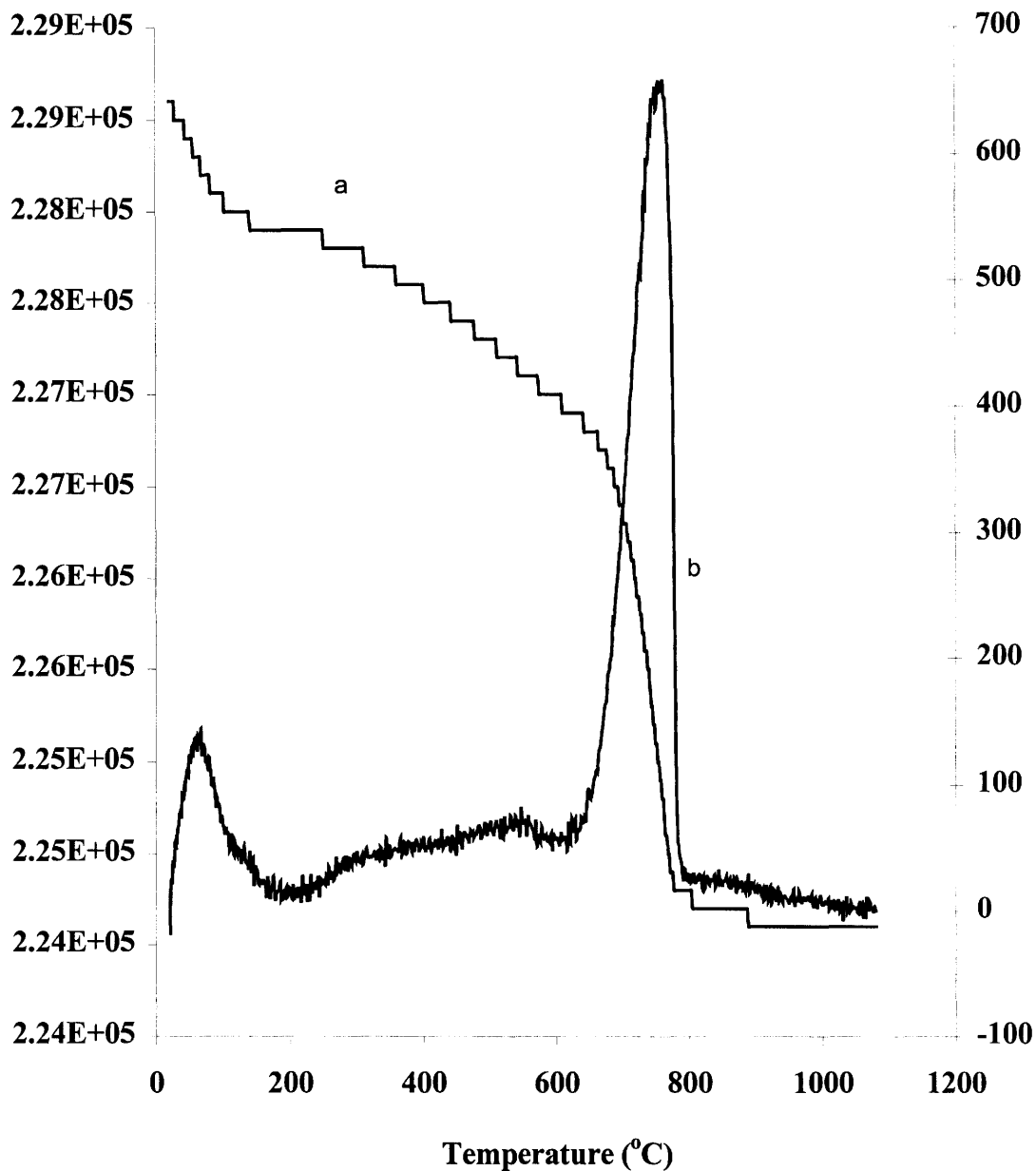


Figure 12. Typical example of a Thermogravimetric (TG)^a [ug] and Derivative Thermogravimetric (DTG)^b [ug/min] curves for Saylorville bottom-lake sediments. Thermal analysis was obtained by using approximately 0.2-g sediment of <2- μ m pore size. The TG measures the change in mass of the sample as it is heated on a controlled temperature program setting and the DTG is obtained through differentiation of the TG curve.

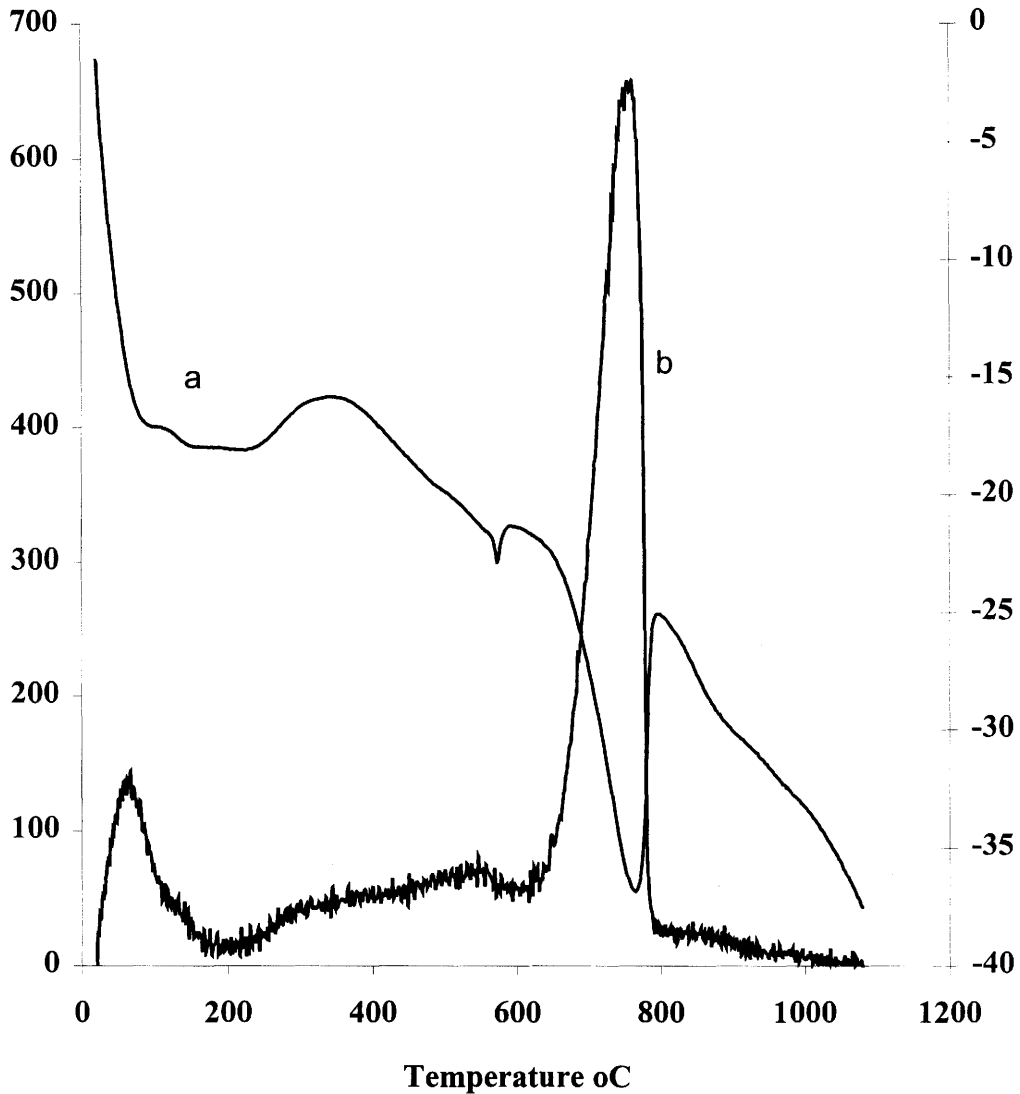


Figure 13. Typical example of a Differential Thermal Analysis (DTA) [uV]^a and Derivative Thermographic (DTG)^b [ug/min] curves for Saylorville bottom-lake sediments. Thermal analysis was obtained by using approximately 0.2-g sediment of <2 μm pore size. The TG measures the change in mass of the sample as it is heated on a controlled temperature program setting and the DTA measures the change in temperature. This change in temperature is plotted on the ordinate, with endothermic peaks pointing downwards and temperature of the sample is plotted on the x-axis.

principal of hard and soft acids and bases (Sullivan, 1977). The principle of hard and soft bases (HSAB) is useful for understanding a vast variety of chemical phenomena such as solution equilibrium, solubility, gas phase equilibrium, hydrogen bonding, and metal-ion-surface behavior (Pearson, 1968a).

According to Lewis (1923) an acid is a substance that can accept an electron pair from a base and a base is a substance that can share its electrons with an acid. However, with this interpretation being too broad, many classifications came about, the most well known and used being originated by Pearson (1963). Pearson (1963) classified these acids as follows: hard acids are usually small in size, with high positive charge, high electronegativity, low polarizability and do not contain unshared pairs of electrons in their outer shells; soft acids are the opposite of hard acids; hard bases are those with high electronegativity, low polarizability, and hard to oxidize and; soft bases are those that have low electronegativity and high polarizability and are very easy to oxidize. However, borderline species do occur, and these can behave in either way depending on the solution environment (Pearson, 1968a).

The principle behind the HSAB theory is that hard acids tend to associate with hard bases and soft acids with soft bases. This finding makes it possible to predict stable complex formation in a lake-sediment system. For example, if the exchanger site is a hard base, then the theory leads us to predict that if two chemical species are present in solution, e.g., Na^+ and Cd^{2+} , then Na^+ will be preferred over Cd^{2+} . Therefore, by knowing the relative 'hardness' or 'softness' of various species in an aqueous-sediment environment, then the stability of complexes formed can be predicted by HSAB theory.

The data in Tables 13-16 and 17-20 show extractable cations present in the four lake-sediments. An interesting piece of information coming from the data in Tables 14-17 is the extractable Na^+ by Mehlich III. Commonly, agricultural soils in Iowa contain a very small quantity of Na^+ in relation to the Na^+ present in the sediments. Data of exchangeable sodium percentage (ESP) (Tables 14 – 17), an index of soil colloid dispersion, show that ESP (corrected for calcite-calcium) varied from approximately 10 to 30 (sample BC 1 was not included since calcite-Ca was greater than Mehlich III Ca). Note that ESP values greater than approximately 10 signify soil colloid dispersion (US Salinity Lab. staff, 1954). This suggested that dispersion in Iowa lakes would be affected by Na^+ inputs. Potential sources of this Na^+ are manures applied to agricultural fields and/or road de-icing salts, e.g., NaCl.

Fixation is one of the soil processes that influences the availability of ions. In the case of K^+ , fixation occurs when it cannot be easily removed from the soil or sediment by classical ion exchange, as potassium is tightly bound in interlayer position of 2:1 phyllosilicates (Liu et al., 1997). The chemistry of K^+ and ammonium (NH_4^+) in soils is closely related as both ions have low hydration energies and similar ionic radii. The two ions can comfortably fit in the ditrigonal holes in the basal oxygen plane of the 2:1 phyllosilicates, and collapse the clay-interlayers, hence are referred to as ‘fixed’ or ‘confined’. Ion fixation reduces bioavailability and/or release to water. However, it may be released by stronger means (Liu et al., 1997). In this thesis fixed K^+ or NH_4^+ would be referred to as ‘confined’. ‘Confined’ implies temporarily fixed whereas ‘fixed’ implies a permanent condition.

Table 21 shows forms of potassium in the four lakes. The data suggest that most of the K^+ in these lake systems exist in non-exchangeable or ‘fixed’ form. High K^+

Table 13. Extractable cations for Big Creek lake sediments using various extraction procedures at two sampling dates.

Procedure [§]	Na	K	Mg	Ca ^φ	Sr	Ba	Ti	Mn	Fe	Si	Al	Σ _{xi}	ESP ^e
-----cmol _c /kg-----													(%)
Mehlich III^a													
1	7.78	0.73	6.30	53.4	- ^d	-	-	2.69	2.95	-	-	73.85	52.3^f
2	6.80	0.73	6.00	17.5	-	-	-	1.90	4.09	-	-	37.02	29.15
HNO₃^b													
1	0.67	0.72	24.4	50.4	0.01	0.08	0.02	1.57	27.7	2.14	14.9	122.6	
2	0.66	0.89	4.38	7.24	0.01	0.04	0.03	0.57	9.35	0.59	16.5	40.30	
Na₂CO₃^c													
1	-	167.0	84.0	280.8	1.49	0.02	13.0	8.61	279.0	412.7	363.6	1610	
2	-	170.5	55.8	182.7	1.47	0.02	14.5	6.38	187.8	418.8	391.5	1430	

§ 1,2 = August and October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique was used for determination of total ions in sediments (Jackson, 1958).

^d not determined.

^φ contain calcium from calcite.

^e ESP = Exchangeable Sodium Percentage = ExNa/ΣEx (cations) *100.

Ex(cation) being sum of Mehlich III cations except Ca.

ExCa = Mehlich III Ca minus calcite Ca.

^f probable error in calcite concentration.

All analysis carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 14. Extractable cations for Lake Laverne sediments using various extraction procedures at two sampling dates.

Procedure [§]	Na	K	Mg	Ca [†]	Sr	Ba	Ti	Mn	Fe	Si	Al	Σ_{xi}	ESP ^e
	-----cmol _c /kg-----												(%)
Mehlich III^a													
1	7.63	1.28	7.99	64.1	- ^d	-	-	2.12	5.90	-	-	89.02	45.2
2	7.48	1.12	6.96	48.1	-	-	-	1.30	7.84	-	-	72.80	41.4
HNO₃^b													
1	5.68	1.19	42.8	101.5	0.05	0.06	0.02	0.70	12.3	5.50	18.4	188.2	
2	12.2	1.03	33.9	91.4	0.05	0.05	0.02	0.78	10.9	4.06	18.3	172.3	
Na₂CO₃^c													
1	-	160.7	130	456	1.60	0.01	14.0	4.83	166.4	396	407	1592	
2	-	147.8	72.7	326	1.65	0.00	11.2	3.03	121.1	379	382	1444	

§ 1,2 = August, October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique was used for total ion determination in lake sediments (Jackson, 1958).

^d not tested.

[†] contain calcium from calcite.

^e ESP = Exchangeable Sodium Percentage = ExNa/ΣEx (cations) * 100.

Ex(cation) being sum of Mehlich III cations except Ca

ExCa = Mehlich III Ca minus calcite Ca.

All analysis carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 15. Extractable cations for Little Wall lake sediments using various extraction procedures at two sampling dates.

Extractant [§]	Na	K	Mg	Ca [†]	Sr	Ba	Ti	Mn	Fe	Si	Al	Σ _{xi}	ESP ^e
	-----cmol/kg-----												(%)
Mehlich III^a													
1	8.02	0.58	5.78	71.7	- ^d	-	-	0.60	2.62	-	-	89.33	12.67
2	7.60	0.43	3.92	48.5	-	-	-	0.48	2.48	-	-	63.41	24.17
HNO₃^b													
1	1.73	0.40	26.0	54.1	0.02	0.02	0.04	0.19	3.85	2.47	5.21	94.03	
2	0.89	0.26	25.0	51.4	0.02	0.01	0.04	0.19	3.17	2.12	4.36	87.46	
Na₂CO₃^c													
1	-	132.2	85.5	266.5	1.59	0.07	8.78	2.22	79.9	331.2	273.9	1182	
2	-	142.7	77.0	255.6	1.64	0.01	10.5	2.05	74.6	326.5	297.1	1188	

§ 1,2 = August and October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique was used for determination of total ions in sediments (Jackson, 1958).

^d not tested.

[†] contain calcium from calcite.

^e ESP = Exchangeable Sodium Percentage = ExNa/ΣEx (cations) *100.

Ex(cation) being sum of Mehlich III cations except Ca.

ExCa = Mehlich III Ca minus calcite Ca.

All analysis carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 16. Extractable cations for Saylorville lake sediments using various extraction procedures at two sampling dates.

Extractant [§]	Na	K	Mg	Ca [†]	Sr	Ba	Ti	Mn	Fe	Si	Al	Σ _{xi}	ESP ^c
	-----cmol _c /kg-----												(%)
Mehlich III^a													
1	7.58	0.26	8.91	132.0	- ^d	-	-	1.29	0.78	-	-	150.82	11.36
2	7.35	0.48	6.92	101.1	-	-	-	0.52	0.42	-	-	116.79	10.03
HNO₃^b													
1	0.88	0.20	22.7	65.1	0.02	0.02	0.04	0.47	3.82	2.07	3.91	99.23	
2	0.64	0.16	16.6	49.6	0.01	0.02	0.05	0.30	3.66	1.43	3.79	76.26	
Na₂CO₃^c													
1	-	151.3	86.9	389.4	1.88	0.03	6.29	3.95	110.6	361.0	345.4	1457	
2	-	146.5	57.2	275.9	1.70	0.00	4.38	2.06	53.1	521.2	338.9	1401	

§ 1,2 = August and October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique was used for determination of total ions in sediments (Jackson, 1958).

^d means not tested.

[†] Contain calcium from calcite.

^c ESP = Exchangeable Sodium Percentage = ExNa/ΣEx (cations) *100.

Ex(cation) = sum of Mehlich III cations except Ca.

ExCa = Mehlich III Ca minus calcite Ca.

All analyses were carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 17. Extractable heavy metals and hard bases for Big Creek lake-sediments using various extraction procedures at two sampling dates.

Extractant [§]	Soft Cations / Heavy Metals ^e			Hard Bases ^e
	Cu	Pb	Zn	SO ₄ -S
	-----cmol _c /kg-----			(cmol _c /kg)
Mehlich III^a				
1	0.02	- ^d	0.03	0.17
2	nd	-	0.01	0.12
HNO₃^b				
1	nd ^f	nd	0.03	0.30
2	nd	nd	0.03	0.57
Na₂CO₃^c				
1	0.14	nd	0.69	-
2	0.40	nd	0.45	-

§ 1,2 = August and October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique analyzed for total ions in sediments (Jackson, 1958).

^d not tested.

^e classification according to Sullivan, 1977. Other hard bases such as CO₃⁻, NH₃, NO₃⁻, and PO₄-P can be found in Tables 12, 22 and 23 respectively.

^f - non detectable.

All analyses were carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 18. Extractable heavy metals and hard bases for lake Laverne sediments using various extraction procedures at two sampling dates.

Extractant [§]	Soft Cations / Heavy Metals ^e			Hard Bases ^e
	Cu	Pb	Zn	SO ₄ -S
	-----cmol _c /kg-----			(cmol _c /kg)
Mehlich III^a				
1	0.01	- ^d	0.04	0.58
2	nd ^f	-	0.04	0.29
HNO₃^b				
1	0.01	nd	0.06	0.80
2	0.02	nd	0.05	1.15
Na₂CO₃^c				
1	0.17	nd	0.55	-
2	0.25	nd	0.45	-

§ 1,2 = August, October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique analyzed for total ions in sediments (Jackson, 1958).

^d means not tested.

^e classification according to Sullivan, 1977. Other Hard bases such as CO₃⁻, NH₃, NO₃⁻, and PO₄-P can be found in Tables 12, 22 and 23 respectively.

^f non detectable.

All analyses were carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 19. Extractable heavy metals and hard bases for Little Wall lake- sediments using various extraction procedures at two sampling dates.

Procedure [§]	Soft Cations / Heavy Metals ^e			Hard Bases ^e
	Cu	Pb	Zn	SO ₄ -S
	-----cmol _c /kg-----			(cmol _c /kg)
Mehlich III^a				
1	nd ^f	- ^d	0.02	0.58
2	nd	-	0.02	0.05
HNO₃^b				
1	nd	nd	0.02	2.20
2	nd	nd	0.02	0.97
Na₂CO₃^c				
1	3.37	nd	2.71	-
2	2.17	nd	0.18	-

§ 1,2 = August and October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique was used for determination of total ions in sediments (Jackson, 1958).

^d not determined.

^e classification according to Sullivan, 1977. Other Hard bases such as CO₃⁻, NH₃, NO₃⁻, and PO₄-P can be found in Tables 12, 22 and 23 respectively.

^f non-detectable.

All analyses were carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 20. Extractable heavy metals and hard bases for Saylorville lake-sediments using various extraction procedures at two sampling dates.

Extractant [§]	Soft Cations / Heavy Metals ^e			Hard Bases ^e
	Cu	Pb	Zn	SO ₄ -S
	-----cmol/kg-----			(cmol/kg)
Mehlich III^a				
1	nd ^f	- ^d	0.01	0.05
2	nd	-	0.02	0.06
HNO₃^b				
1	nd	nd	0.01	0.38
2	nd	nd	0.01	0.29
Na₂CO₃^c				
1	1.08	nd	1.42	-
2	1.15	nd	0.47	-

[§] 1,2 = August and October samplings, respectively.

^a Mehlich III is a mixture of NH₄F-EDTA and nitric acid (Mehlich, 1984).

^b 0.1 M nitric acid used to digest sediment samples (Helmke and Sparks, 1996).

^c Na₂CO₃ fusion technique was used for determination of total ions in sediments (Jackson, 1958).

^d means not tested.

^e classification according to Sullivan, 1977. Other Hard bases such as CO₃⁻, NH₃, NO₃⁻, and PO₄-P can be found in Tables 12, 22 and 23 respectively.

^f non-detectable

All analyses were carried out by use of an Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

Table 21. Forms of Potassium in the lake-water and -sediments for the four studied Iowa lakes at two sampling dates.

Sample ID [§]	Solution K ^a (mmol/l)	Extractable K with		
		HNO ₃ ^a	HNO ₃ ^b	Na ₂ CO ₃ ^a
		-----cmol/kg-----		
Big Creek – 1	0.19 ± 0.01	0.72 ± 0.01	0.96 ± 0.05	166.8 ± 4.61
Big Creek – 2	3.29 ± 0.19	0.89 ± 0.01	1.19 ± 0.04	176.1 ± 1.72
Laverne – 1	0.06 ± 0.01	1.19 ± 0.21	1.53 ± 0.26	160.7 ± 9.06
Laverne – 2	1.51 ± 0.02	1.01 ± 0.08	1.36 ± 0.04	147.8 ± 3.49
Little Wall – 1	0.09 ± 0.01	1.19 ± 0.00	0.67 ± 0.06	132.2 ± 4.80
Little Wall – 2	0.43 ± 0.02	1.03 ± 0.03	0.53 ± 0.07	142.7 ± 1.27
Saylorville – 1	0.23 ± 0.01	0.20 ± 0.05	0.41 ± 0.00	151.3 ± 8.83
Saylorville – 2	0.21 ± 0.01	0.16 ± 0.09	0.39 ± 0.09	146.5 ± 0.23

[§] 1,2 = August and October samplings, respectively.

^a Analyzed by Inductively Coupled Plasma Emission Spectrophotometer (ICP-AES Thermo Jarrell Ash Model 61E).

^b Analyzed by Atomic Absorption Spectrophotometer (Perkin Elmer, Aanalyst-100 model).

concentrations can collapse the interlayer and trap the NH_4^+ ion in the clay interlayer (Liu et al., 1997), but may also cause lake-colloid dispersion due to high monovalent cation ratios on the external clay surfaces (Evangelou, 1998 and references therein). The data in Table 22 show ammonium and ammonium forms associated with the lake water and sediments. It is shown in Table 22 that lake sediments were associated with relatively large quantities of clay interlayer-confined ammoniacal-nitrogen ($\text{NH}_4\text{-N}$) (0.45 to 2.55 meq $\text{NH}_4\text{-N}/100\text{-g}$ sediment or 63 to 357 mg $\text{NH}_4\text{-N}/\text{kg}$ sediment), whereas exchangeable ammonium was relatively low. It varied from 0.04 to 0.18 meq $\text{NH}_4\text{-N}/100$ g sediment or 5.5 to 25 mg $\text{NH}_4\text{-N}/\text{kg}$ sediment. Midwestern soils often receive nutrients during fertilization. Liu et al. (1997) determined the fixed or 'confined' and exchangeable NH_4^+ and K^+ in typical upper midwestern agricultural soils after long-term (30-yr) fertility management, given different N-fertilizer treatments. The exchangeable ammonium ranged from around 4 kg/ha to ~14 kg/ha which is equivalent to 2 mg/kg – 7 mg/kg (or 0.014 meq/100g – 0.05 meq/100g) assuming 1 ha. furrow slice of soil weighs 2×10^6 kg. Likewise, exchangeable K^+ ranged from 50 kg/ha to ~ 400 kg/ha, equivalent to 25 mg/kg to 200 mg/kg sediment (or 0.06 meq/100g - ~0.5 meq/100g). They found that levels of exchangeable and fixed NH_4 and fixed K^+ were similar for all treatments, however, exchangeable K^+ was significantly higher in those plots that received high doses of N fertilizer and those that received no N fertilizer. This suggested that levels of fixed NH_4 are constant throughout long-term fertility management, whereas, long-term fertility management influences levels of exchangeable K^+ . Nitrate in solution was below the maximum contaminant level of 10 mg/l $\text{NO}_3\text{-N}$.

Table 23 show phosphate and its forms associated with lake water and sediments. Inorganic phosphorus ($\text{PO}_4\text{-P}$) varied from 6.2 to 112 mg $\text{PO}_4\text{-P}/\text{kg}$ sediment whereas total P

Table 22. Ammonium and nitrate content of the lake-water and -sediments and forms or sinks of ammonium for the four studied lakes.

Sample ID [§]	Solution phase (Lake water)		Solid Phase (Sediments)	
	NH ₄ -N ^a	NO ₃ -N ^b	Exchangeable NH ₄ ⁺	Confined NH ₄ ⁺
	-----meq/L-----		-----meq NH ₄ -N /100g-----	
Big Creek – 1	nd ^c	0.011	0.062 ± 0.005	1.75 ± 0.05
Big Creek – 2	0.010	0.005	0.139 ± 0.007	3.42 ± 0.13
Laverne – 1	nd	0.012	0.140 ± 0.005	2.55 ± 0.11
Laverne – 2	0.036	nd	0.183 ± 0.076	1.45 ± 0.03
Little Wall – 1	0.006	0.570	0.043 ± 0.002	1.98 ± 0.19
Little Wall – 2	0.012	nd	0.041 ± 0.002	1.34 ± 0.11
Saylorville – 1	nd	0.05	nd	0.58 ± 0.02
Saylorville – 2	nd	0.103	nd	0.45 ± 0.03

[§] 1,2 = August and October samplings, respectively.

^a determined by using a universal microplate reader (Bio-TEK Instruments Inc, Model Elx 800, Winooski, VT) employing the modified Berthlot reaction (Ngo et al., 1982).

^b determined by using ion specific electrode (QuickChem Automatic Ion analyzer , Milwaukee, WI).

nd = non detectable

Table 23. Phosphate content of lake-water and -sediments and forms or sinks of P for the four studied lakes.

Sample ID [§]	Solution phase (Lake water)	Solid Phase (Sediments)			
	PO ₄ -P (mmol/L)	Extractable PO ₄ -P ^a	Total P ^b	Organic P ^c	Inorganic P ^d
-----mg P/kg -----					
Big Creek – 1	2.50E-04	37.2	2149	26.6	2123
Big Creek – 2	4.17E-03	111.6	2018	68.4	1949
Laverne – 1	3.50E-04	24.8	1986	44.3	1942
Laverne – 2	1.33E-03	9.30	1851	23.4	1828
Little Wall – 1	2.67E-04	34.1	2432	26.6	2405
Little Wall – 2	6.34E-03	18.6	2131	15.6	2116
Saylorville – 1	1.00E-03	6.20	1039	2.8	1037
Saylorville – 2	5.17E-03	6.20	774	nd ^e	774

[§] 1,2 = August and October samplings, respectively.

^a Extractable P by Mehlic III (Mehlic, 1984).

^b Total P by Na₂CO₃ fusion - includes organic and inorganic P (Jackson, 1958).

^c Organic P by Ignition method (Saunders and Williams, 1955).

^d Inorganic P determined by subtracting organic P from Total P.

(organic plus inorganic) varied from 1,851 to 2,432 mg P/kg sediment. These are typical soil levels (Dick and Tabatabai, 1977). It can be concluded that the surfaces of the eroded sediments appear to have high loads of 'confined' or 'fixed' ammonium and relatively high loads of inorganic and organic phosphorus.

Lake Eutrophism

According to Downing and McCauley (1992) and references therein, availability of nutrients, especially N and P promote lake eutrophication with P being the most limiting in freshwater systems. Chappell and Evangelou (2000 a,b and references therein) showed that N in the form of soluble NH_4^+ is readily bioavailable. They further went on to show that exchangeable NH_4^+ -N is less readily available and that the confined or fixed form is practically non-bioavailable. This piece of information is important as, research has shown that depending on the availability of N, the ratio to different form of phosphates contained in the lake system will make it possible to predict lake eutrophication (Downing, 1997). This is under the assumption that no nutrient or nutrient load is limiting.

The following conclusions were drawn from epilimnetic total mass of N (TN) and total mass of P (TP) loads in world lakes (Downing and McCauley, 1992 and references therein). Lakes with low nutrient content, referred to as oligotrophic lakes, exhibit TN:TP ratios from 21 to 240. Lakes with average nutrient load, referred to as mesotrophic lakes exhibit TN:TP ratios in the range of 17 to 96, while lakes with high nutrient loads, referred to as eutrophic will show TN:TP ratios in the range of 4 to 71. Finally, lakes extremely rich in nutrients referred to as hypereutrophic exhibit TN:TP ratios in the range of 0.5 to 9. In general, the range of N:P mass ratio (TN:TP) found in lake-nutrient sources differs from that

found in aquatic organisms. On the other hand, nutrient sources of lakes exhibit a wide N:P ratio, ranging from 20 to greater than 200 (Downing and McCauley, 1992 and references therein). The disparity between N:P mass ratios should influence algal production and biomass. Generally, based on TN:TP ratios, sewage is expected to be responsible for hypereutrophic conditions whereas runoff from unfertilized fields is expected to be responsible for oligotrophic conditions (Downing and McCauley, 1992 and references therein). Based on the above ratios, Table 24 was developed to predict lake eutrophism for the four lakes studied based on potential nutrient content of epilimnetic water due to lake-bottom sediment nutrient content. From the data in Table 24 table, three systems can be predicted. The first system would range from eutrophic to hypereutrophic under unlimited nutrient loads if TN and TP are suspended in the epilimnion. The second system would be oligotrophic if TN and organic P are suspended in the epilimnion and inorganic P is not suspended. The third system would be hypereutrophic if TN and inorganic P only are suspended in the epilimnion. It is apparent from this characterization that under unlimited nutrient loads in the lake system eutrophism would depend on the form of P in the dispersed mode, i.e., available in the epilimnion. A potential limitation for using the above TN:TP ratio under unlimited nutrient loads for predicting potential lake eutrophication is the fact that these ratios are assumed to represent constant epilimnetic nutrient levels and this would require the assumption that eroded sediments represent epilimnetic dispersed solids.

Quantity/Intensity Relationships (Q/I)

From the solution and solid phase data it is certain that lake-waters vary in chemical composition. This variation can be attributed to the water's chemical characteristics and

Table 24. Classification of studied Iowa lake-water on the basis of N:P ratios in their potential epilimnetic water.

Sample ID	Labile -N:P^a	TN:TP^b	TN:Organic P^c	TN:Inorganic P^d
Big Creek	0.03	1.10	48.42	1.13
Laverne	0.10	1.17	56.69	1.19
Little Wall	0.16	0.89	59.59	0.91
Saylorville	1.13	1.38	323.9	1.38

^a Labile N: P refers to readily exchangeable and extractable Nitrogen: Phosphorus. Quantity very small, therefore cannot maintain eutrophism.

^b TN:TP refers to Total Nitrogen:Total Phosphorus ratio. Lake systems predict eutrophism to hypereutrophism if the two forms are suspended in the epilimnion.

^c TN: Organic P refers to Total Nitrogen: Organic Phosphorus ratio. Lake systems predict oligotrophism if the two forms are suspended in the epilimnion and when inorganic P is not suspended.

^d TN: Inorganic P refers to Total Nitrogen: Inorganic P ratio. Lake systems predict eutrophism to hyperutrophism if the two forms are suspended in the epilimnion and when organic P is not suspended.

mineralogy of sediments. Several processes, involving water, dissolved chemical constituents and sediments, such as dissolution and precipitation, are always in operation and their tendency to reach an equilibrium state is a controlling factor (Meybeck and Helmer, 1997). Dissolution and exchange of ions between the two sinks (solution and solid) can be thought of as a continuous process, triggered and perhaps regulated by mineral composition of natural water systems. Major constituents contained in the four lake-waters are constantly in contact with the solid phase, hence a form of an exchange mechanism may be in place. The sediments from the four lakes contained considerable amounts of confined ammonium and phosphate and with time, these can be released into the lake-water and may contribute to lake eutrophication. The ease by which nutrients become available depends on their chemical form.

The data in Figs. 14 through 17 show NH_4^+ Q/I plots. These plots are slightly modified from the traditional Q/I plots (Beckett, 1964). For example in the traditional K^+ Q/I plot the x-axis is represented by the concentration ratio of the monovalent cation (e.g., $\text{CR}_K = \text{K} / (\text{Ca} + \text{Mg})^{1/2}$ in units of $(\text{mmol L})^{-1/2}$). However, since Ca^{2+} and Mg^{2+} were kept relatively constant in this study (verified by analyzing Ca^{2+} and Mg^{2+} concentration under the various NH_4^+ levels) for practical purposes they were omitted. This omission provided the advantage of observing the behavior of NH_4^+ with respect to exchangeable and solution NH_4^+ . Another way to evaluate these plots (Figs. 14 to 17) was to assume that the slope of the line ($\text{Ads NH}_4^+ / \text{NH}_4\text{-N}$) represents the distribution coefficient or K_d . This K_d appeared to be significantly less than 1 for all the sediment samples, which is very small. The negative y-intercept represented residual exchangeable $\text{NH}_4\text{-N}$ whereas the x-intercept represented the

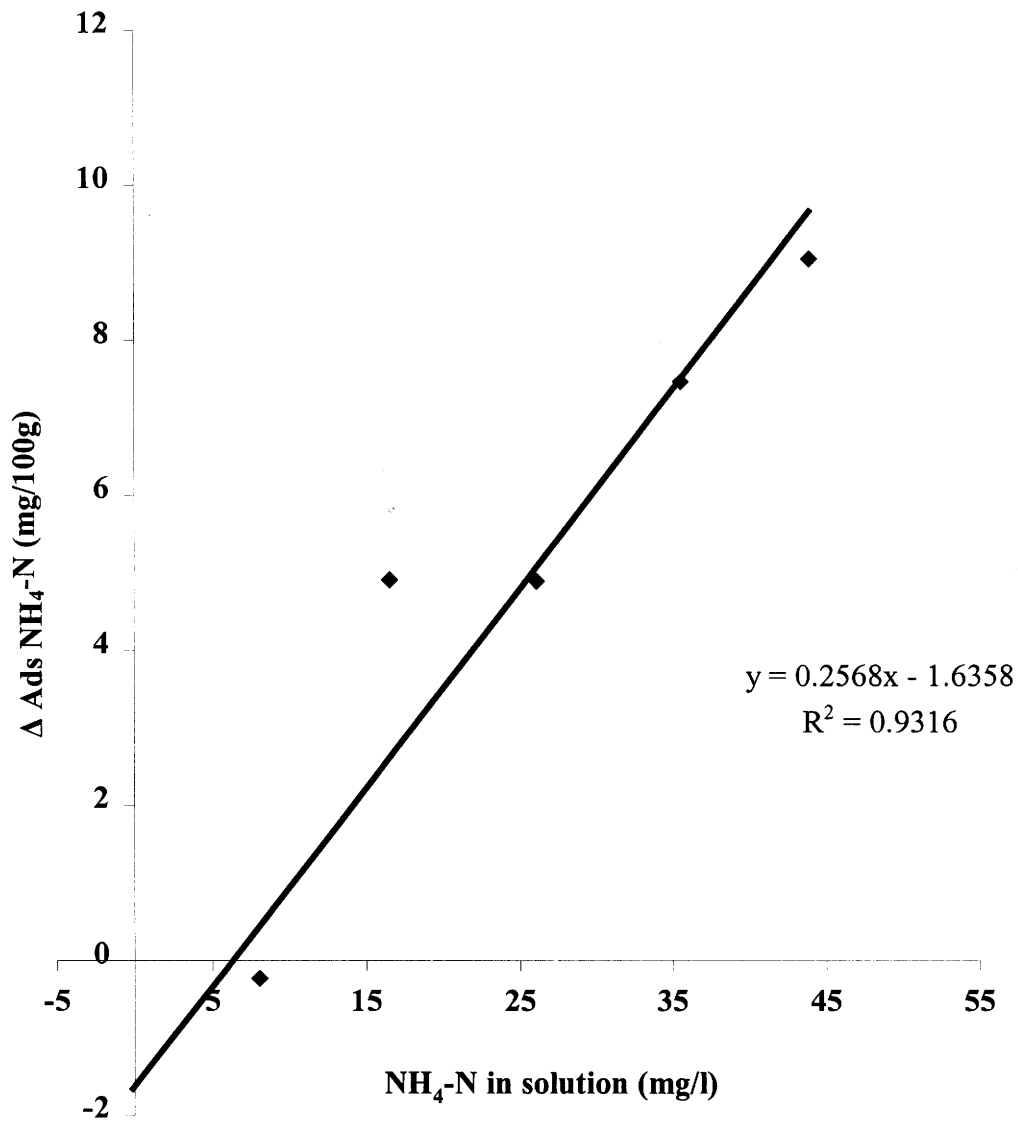


Figure 14. Ammonium quantity-intensity (Q/I) plot for Big Creek lake system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl_2 and $\text{NH}_4\text{-N}$ concentrations in the range 0 to 2.78 mmol/L. The quantity (Q) by which the sediment gained or lost NH_4^+ in reaching equilibrium (Ads $\text{NH}_4\text{-N}$) was then plotted against the ammonium in solution (mg/l), where the slope, r^2 and y-intercept were obtained.

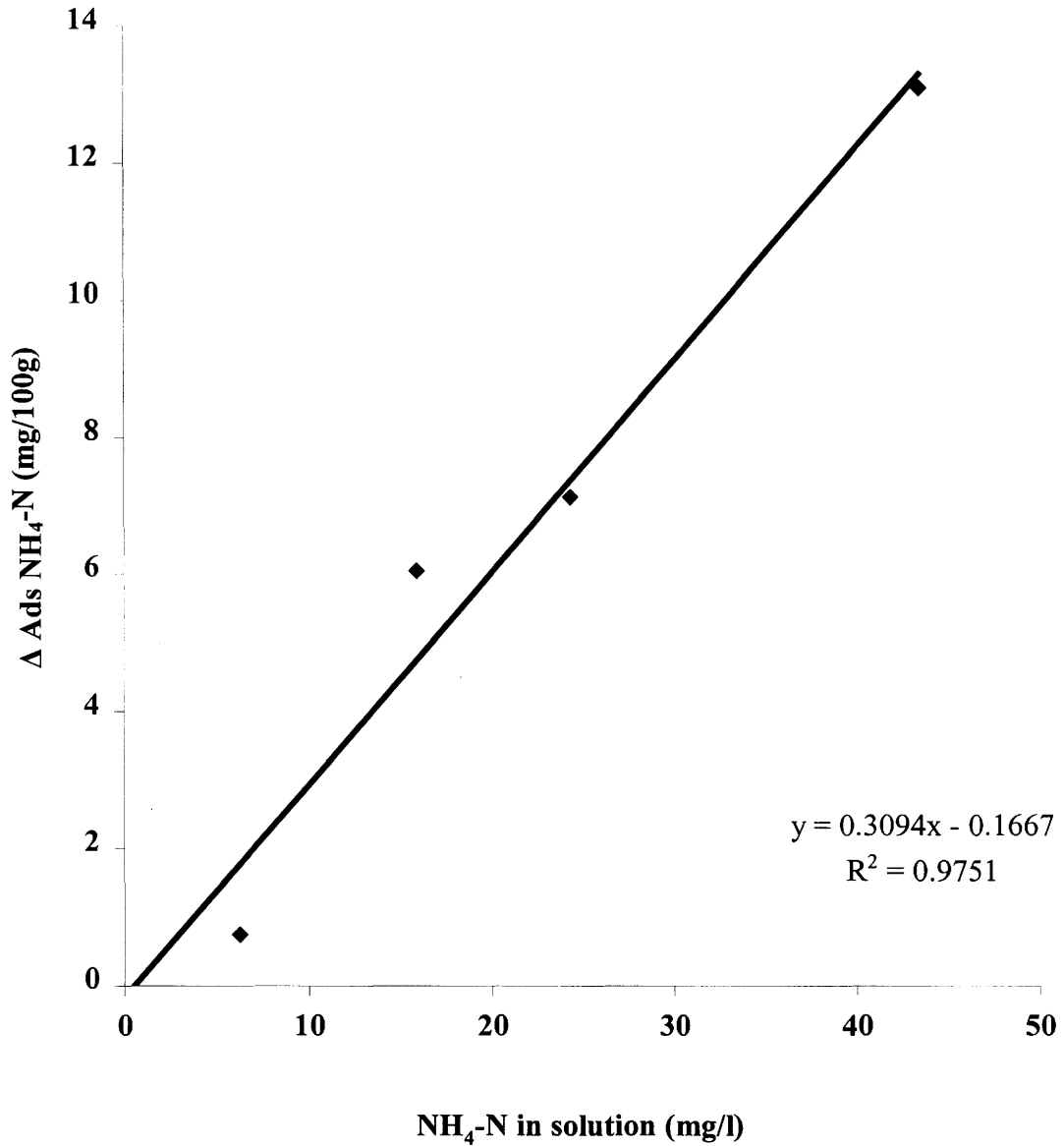


Figure 15. Ammonium quantity-intensity (Q/I) plot for lake Laverne system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl₂ and NH₄-N concentrations in the range 0 to 2.78 mmol/L. The quantity (Q) by which the sediment gained or lost NH₄⁺ in reaching equilibrium (Ads NH₄-N) was then plotted against the ammonium in solution (mg/l), where the slope, r² and y-intercept were obtained.

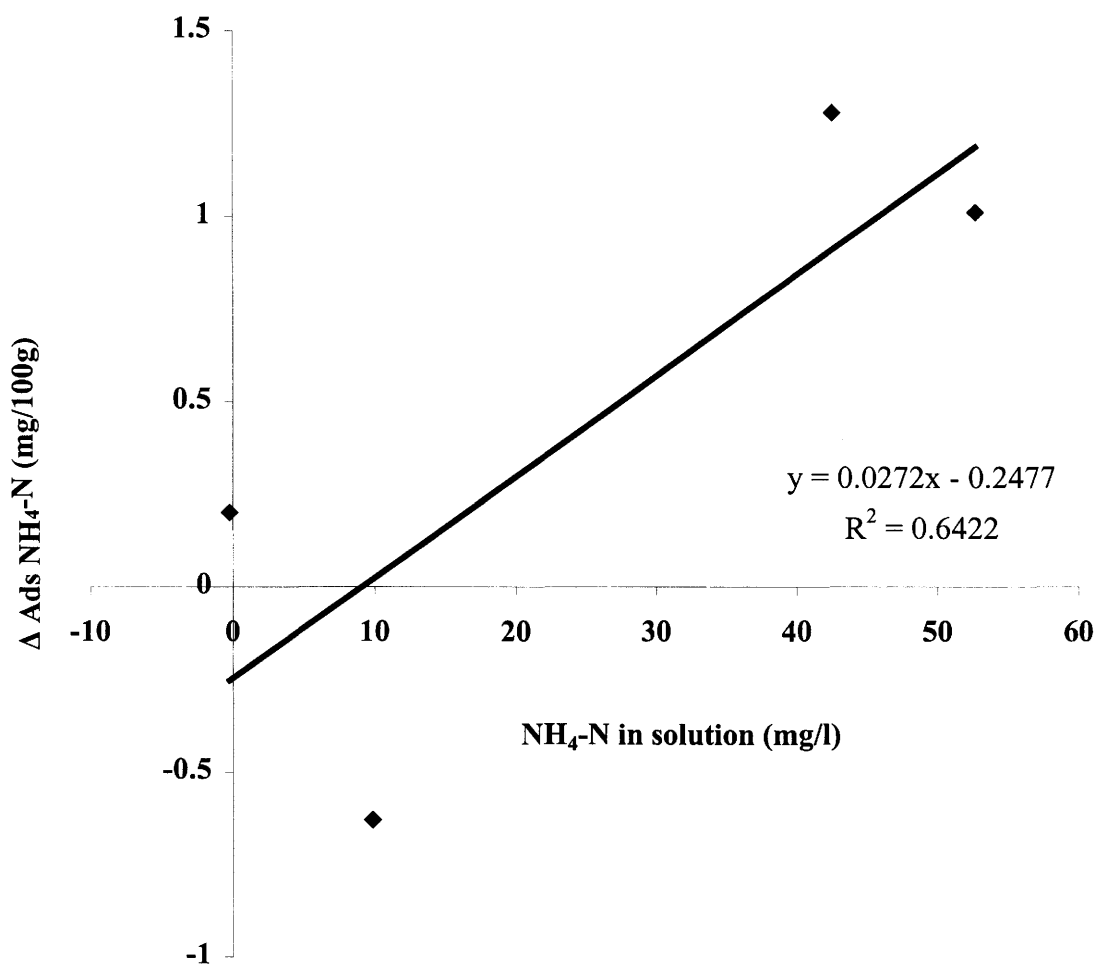


Figure 16. Ammonium quantity-intensity (Q/I) plot for Little Wall lake system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl_2 and $\text{NH}_4\text{-N}$ concentrations in the range 0 to 2.78 mmol/L. The quantity (Q) by which the sediment gained or lost NH_4^+ in reaching equilibrium (Ads $\text{NH}_4\text{-N}$) was then plotted against the ammonium in solution (mg/l), where the slope, r^2 and y-intercept were obtained.

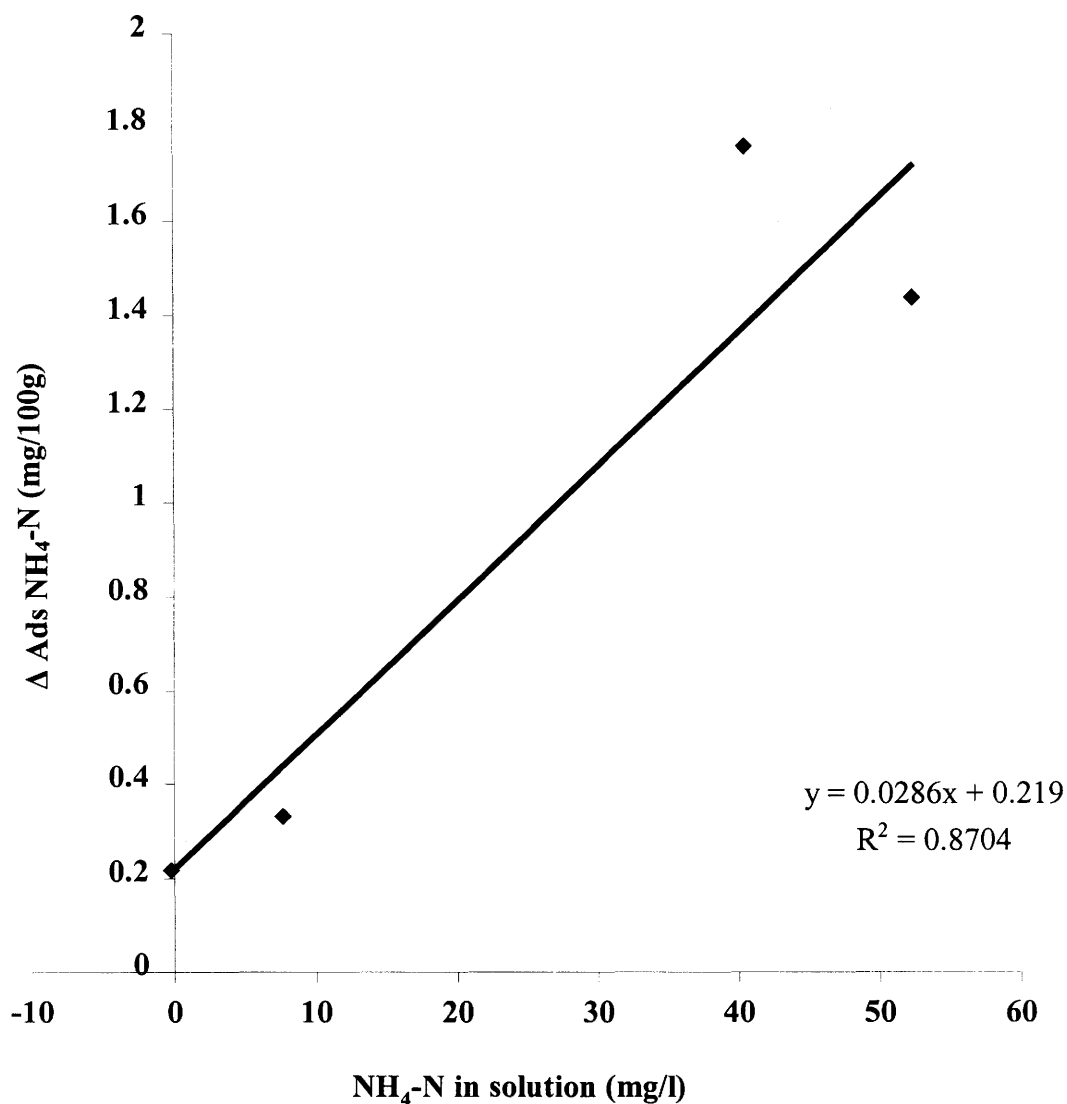


Figure 17. Ammonium quantity-intensity (Q/I) plot for Saylorville lake system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl_2 and $\text{NH}_4\text{-N}$ concentrations in the range 0 to 2.78 mmol/L. The quantity (Q) by which the sediment gained or lost NH_4^+ in reaching equilibrium (Ads $\text{NH}_4\text{-N}$) was then plotted against the ammonium in solution (mg/l), where the slope, r^2 and y-intercept were obtained.

amount of $\text{NH}_4\text{-N}$ in the solution phase. Both quantities appeared to be very small. Additionally, Saylorville lake appeared to have no residual solution or exchangeable NH_4^+ .

The theoretical meaning of $\text{NH}_4\text{-N}$ Q/I, described previously, could also be used to describe the behavior of $\text{PO}_4\text{-P}$ in the lake systems. Figures 18 through to 21 show curves for PO_4 Q-I's. For example, data in Fig. 18 and 21 show that the relationship between solution and adsorbed P is a linear one. This relationship is described by a slope, which varies from approximately 20 for Big Creek lake (Fig. 18) to 3.83 for Saylorville lake (Fig. 21). The slope describes the adsorption coefficient, K_d . Note, that K_d for $\text{NH}_4^+\text{-N}$ was less than 1 but, the K_d of $\text{PO}_4\text{-P}$ is much greater than 1. This was related to the bonding mechanism between NH_4^+ and sediment surfaces (electrostatic) and $\text{PO}_4\text{-P}$ and sediment surfaces (a relatively high degree of covalency). These plots (Fig. 18 to 21) also revealed that the concentration of $\text{PO}_4\text{-P}$ in the lake-water at equilibrium varied from approximately 0.162 mg/L or 162 $\mu\text{g/L}$ (Fig. 18) to 0.05 mg/L or 50 $\mu\text{g/L}$ (x-intercept). Note that $\text{PO}_4\text{-P}$ concentrations at around 100 $\mu\text{g/L}$ describe the lake-system as eutrophic. The y-intercept in Fig. 21 shows that the available quantity (labile) of $\text{PO}_4\text{-P}$, is around 0.17 mg/100g, which is very small. A similar extrapolation for Fig. 18 could not be made because of the poor r^2 of the data.

Interesting $\text{PO}_4\text{-P}$ adsorption plots are presented in Figs. 19 and 20. These two figures show that the quantity of $\text{PO}_4\text{-P}$ in solution remained constant, or independent of added $\text{PO}_4\text{-P}$, at 200 $\mu\text{g/L}$. This implied that a reaction other than adsorption described solution $\text{PO}_4\text{-P}$. A possible explanation is that $\text{PO}_4\text{-P}$ in solution was controlled by the solubility of a Ca-PO_4 mineral. Considering that the lake-water Ca^{2+} concentration was much greater than $\text{PO}_4\text{-P}$, then, any new added $\text{PO}_4\text{-P}$ in the lake-water would precipitate due to a common-ion effect induced by the dissolved Ca^{2+} . Since the added $\text{PO}_4\text{-P}$ was much smaller

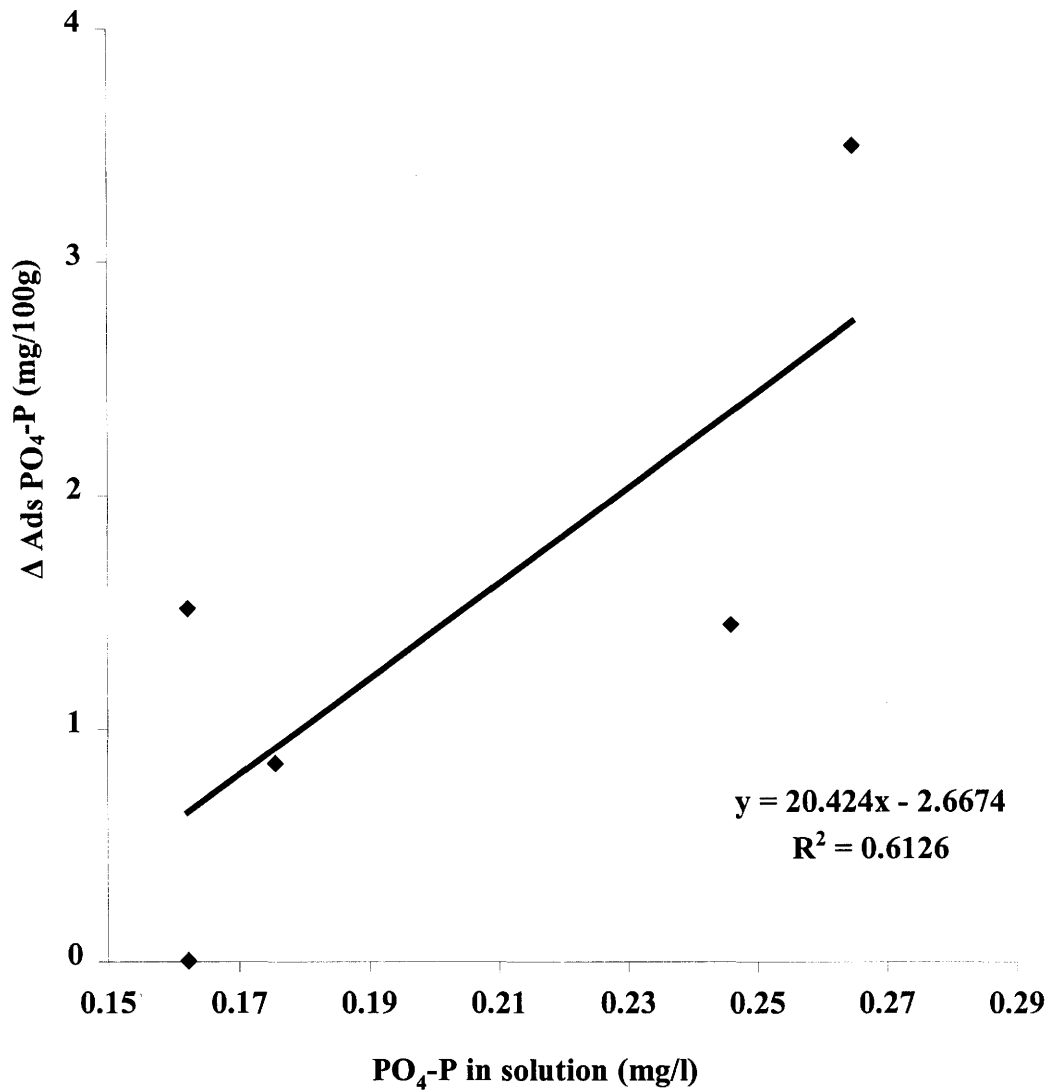


Figure 18. Phosphate quantity-intensity (Q/I) plot for Big Creek lake system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl_2 to maintain ionic strength and $\text{PO}_4\text{-P}$ concentrations in the range 0 to $1.58\text{E-}2$ mmol/L. The quantity (Q) by which the sediment gained or lost $\text{PO}_4\text{-P}$ in reaching equilibrium ($\Delta \text{ Ads PO}_4\text{-P}$) was then plotted against the phosphate concentration in lake water (mg/l), where the slope, r^2 and y-intercept were obtained.

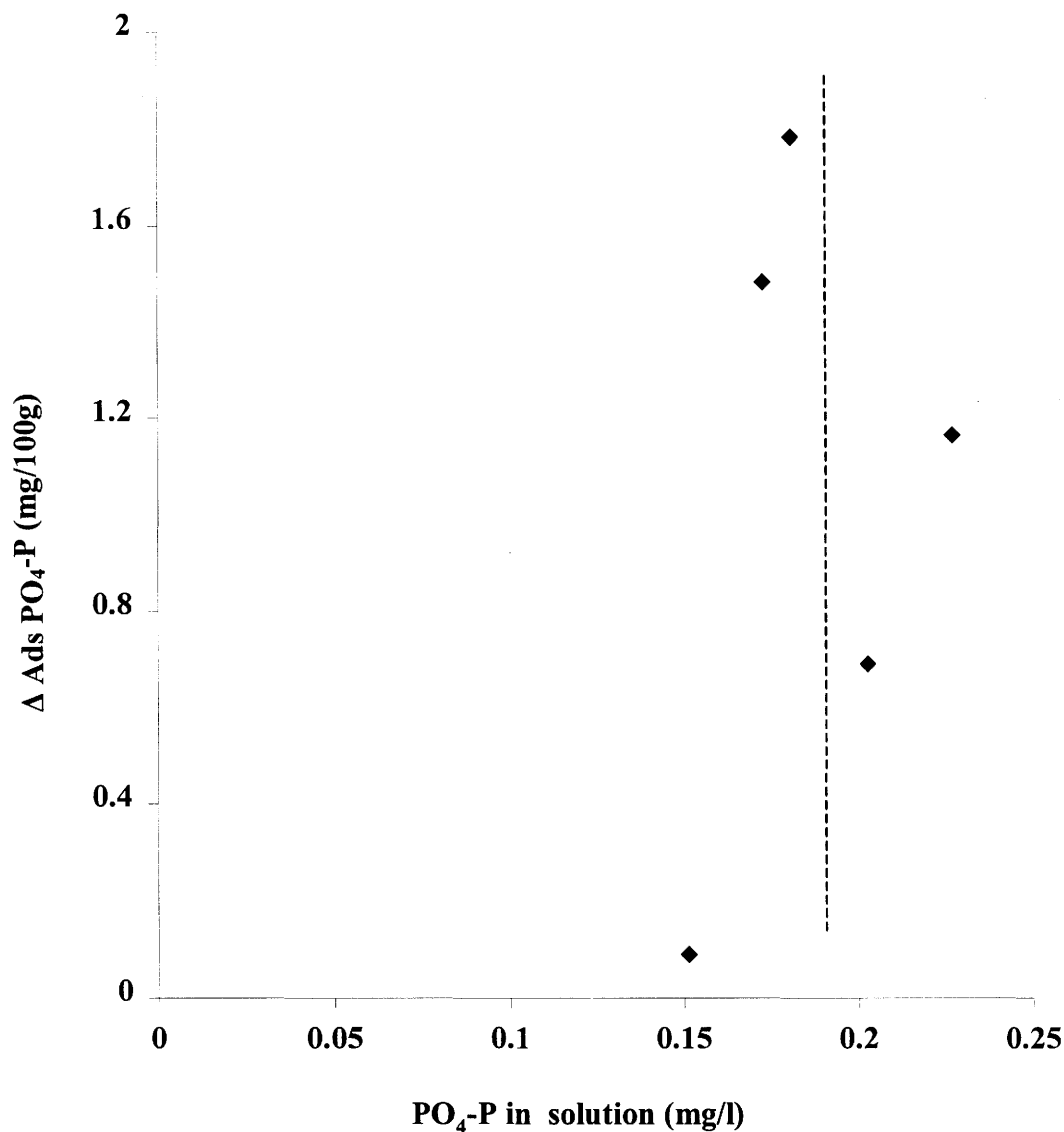


Figure 19. Phosphate quantity-intensity (Q/I) plot for lake Laverne system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl₂ to maintain ionic strength and PO₄-P concentrations in the range 0 to 1.58E-2 mmol/L. The quantity (Q) by which the sediment gained or lost PO₄-P in reaching equilibrium (Ads PO₄-P) was then plotted against the phosphate concentration in lake water (mg/l), where the slope, r^2 and y-intercept were obtained.

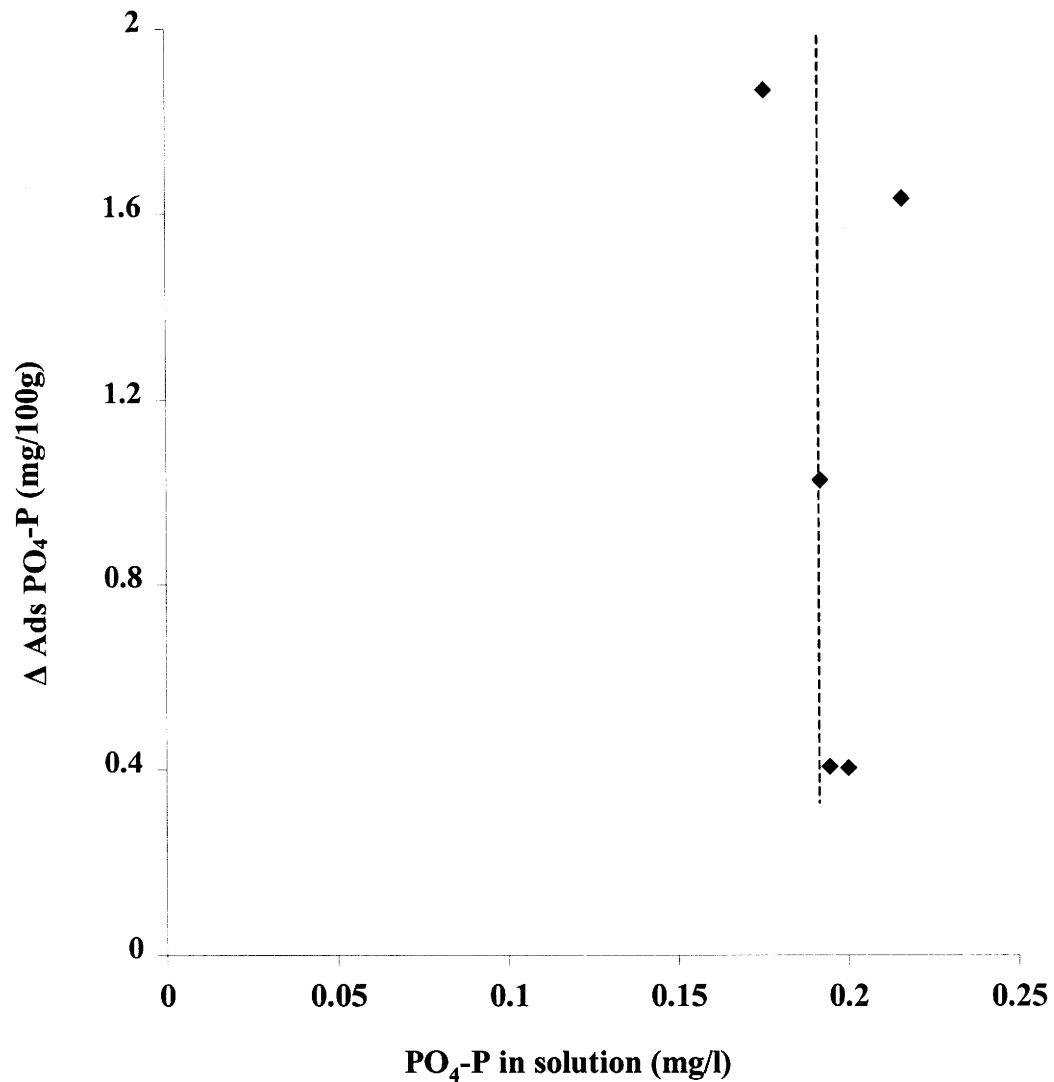


Figure 20. Phosphate quantity-intensity (Q/I) plot for Little Wall lake system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl_2 to maintain ionic strength and $\text{PO}_4\text{-P}$ concentrations in the range 0 to $1.58\text{E-}2$ mmol/L. The quantity (Q) by which the sediment gained or lost $\text{PO}_4\text{-P}$ in reaching equilibrium ($\Delta \text{ Ads PO}_4\text{-P}$) was then plotted against the phosphate concentration in lake water (mg/l), where the slope, r^2 and y-intercept were obtained.

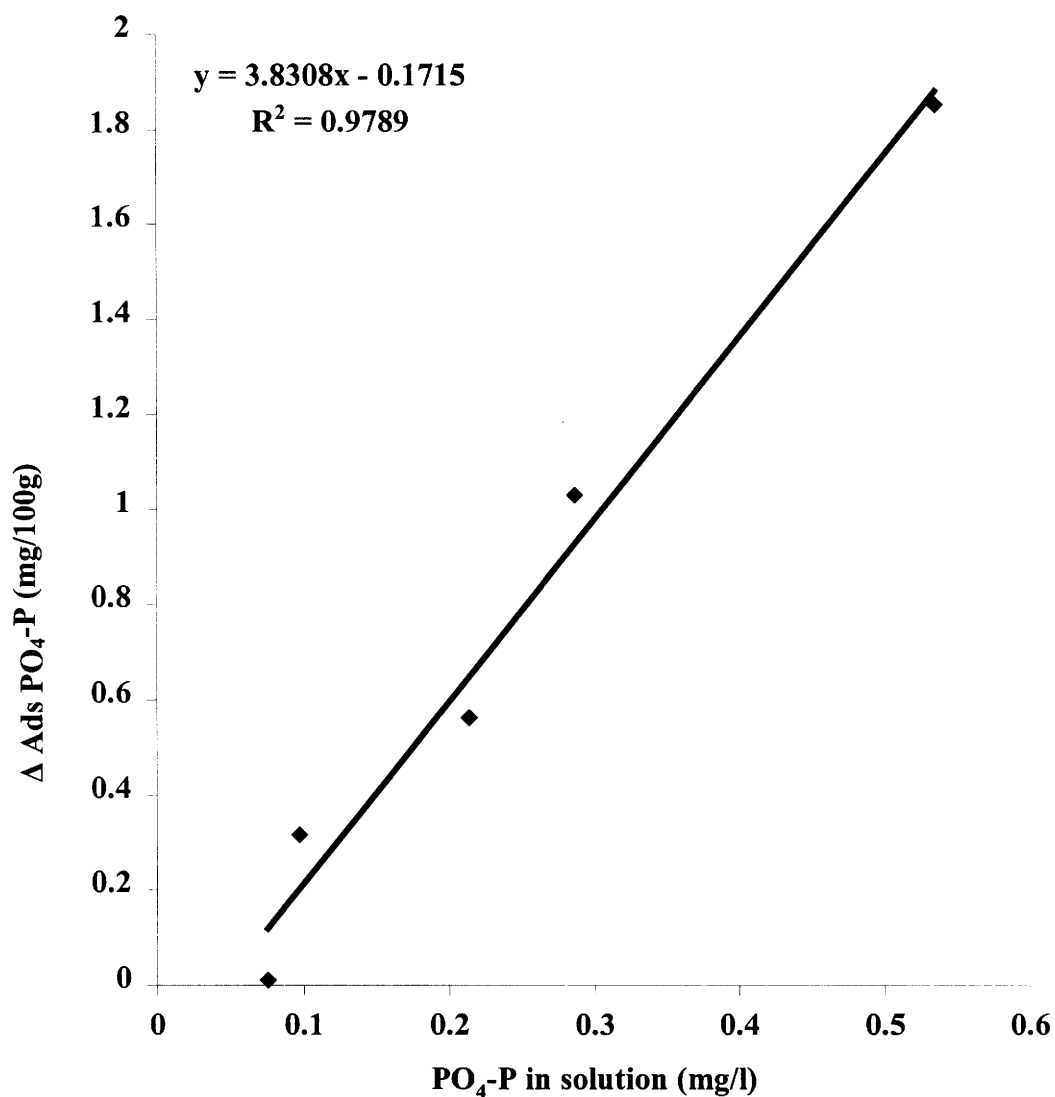


Figure 21. Phosphate quantity-intensity (Q/I) plot for Saylorville lake system. Q/I plot was obtained from samples containing 1.5 mmol/L CaCl₂ to maintain ionic strength and PO₄-P concentrations in the range 0 to 1.58E-2 mmol/L. The quantity (Q) by which the sediment gained or lost PO₄-P in reaching equilibrium (Ads PO₄-P) was then plotted against the phosphate concentration in lake water (mg/l), where the slope, r^2 and y-intercept were obtained.

than the amount of Ca^{2+} dissolved, $\text{PO}_4\text{-P}$ remained constant in solution. Assuming that this $\text{PO}_4\text{-P}$ is readily bioavailable, especially when the sediments of the lake(s) become dispersed in the epilimnion, then such lakes would exhibit a high potential of becoming eutrophic, assuming no other nutrient is limiting. Table 25 shows prediction equations obtained from plots of adsorbed $\text{NH}_4\text{-N}$ vs. solution NH_4 and adsorbed $\text{PO}_4\text{-P}$ vs. solution PO_4 for all four lakes. The concentration of the major cations (Ca, Mg, Na, and K), were determined after running the quantity-intensity tests. These concentrations are shown in Table 26, which show constant quantities.

Table 25. Prediction equations of Ads. NH₄-N vs. NH₄-N in solution and Ads. PO₄-P vs. PO₄-P in solution in the binary mode for the four lake sediments.

Sample ID	Q/I plot ^a	Prediction Equation	r² value	Slope	y-intercept
Big Creek	NH ₄ -N	$y = 0.26 x - 1.64$	0.932	0.26	-1.64
	PO ₄ -P	$y = 20.42 x - 2.67$	0.613	20.42	-2.67
Laverne	NH ₄ -N	$y = 0.31 x - 0.17$	0.975	0.31	-0.17
	PO ₄ -P	$y = 6.78 x - 0.23$	0.086	6.78	-0.23
Little Wall	NH ₄ -N	$y = 0.029 x - 0.69$	0.333	0.029	-0.69
	PO ₄ -P	$y = -7.46 x + 2.53$	0.026	-7.46	+2.53
Saylorville	NH ₄ -N	$y = 0.03 x + 0.22$	0.870	0.03	+0.22
	PO ₄ -P	$y = 3.83 x - 0.17$	0.979	3.83	-0.17

^a Quantity-Intensity plot for Ads. NH₄-N vs. solution NH₄-N and Ads PO₄-P vs. solution PO₄-P in all four lake sediments.

Table 26. Major cation concentrations after equilibration during the Quantity-Intensity experiments.

Sample ID [§]	Ca	Mg	Na	K
	(mg/L)			
BCcontrolA	8.54	24.69	7.82	3.74
BCcontrol B	7.35	27.65	9.78	5.22
BCT1 A	8.55	27.50	8.73	4.23
BCT1 B	7.32	27.41	9.14	5.64
BCT2 A	8.40	24.26	8.23	3.63
BCT2 B	7.43	28.78	8.96	6.47
BCT3 A	8.39	24.02	8.33	3.95
BCT3 B	7.60	31.39	10.42	6.75
BCT4 A	8.16	24.63	8.80	4.06
BCT4 B	7.74	29.32	9.26	6.81
BCT5 A	8.24	26.18	8.94	3.73
BCT5 B	7.71	28.42	9.46	6.48
LavControl A	11.27	30.30	26.95	24.82
LavControl B	11.49	31.50	23.66	11.34
LavT1 A	11.41	30.80	22.22	8.64
LavT1 B	11.29	32.10	24.00	13.15
LavT2 A	11.15	31.80	22.39	8.50
LavT2 B	11.33	31.50	23.66	13.04
LavT3 A	11.22	31.50	21.17	8.01
LavT3 B	11.19	32.80	26.14	13.73
LavT4 A	11.28	30.20	26.70	8.84
LavT4 B	11.50	33.10	25.53	13.47
LavT5 A	10.83	30.30	22.98	8.36
LavT5 B	11.59	33.50	24.30	13.59

§ BC = Big Creek, Lav = Laverne

T = Treatment, 1,2,3,4 and 5 = treatment number

Table 26 (continued)

Sample ID [§]	Ca	Mg	Na	K
	(mg/L)			
LWcontrol B	7.73	35.40	19.10	14.15
LWT1 A	7.92	34.80	20.72	12.71
LWT1 B	7.82	36.70	19.59	14.74
LWT2 A	7.65	33.10	18.56	12.78
LWT2 B	7.79	35.90	19.64	14.66
LWT3 A	7.67	33.90	19.03	12.77
LWT3 B	7.79	36.40	21.20	14.86
LWT4 A	7.50	32.80	18.60	12.89
LWT4 B	7.90	35.40	19.77	14.39
LWT5 A	7.47	31.20	18.45	12.31
LWT5 B	7.79	36.00	19.74	14.34
SControl A	12.58	30.10	26.80	7.23
SControl B	12.21	30.10	26.10	7.13
ST1 A	12.50	30.10	25.32	6.59
ST1 B	12.31	30.20	25.92	7.12
ST2 A	12.08	28.63	25.55	6.43
ST2 B	12.00	29.87	25.06	6.83
ST3 A	12.16	30.20	26.20	44.18 ^a
ST3 B	12.48	30.10	26.80	7.43
ST4 A	12.01	28.73	24.89	6.39
ST4 B	12.17	31.30	34.30	7.98
ST5 A	12.01	30.80	27.10	12.35
ST5 B	12.04	30.40	27.30	7.07

^a = possible contamination

§ LW = Little Wall, S = Saylorville

T = Treatment, 1,2,3,4 and 5 = treatment number

CONCLUSIONS

The results from the four lakes studied suggested that pH was most likely controlled by the Ca-Mg-CO₃ equilibrium system. All four lake-systems contained free carbonates as well as clay minerals such as kaolinite, smectite, quartz and traces of chlorite. Equilibrium states simulated with the GEOCHEM-PC showed that calcium, magnesium and phosphate concentration maybe regulated by various solid phases including CaCO₃, MgCO₃, Fe-OH-PO₄, and Ca₃(PO₄)₂.

Based on the data obtained from this study, it can also be concluded that lake eutrophication would depend on water chemistry, surface chemistry of lake-sediments, and interactive chemistry between water-chemical constituents and surfaces of lake-sediment colloids, and epilimnetic TN:TP ratios as dictated by dispersion/flocculation processes. Clay and humic substances due to their surface reactivity and structural composition are commonly associated with metal-cations (e.g., non-heavy and heavy metals), oxyanions (e.g., inorganic phosphorus), and organic phosphorus. Metals and inorganic P may influence CEC and sediment dispersion/flocculation behavior.

Smectites known also as 2:1 expanding clays, were found to be present in all lake-sediments. They possess an external surface as well as an internal surface. The internal surface produces what is known a cation confinement effect. The study showed that lake-sediment smectites have the potential to accumulate by confinement large quantities of NH₄⁺. This NH₄⁺ confinement is commonly potassium-induced. However, K⁺ also has the potential to liberate NH₄⁺ from the internal clay surface but restricts most other cations from being able to displace 'confined' NH₄⁺. Because of the potential of smectite-colloids to adsorb on

to their surfaces large quantities of nutrients, in addition to increasing water potential turbidity through dispersion, they may also increase lake eutrophication potential.

PART II: THE SOIL COLLOIDAL PHASE AND SUSPENDED SOLIDS

INTRODUCTION

Commonly, soil colloids are particles less than 2- μm in average diameter and carry surface electrical charges (Evangelou, 1998 and references therein). Overall colloids are involved in many processes including serving as sinks for nutrients or pollutant, transporting nutrients or pollutants, inhibiting light penetration and diminishing aquatic life. Colloid behavior in water is controlled by dispersion-flocculation processes, which generally are influenced by the surface electrical potential of colloids, solution composition, pH, and type/proportionality of cations (Arora and Coleman, 1979 and references therein). Dispersion refers to the process under which colloids tend to stay apart from each other and not form flocs, while flocculation is aggregation of colloids or the process of floc formation.

MATERIALS AND METHODS

The lake-water and bottom sediments used in this study were obtained from the four studied lakes. Details of the lake-water and bottom sediments were described in the previous part.

Lake-Water Sediment Settling Characteristics

Settling characteristics of suspended colloidal matter in lake-water were investigated as follows: Duplicate samples of unfiltered lake-water were placed in 50-ml test tubes (13-cm height); they were covered with parafilm and mixed with the aid of a vortex mixer (Lab-line Instruments Inc., model 260, Melrose Park, ILL USA). Immediately, a sample of the unfiltered lake-water was placed in a polystyrene cuvette of 3.5-cm x 1-cm x 1-cm. Settling or optical density with respect to time was taken using a UV/VIS spectrophotometer (Varian Instruments, Cary50 Bio model, Walnut Creek, CA, USA). The UV/VIS settings were as follows; total time period for the experiment was up to 300 minutes with readings taken at 2-minute intervals at a wavelength of 560 nm. The selection of this wavelength was based on the assumption that nothing other than suspended colloids will absorb the chosen wavelength. The following relationship was used to relate absorbance to suspended solids or colloids

$$A = kC \quad [30]$$

where A is absorbance, k is the absorption coefficient and C being the concentration of suspended solids. The relationship is linear and therefore it directly allowed estimation of percent optical density by dividing absorbance at any time t by absorbance at t=0 times one hundred.

Sediment Settling Characteristics and Estimation of Suspended Matter

Sediment settling characteristics and estimation of colloidal suspended matter was carried out on lake air-dried sediments. Duplicate sediment samples of 1.0 g were placed in 50-ml test-tubes (13-cm height), and deionised water was added. The test-tubes were covered with parafilm and mixed with the aid of a vortex (Lab-line Instruments Inc. model 260, Melrose Park, ILL USA). Measurements of pH and EC were taken using a dual pH/Ion/Conductivity meter (Accumet Fischer, AR50 model, Pennsylvania, USA). After the sand and silt portion of the suspension was allowed to settle for 5-minutes, an aliquot was taken from the top few centimeters of the test-tube. Kinetics of settling of the suspended colloidal particles were then investigated by running the sample using a UV/VIS spectrophotometer (Varian Instruments, Cary50 Bio model, Walnut Creek, CA, USA) at 560 nm (Evangelou, 1990). The UV/VIS settings were as follows: total time period for the experiment was up to 300 minutes with readings taken at 2-minute intervals at a wavelength of 560 nm.

Lake Dispersion Sensitivity Indices

Any form of lake disturbance, be it natural or man-made, is bound to cause re-suspension of the settled colloidal matter from the lake-bottom sediments. The aim of this test therefore, was to evaluate the rate of settling of the disturbed colloidal particles in case of any form of disturbance to the lake system, such as boating, windstorming, etc. Sediment settling characteristics of colloidal matter were determined as follows: Duplicate 1.0 g sediment samples were placed in a 50-ml test-tubes and 20-ml of lake water added and mixed by aid of a vortex mixer (Lab-line Instruments Inc., model 260, Melrose Park, ILL USA).

Measurements of pH and EC were made with an Accumet AR 50 dual channel pH/Ion/Conductivity meter (Accumet Fischer, AR50 model, Pennsylvania, USA). After the larger sediment particles were allowed to settle for 5 minutes, a sample was taken from the upper portion of the test-tube (1-cm) and kinetics of colloid settling run on a UV/VIS spectrophotometer (Varian Instruments, Cary50 Bio model, Walnut Creek, CA, USA) using a polystyrene cuvette of 3.5-cm x 1-cm x 1-cm. The UV/VIS settings were as specified previously. After this run, the colloid suspension sample was poured back into the test-tube.

In order to evaluate the influence of dilution on colloid settling the test-tube sample was then shaken vigorously and the test-tube suspension was diluted at a ratio of 1:3 with deionised water (5-ml sample and 15-ml deionised water were placed in a 50-ml test-tube). This suspension dilution was supposed to simulate rainfall events in the lakes. The larger particles were then allowed to settle for 5-min and a colloid suspension sample was taken from the upper portion of the test-tube (1-cm). Settling characteristics of this sample with respect to time were then run on a UV/VIS spectrophotometer (Varian Instruments, Cary50 Bio model, Walnut Creek, CA, USA) following the same settings as previously described.

In order to evaluate the influence of solution concentration, 3 meq/L of CaCl_2 was used as follows: To a test tube containing sediment sample and normal lake water, a volume equivalent to 3 meq/L of CaCl_2 was added to simulate anthropogenic inputs. The sample was then shaken vigorously and larger particles were then left to settle for 5-min prior to removing a sub-sample of the colloid suspension, and a sample was taken from the upper 1-cm of the test-tube. The settling characteristics of this sample with respect to time were then run on a UV/VIS spectrophotometer (Varian Instruments, Cary50 Bio model, Walnut Creek,

CA, USA) using the same settings as previously described. In all runs pH and EC measurements of the lake-sediment colloid suspensions were taken.

RESULTS AND DISCUSSIONS

Suspended Solids

Suspended matter in a body of water consists of silt, clay, and fine particles of organic and inorganic matter, soluble organic compounds and some microscopic organisms. These particles may vary in size but it is commonly accepted that suspended matter is that fraction that will not pass through a 0.45 μm pore diameter filter (USEPA, 1996, WHO, 1984). Therefore, the type and concentration of suspended matter controls water turbidity, which sometimes is used as an indirect measurement of total suspended solids. As previously discussed, suspended solids or colloidal particles find their way into surface waters and carry large amounts of nutrients like ammonium and phosphate in the adsorbed form. Availability and forms of N has been previously discussed. Like N, most of the inorganic/organic P in lake systems is attributed to eroding soil colloids during rainstorm (Goolsby et.al, 1999). Dispersion potential as well as bioavailability of such P would depend on the nature of colloid(s) (Stumm and Morgan, 1981 or 1997).

The data in Fig. 22 show the relationship between total suspended solids of the four lakes tested and absorbance at a wavelength of 560 nm (Evangelou, 1990). These data indicate that all four lakes produced identical relationships. This suggested that direct lake-water absorbance measurements may have the same significance for all lakes with respect to turbidity. The fact that all four lakes provided an indistinguishable relationship between suspended solids and absorbance suggested that the sediments of all four lakes had similar mineralogy. X-ray diffractograms revealed that the sediments of all four lakes were composed of mixed mineralogy, dominated mostly by smectites.

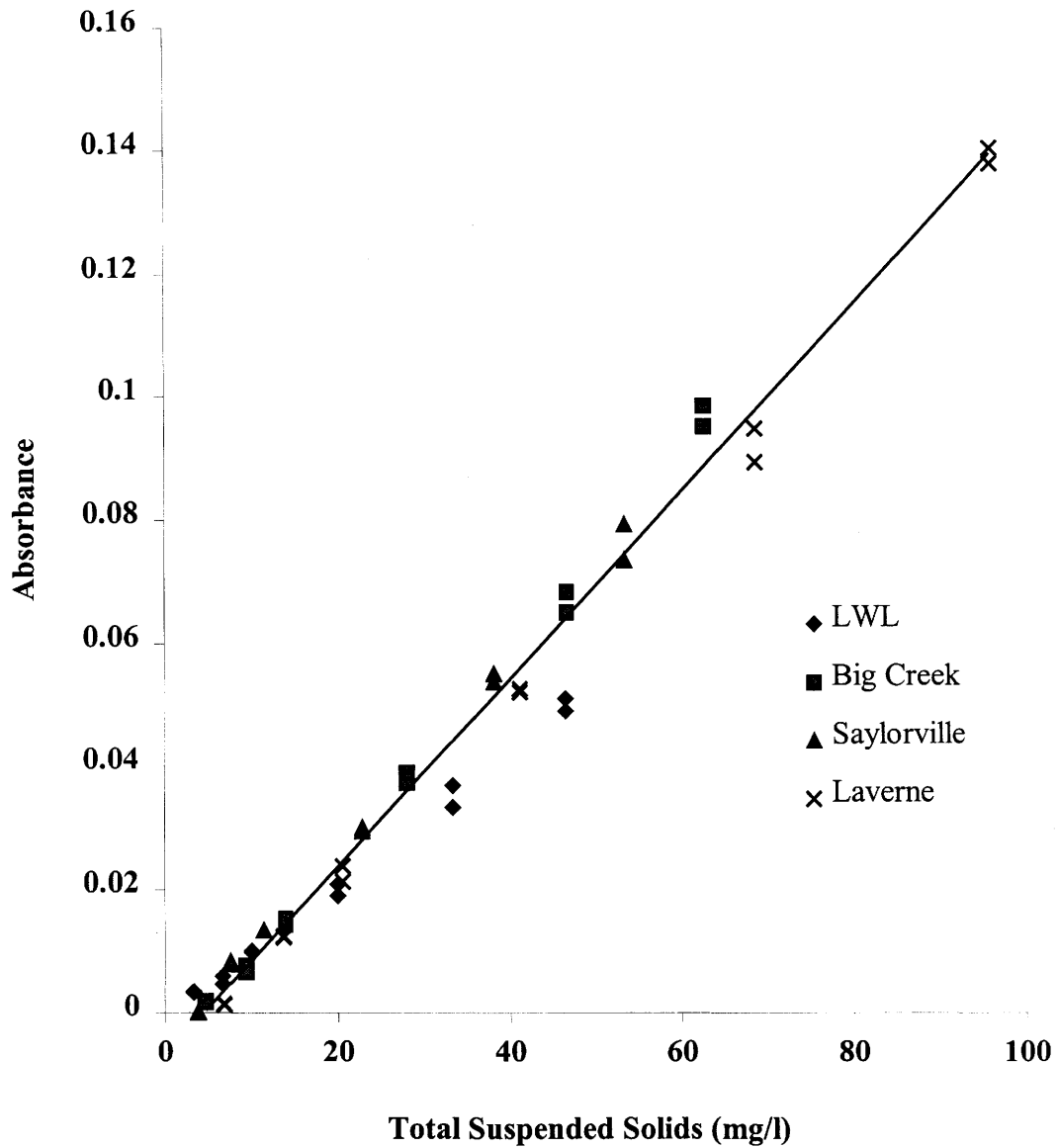


Figure 22. Plot showing relationship between total suspended solids (TSS) and absorbance for the four lakes. The simple scan readings were taken on a UV/VIS spectrophotometer set at 560 nm (Varian Instruments, Cary50 Bio model, Walnut Creek, CA).

As previously discussed three factors control soil or lake-sediment dispersion. The first factor is the colloid's surface charge density; the second factor is the ionic strength of the solution bathing the colloidal particles, and the third factor is the type of cations present on the mineral or colloidal surfaces (Legerwerff et al., 1969; Marsi and Evangelou, 1991a,b,c; Quirk and Schofield, 1955; U.S Salinity Laboratory staff, 1954). Uehara and Gilman (1980) related the surface charge of certain colloids to pH, details of which have been previously discussed. In the case of the first factor, the presence of potential determining ions (PDIs) may change the surface electrical potential of colloids and thus PZC of colloids will also change. One important PDI in all the lakes tested was inorganic phosphate (Table 11). The latter upon chemisorbing to a colloid's surface will lower the PZC by increasing the surface negative electrical potential (Stumm and Morgan, 1981 or 1997; Evangelou, 1998 and references therein). The second factor, ionic strength involves the interaction of all ions present in the system. Total salt concentration in lake-water can be used as an index for predicting dispersion or flocculation of colloids. However, cations exhibit different clay-dispersing properties because of their difference in preference by colloid surfaces and because of valence effects.

Preference of cations by colloidal surfaces and its influence on clay settling behavior is demonstrated by the sodium adsorption ratio (SAR). Figure 23 shows the relationship between lake-water turbidity (percent optical density) and CR_{Na} or SAR. It can be observed that as SAR increases, lake-water turbidity increases. The United States Salinity laboratory (1954) states that when clay colloidal suspensions exhibit SAR greater than 10, such systems will undergo clay-colloidal dispersion. The data in Fig. 23 show that the lake-sediments tested exhibited high sensitivity to SAR. At a SAR ($SAR = Na^+ / (Ca + Mg)^{1/2}$) of around

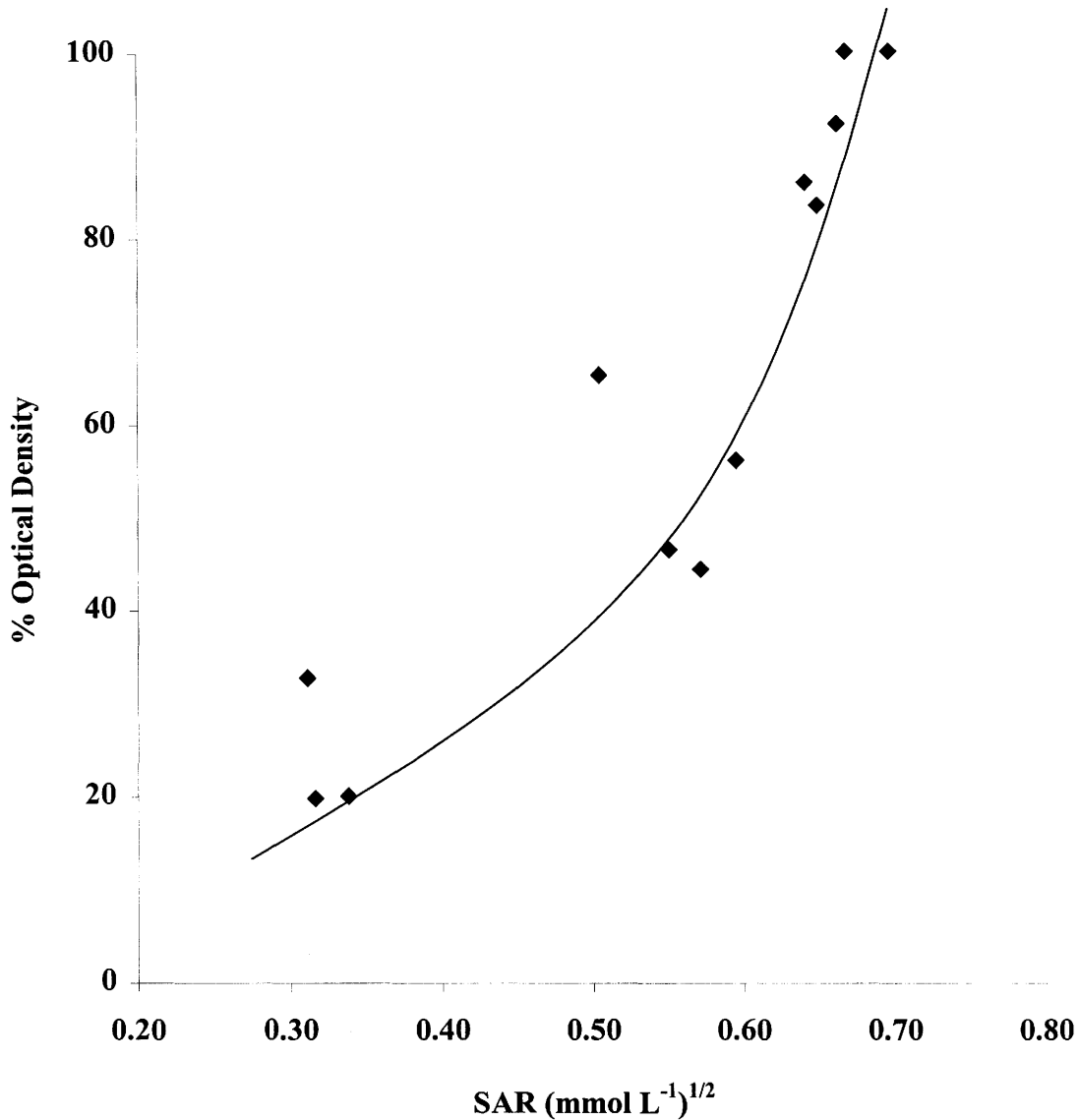


Figure 23. Plot showing relationship between percent optical density of lake water and sodium adsorption ratio ($SAR = Na^+ / [Ca^{2+} + Mg^{2+}]^{1/2}$) of the studied Iowa lakes. Absorbance readings were taken using UV/VIS spectrophotometer at 560 nm (Varian Cary50 Bio model, Walnut Creek, CA). Percent optical density represents suspended solids in the lakes. Percent optical density was measured by taking absorbance readings and normalizing by dividing each absorbance reading with maximum absorbance reading and multiplying by 100.

$0.6 \text{ (mmol L}^{-1}\text{)}^{1/2}$, turbidity increased exponentially. Relationship between optical density (turbidity) and KAR ($\text{KAR} = \text{K}^+ / (\text{Ca} + \text{Mg})^{1/2}$) also suggested that potassium may play a role in dispersion (Fig. 24). A positive relationship between percent optical density and cation adsorption ratio ($\text{CAR} = \text{Na}^+ + \text{K}^+ / (\text{Ca} + \text{Mg})^{1/2}$) (Fig. 25) was also observed. However, there seemed to be no relationship between optical density and temperature (Fig. 26).

Table 27 shows simple linear regression and r^2 values for the relationship between optical density and SAR, KAR, CAR, and temperature. The results indicate that SAR was significantly correlated with optical density ($p < 0.05$), but KAR and temperature were not. Stepwise multi-linear regression analysis was carried out using SAS (1984) to determine which variable(s) can best be used to predict optical density in the four lakes. The results indicate that CAR can best predict optical density at $p < 0.05$ if two outliers are not included (data not included). Inclusion of temperature improved the prediction capability, but the improvement was not statistically significant. Since the best prediction equation should include a minimum number of variables, I concluded that the CAR equation was best model for predicting optical density. Additional support for this conclusion, was provided the plot of predicted optical density vs. experimental optical density data (Fig. 27), which showed that these two parameters are correlated at $p < 0.05$.

Settling Characteristics

According to the DLVO theory, colloid stability depends on the long-range repulsive potential between like-charged particles. This repulsive potential is controlled by the colloid's CEC, which is controlled by pH, specific adsorption, and the ionic strength of the bathing solution (Evangelou, 1998 and references therein). Generally, increasing pH also

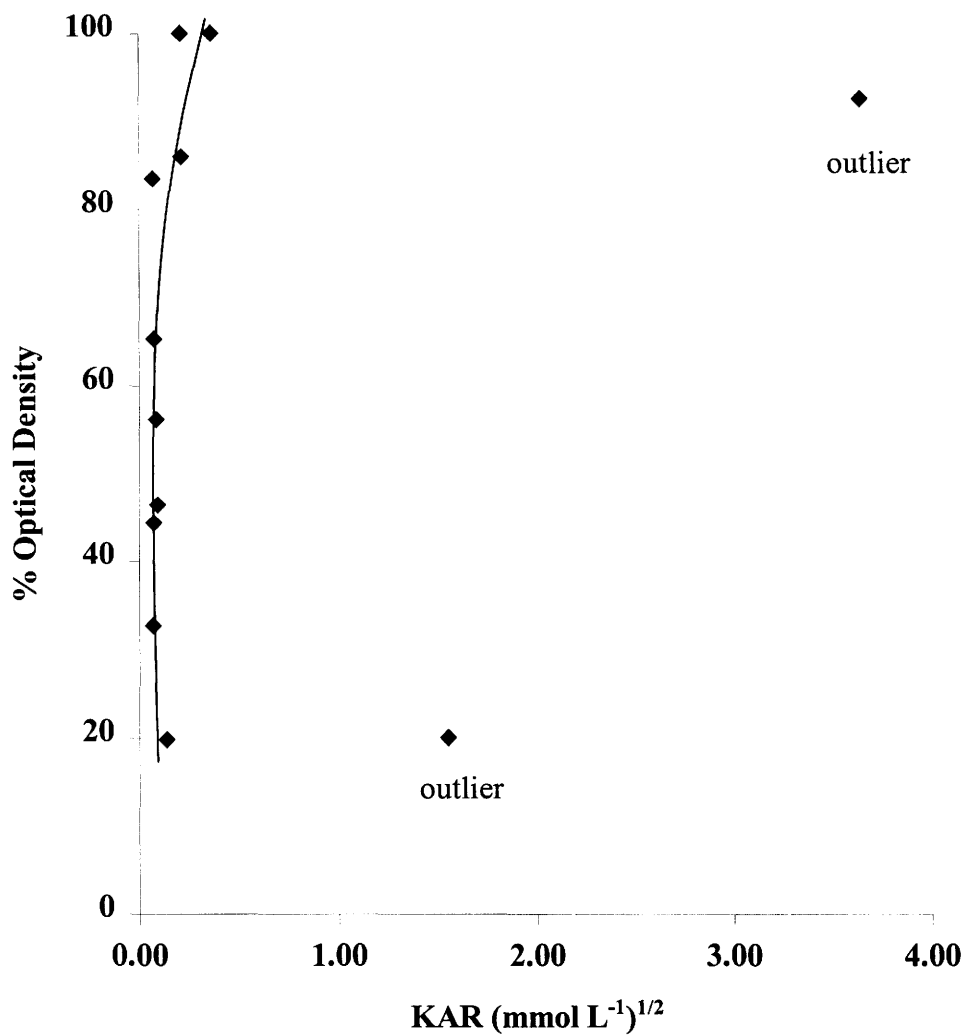


Figure 24. Plot showing relationship between percent optical density representing suspended solids and potassium adsorption ratio ($KAR = K^+ / [Ca^{2+} + Mg^{2+}]^{1/2}$) of the four studied Iowa lakes.

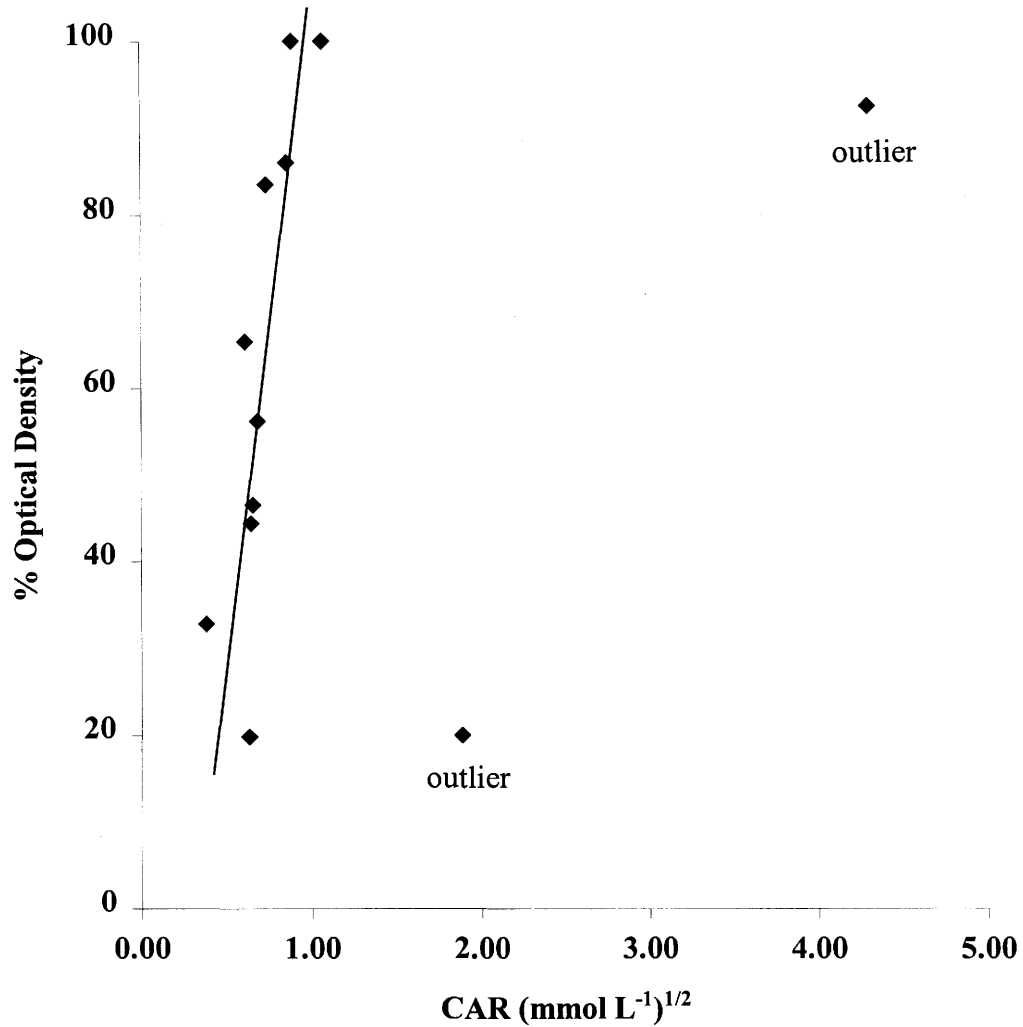


Figure 25. Plot showing relationship between percent optical density representing suspended solids and cation adsorption ratio ($\text{CAR} = [\text{K}^+ + \text{Na}^+] / [\text{Ca}^{2+} + \text{Mg}^{2+}]^{1/2}$) of the four selected Iowa lakes.

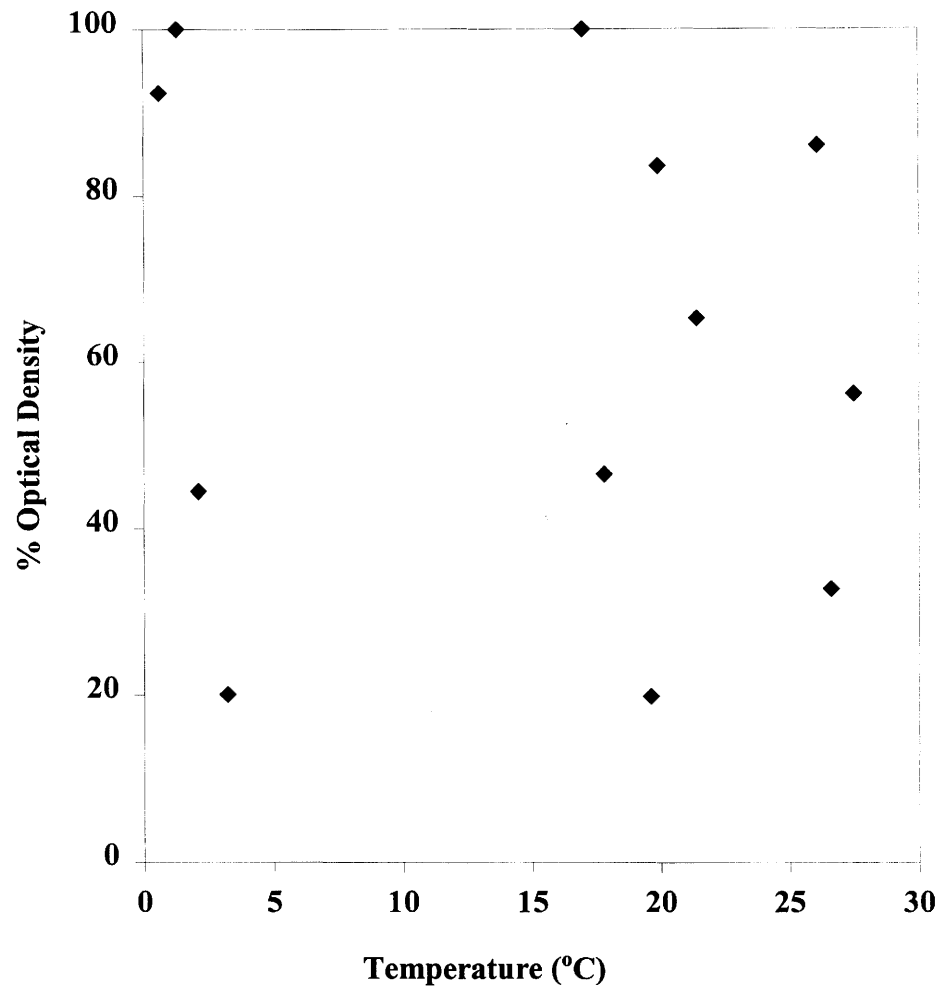


Figure 26. Plot showing relationship between percent optical density, representing suspended solids and temperature for the four lakes.

Table 27. Prediction equations of optical density as a function of SAR, KAR and Temperature from multiple linear regression analysis[§].

Variable	Prediction Equation	r ² value	Pr > F
SAR ^a	$y = 175.551 X - 13.614$	0.400	0.0273*
KAR ^b	$y = 6.865 X + 59.483$	0.029	0.5975
Temp.	$y = -0.343 X + 67.477$	0.015	0.7092
CAR ^c	$y = 181.948 X_1 + 9.466 X_2 - 20.183$	0.455	0.0654*
SAR, Temp.	$y = 173.950 X_1 - 0.162 X_3 - 10.456$	0.403	0.0979*
KAR, Temp	$y = 6.161 X_2 - 0.083 X_3 - 61.034$	0.03	0.8741
CAR and, Temp	$y = 188.248 X_1 + 12.939 X_2 + 0.399 X_3 - 30.393$	0.467	0.1504*

[§] Regression analysis carried out on SAS system.

^a SAR = Sodium Adsorption Ratio

^b KAR = Potassium Adsorption Ratio

^c CAR = Cation Adsorption Ratio

Y = Percent optical density or dispersion.

X1 = Sodium adsorption ratio (SAR)

X2 = Potassium adsorption ratio (KAR)

X3 = Temperature

* significant at P < 0.05 (Snedecor, 1946).

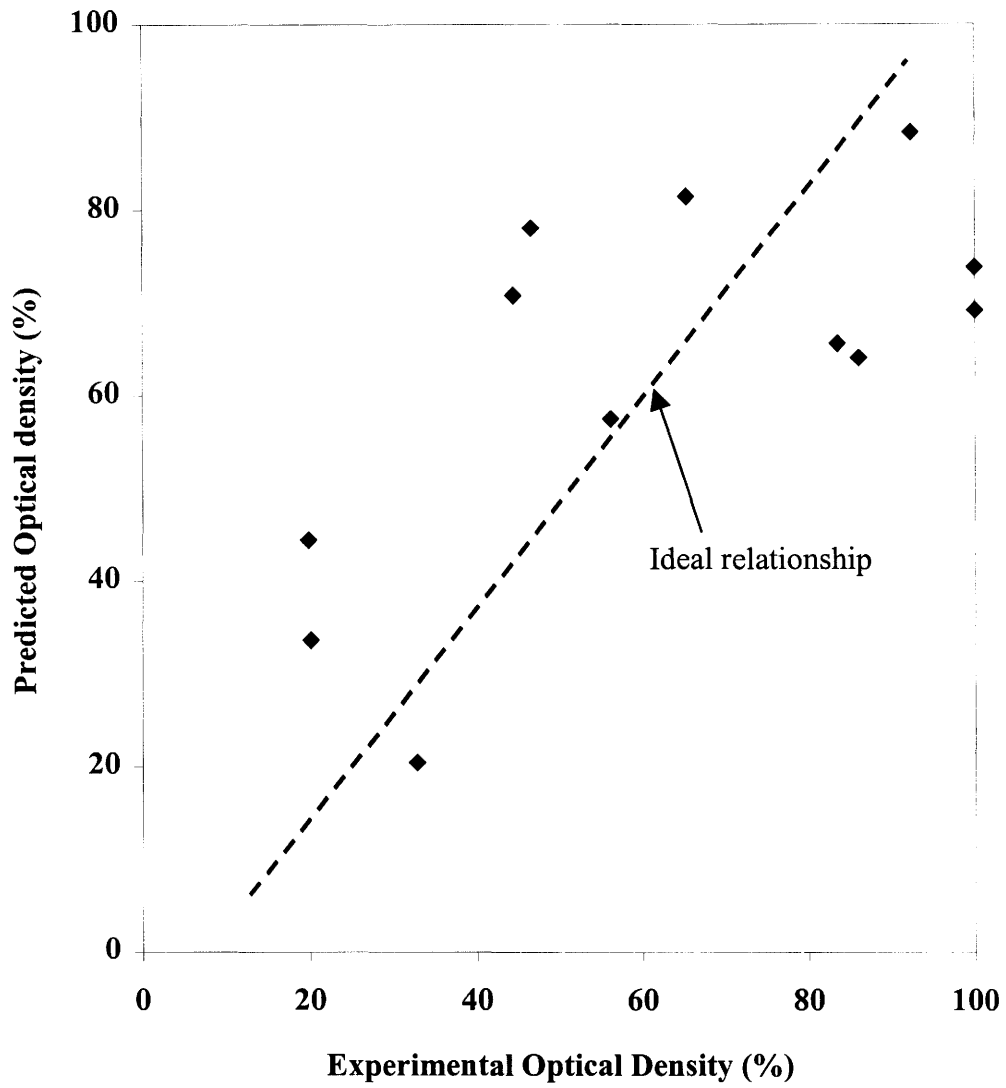


Figure 27. A plot of measured optical density and predicted percent optical density for the four Lakes.

increases repulsion between colloids, resulting in dispersion. Conversely, the reverse of this brings about flocculation. Therefore, the high pH of lake-water coupled with specific adsorption of ions like phosphate, are expected to contribute to the potential of lake sediments to disperse, thus causing an increase in turbidity.

All lake sediments tested contained considerable amount of confined potassium, ammonium and, phosphate. Clay interlayer confinement of ions like K^+ or NH_4^+ may decrease the apparent clay dispersive potential under a given ionic strength. (Evangelou, 1998 and references therein). The analogy is that, since K^+ or NH_4^+ exhibit small radii, many can fit in the interlayer spacing, collapsing the interlayer, and under these conditions the apparent density of this mineral will tend to increase, hence its settling rate will increase. On the other hand, if calcium or any other cation carrying considerable quantity of adsorbed water was to fit in the interlayer spacing, then the clay particle will tend to swell, become bulky, and its apparent density will decrease, thus causing decrease in the settling rate of this particle. However, this observation assumes no true flocculation is taking place in both systems, e.g. K^+/NH_4^+ or Ca^{2+} system, but rather settling of the particles alone. Hence, settling of clay particles would be dictated to a degree much by the saturating cation, assuming that solution ionic strength approaches zero or the double layer is fully expanded. However, the opposite effect will be observed if flocculation was induced by increasing ionic strength. In this case the divalent cation, e.g., Ca^{2+} will act as an effective flocculant, as ionic concentration of the solution was increased by the cation in question.

The data in Fig. 23 showed that the established critical flocculation point (SAR critical) for the studied lake waters is around $0.5 \text{ (mmol L}^{-1}\text{)}^{1/2}$, a relatively low value. The data in Fig. 28 show settling of Iowa smectitic colloids as a function of time under various

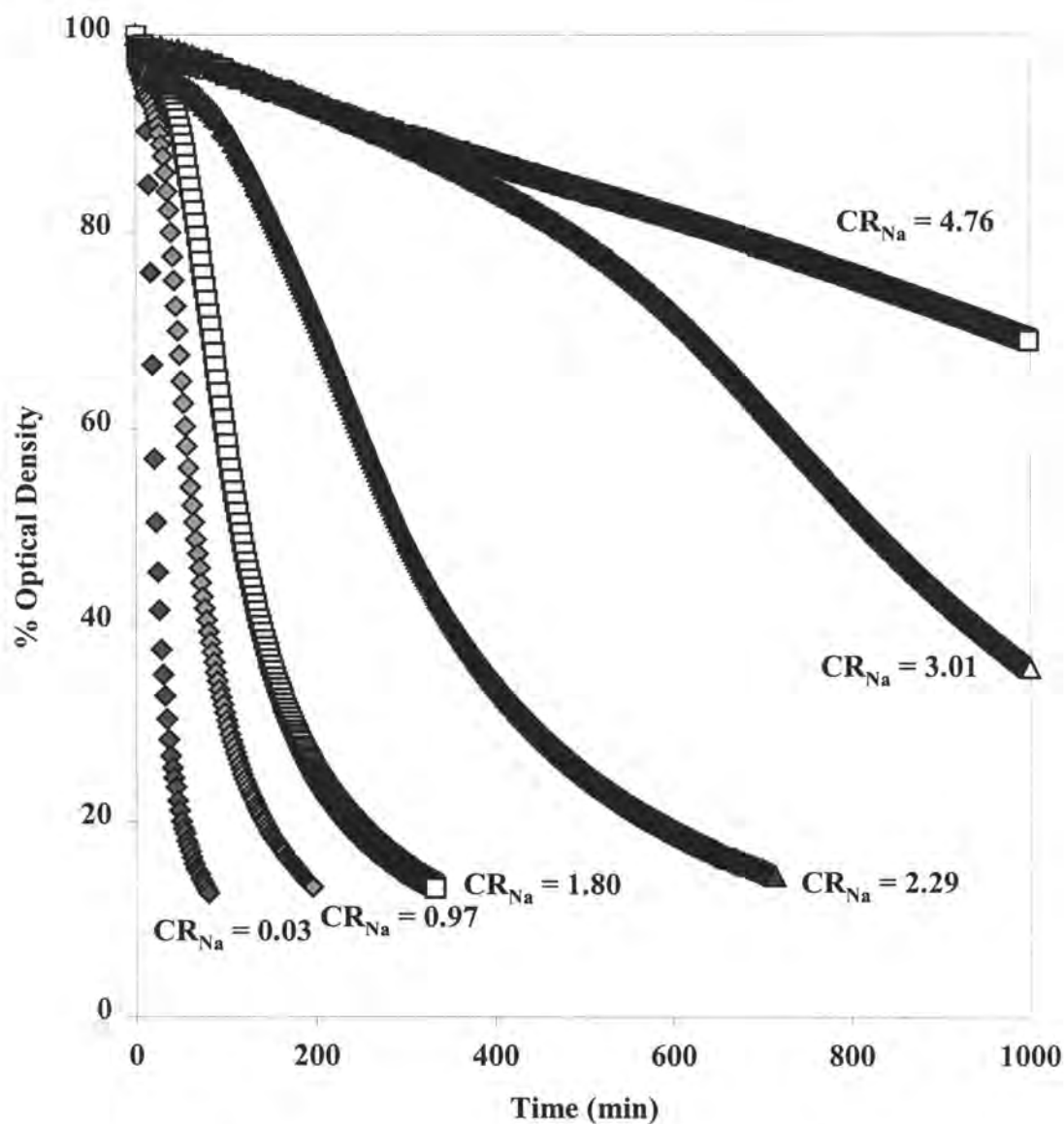


Figure 28. Plot showing settling of smectitic colloids as a function of time under various SAR ($Na^+ / [Ca^{2+} + Mg^{2+}]^{1/2}$ in units of $(mmol L^{-1})^{1/2}$ which is also referred to as CR_{Na} (Pils and Evangelou, 2001 unpublished data).

SAR ($\text{SAR} = \text{Na}^+ / (\text{Ca} + \text{Mg})^{1/2}$) values. Commonly, 2:1 clays or smectites undergo dispersion at an SAR of around 10 (mmol L^{-1})^{1/2}. However, the data in Fig. 29 show that Iowa smectites undergo dispersion at SAR values as low as 2.5 (mmol L^{-1})^{1/2} and no significant difference in settling behavior by the three monovalent cations was observed. Therefore, this enhances the contention that monovalent cations like Na^+ , NH_4^+ or K^+ may indeed act as lake-colloid dispersants (Pils and Evangelou, 2001 unpublished data). The significant lower critical flocculation/dispersion point of Iowa smectite relative to that published in the literature for montmorillonite (also 2:1 clay mineral) is perhaps due to humic coatings of the Iowa smectites. However, more investigation is needed to confirm this point. Based on the established critical flocculation point (SAR critical) for the studied lake-waters (Fig. 23), it can be concluded that any slight monovalent cation concentration change may affect the potential of lake-sediments to disperse or flocculate.

The data in Fig. 30 show that the lake sediments of the four lakes studied, exhibited different settling indices as well as a biphasic settling behavior. The initial phase was a rapid settling rate, or high settling index, approximately equal for all four lakes. The second phase was and a slow settling rate, or low settling index, but with a different plateau for each lake. These data suggested significant differences in water turbidity potential between the four lake- sediments. The results could have a number of explanations. One possible explanation is that the colloids of the four lakes differ in size. According to Stoke's Law, larger particles tend to settle faster than smaller particles. However, small differences in apparent CEC between clay colloids of similar size could have dramatic effects on settling rate (Arora and Coleman, 1979). The difference in colloid CEC could be due to differences in humic substance content and difference in surface electrical potential due to pH and variation in

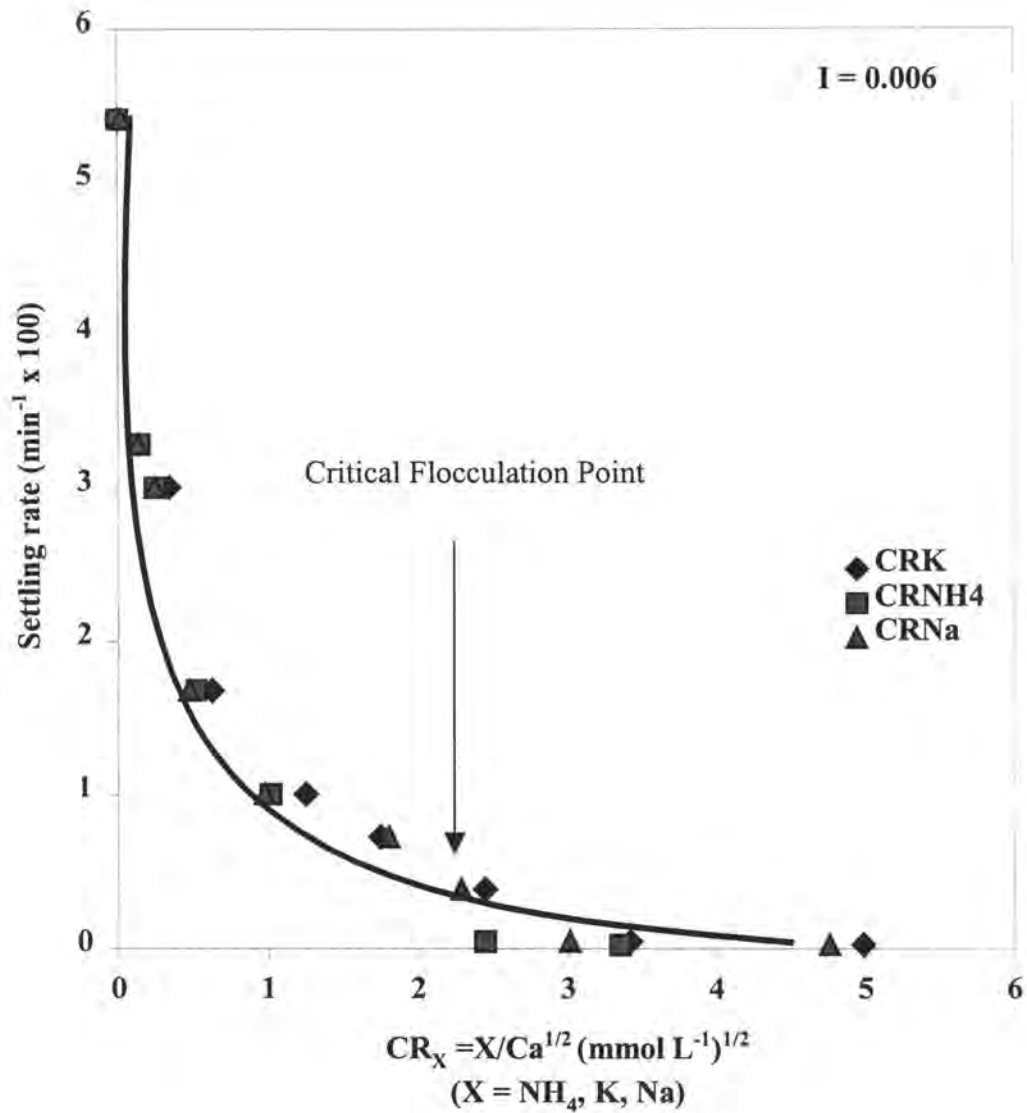


Figure 29. Plot showing sensitivity of Iowa clays to different monovalent cation ratios or CR_x, which is also referred to as XAR ($XAR = X^+ / (Ca + Mg)^{1/2}$ where $X = Na^+, K^+, \text{ or } NH_4^+$) at constant ionic strength. (Pils and Evangelou, 2001 unpublished data).

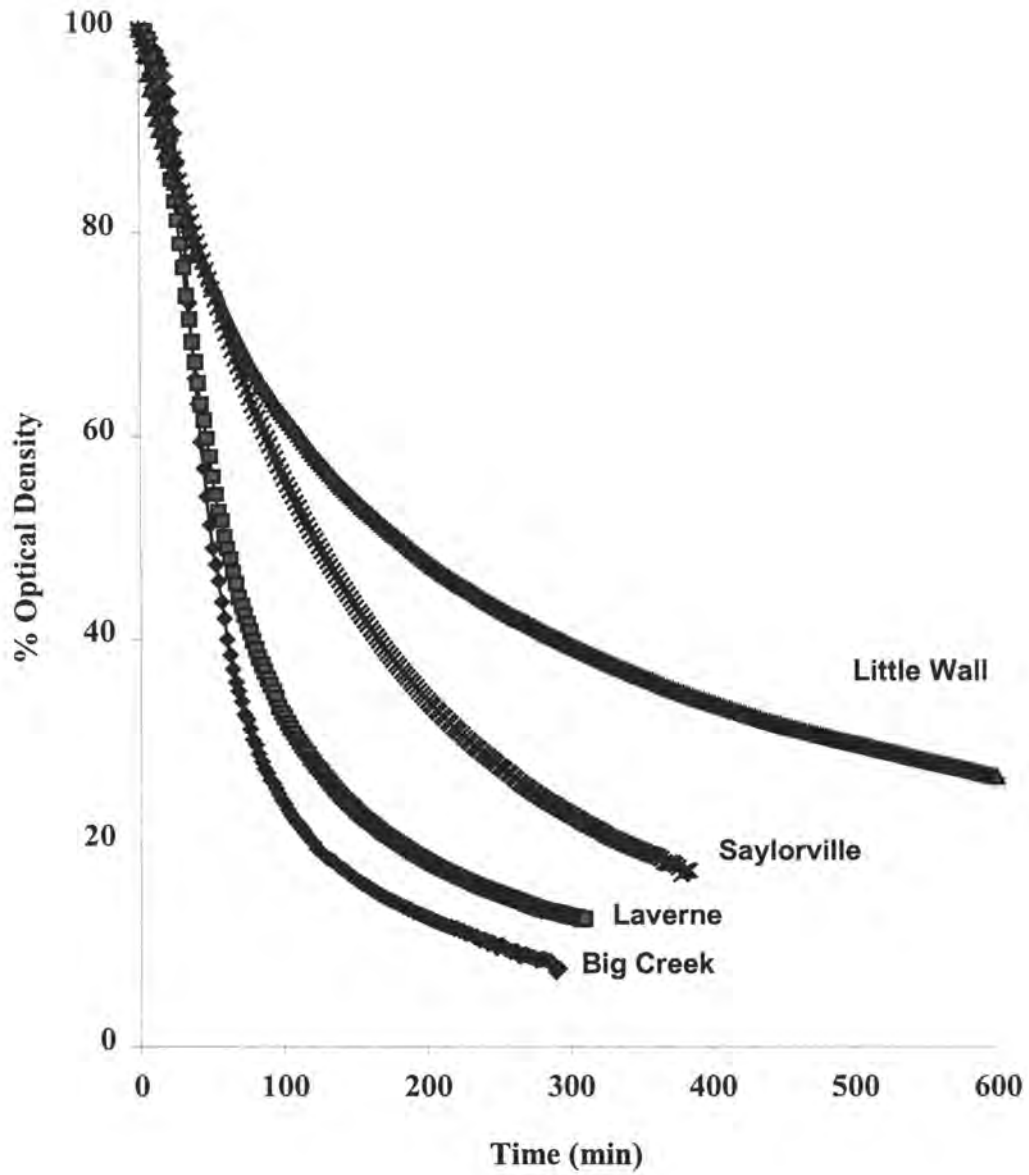


Figure 30. Data showing settling indices for the four lake-colloids. Data shows biphasic behavior with respect to settling of particles for the four lakes.

surface inner-sphere coordination of oxyanions such as phosphate and silicate (Evangelou, 1998).

Lake Dispersion Sensitivity Indices

The data in Fig. 30, as previously pointed out, suggested that Little Wall lake was much more sensitive to disturbances with respect to colloid suspension or turbidity than the Big Creek lake. The potential practical implication of these data was that it will take lake-water sediments at Little Wall longer to settle once disturbed compared to the other lakes. One may use a settling sensitivity test as a function of ionic concentration to predict turbidity potential of lakes under short-term physical disturbances, e.g., motorboats, short wind bursts. The force by which lake-sediment colloids of smectitic nature are attracted to each other is relatively weak; for this reason one does not expect such force to be effective in settling sediment colloids under continued physical disturbance of lake-water. There are, however, other colloid flocculative forces that may overcome physical disturbance of lake-water (Evangelou, 1998 and references therein).

Armed with the knowledge that electrical conductivity (EC) of natural waters can be related to ionic strength (Evangelou and Garyotis, 1984) and considering the double layer theory, an increase in ionic strength means that collision of particles may due to double layer compression, be high enough to induce colloid flocculation. Conversely, dispersion is expected at low ionic concentrations, e.g., influenced by rainy seasons. In my experiments, by simulating different conditions that might be encountered in the lake-environment with respect to settling of colloids, relative settling sensitivity indices were obtained (Fig. 31 to 34). In all four lakes, low ionic concentration was achieved by diluting the original solution

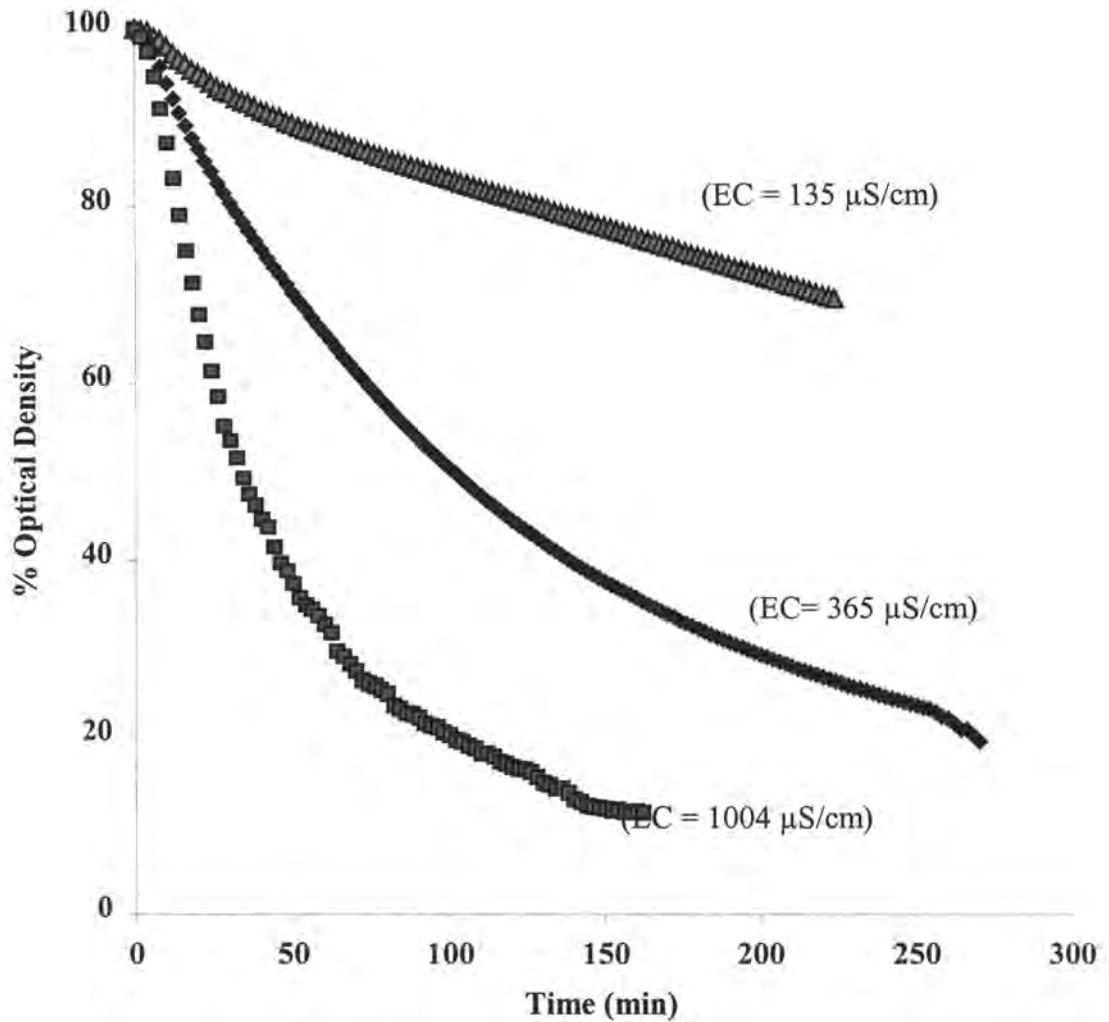


Figure 31. Sensitivity curves for Big Creek lake sediments under different ionic concentrations. Low ionic concentration ($EC = 135 \mu\text{S}/\text{cm}$) normal concentration ($365 \mu\text{S}/\text{cm}$) and high ionic concentration ($1004 \mu\text{S}/\text{cm}$). The low ionic concentration was obtained by diluting normal lake-water with deionised water. The high ionic concentration was achieved by spiking the normal lake-water with $3 \text{ meq}/\text{l CaCl}_2$.

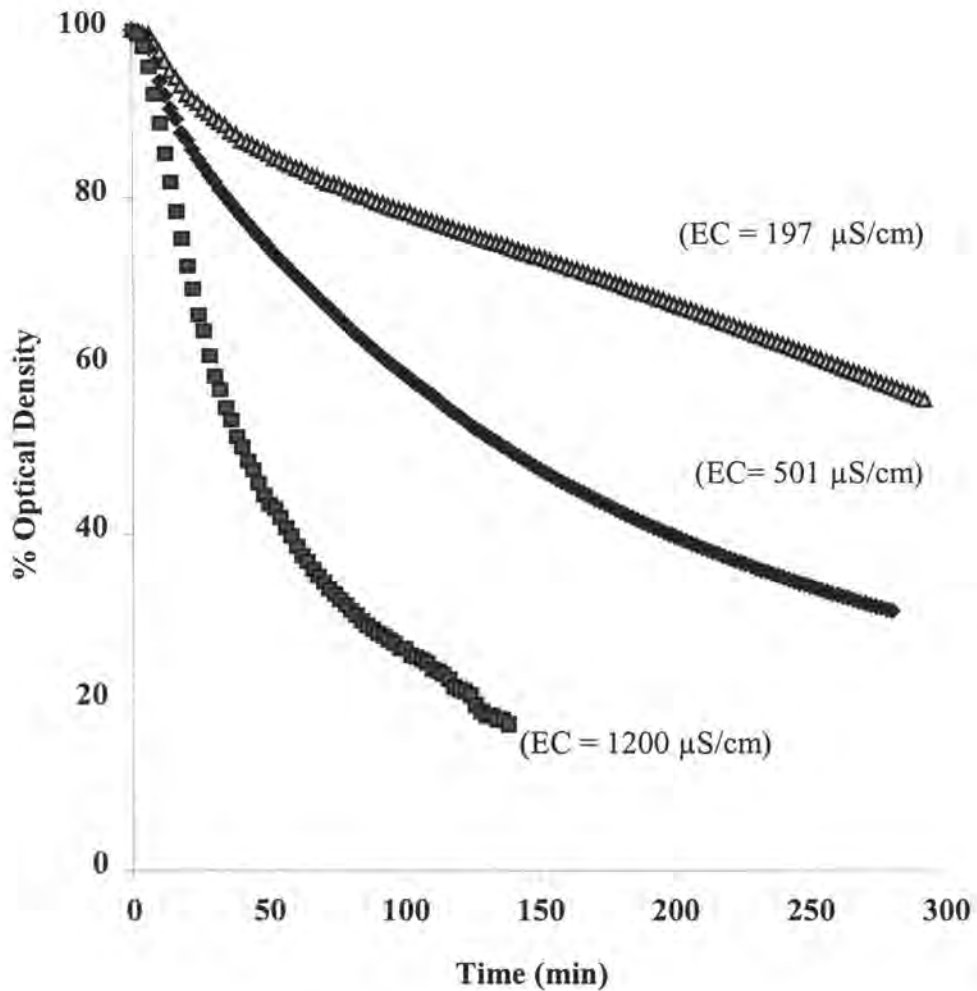


Figure 32. Sensitivity curves for lake Laverne sediments under different ionic concentrations. Low ionic concentration ($EC = 197 \mu\text{S/cm}$) normal concentration ($501 \mu\text{S/cm}$) and high ionic concentration ($1200 \mu\text{S/cm}$). The low ionic concentration was obtained by diluting normal lake-water with deionised water. The high ionic concentration was achieved by spiking the normal lake water with 3 meq/l CaCl_2 .

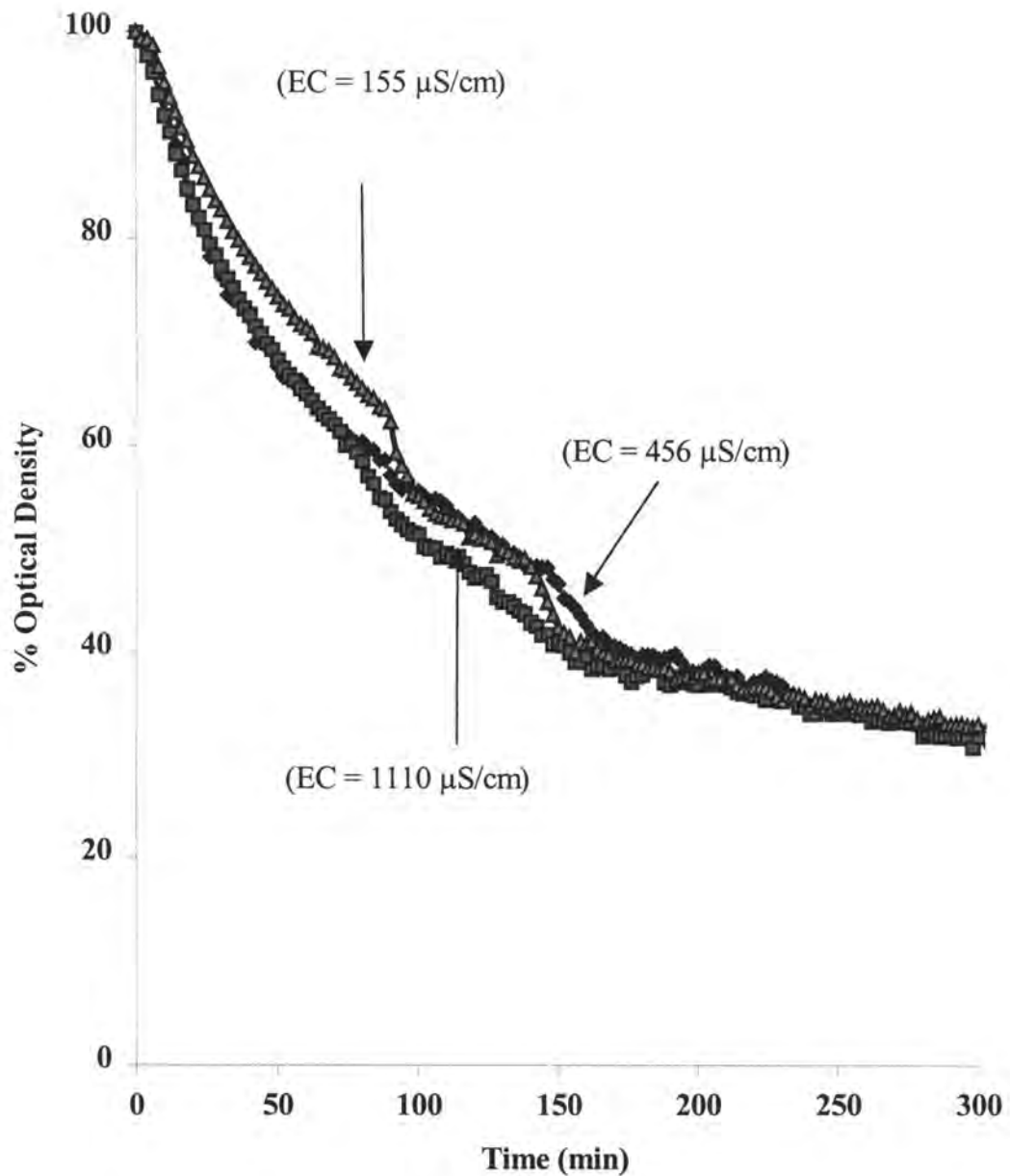


Figure 33. Sensitivity curves for Little Wall lake sediments at different ionic concentrations. Low ionic concentration (EC = 155 $\mu\text{S}/\text{cm}$) normal concentration (EC = 456 $\mu\text{S}/\text{cm}$) and high ionic concentration (EC = 1110 $\mu\text{S}/\text{cm}$). The low ionic concentration was obtained by diluting normal lake-water with deionised water. The high ionic concentration was achieved by spiking the normal lake water with 3 meq/l CaCl_2 .

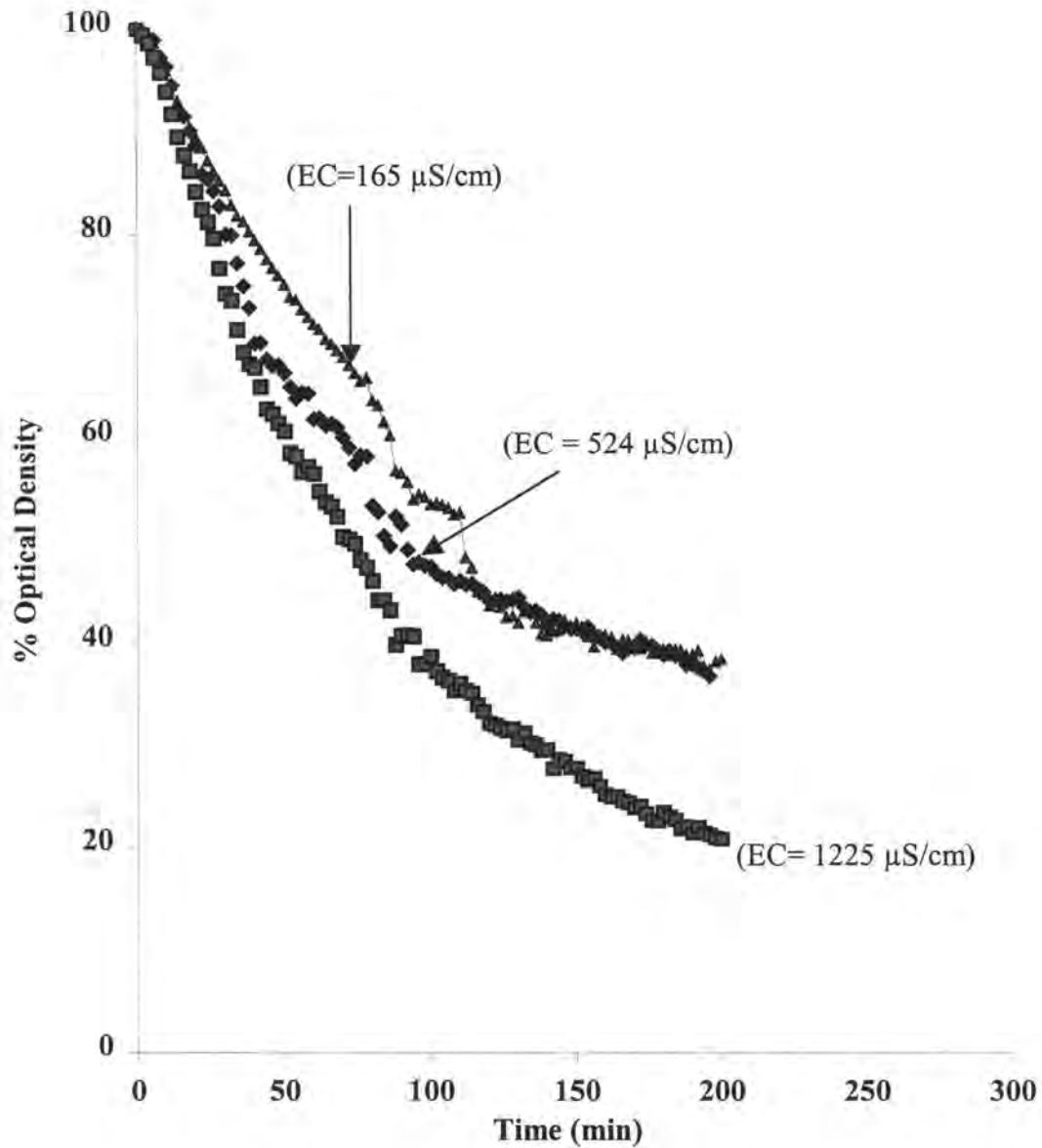


Figure 34. Sensitivity curves for Saylorville lake sediments at different ionic concentrations. Low ionic concentration (EC = 165 $\mu\text{S}/\text{cm}$) normal concentration (524 $\mu\text{S}/\text{cm}$) and high ionic concentration (1225 $\mu\text{S}/\text{cm}$). The low ionic concentration was obtained by diluting normal lake-water with deionised water. The high ionic concentration was achieved by spiking the normal lake-water with 3 meq/l CaCl_2 .

at a ratio of 1:3 with deionised water. The purpose of this dilution process was to simulate rainfall events. High ionic concentration of lake-water samples was achieved by spiking the normal solution with 3 meq/L CaCl_2 , thus simulating anthropogenic inputs into the lake system. For Big Creek low ionic concentration was EC at 135 $\mu\text{S}/\text{cm}$, normal ionic concentration at 365 $\mu\text{S}/\text{cm}$, and high ionic concentration at 1004 $\mu\text{S}/\text{cm}$. For lake Laverne low ionic concentration was EC at 197 $\mu\text{S}/\text{cm}$, normal ionic concentration at 501 $\mu\text{S}/\text{cm}$, and high ionic concentration at 1200 $\mu\text{S}/\text{cm}$. For Little Wall low ionic concentration was EC at 155 $\mu\text{S}/\text{cm}$, normal ionic concentration at 456 $\mu\text{S}/\text{cm}$, and high ionic concentration at 1100 $\mu\text{S}/\text{cm}$. Finally, for Saylorville lake low ionic concentration was EC at 165 $\mu\text{S}/\text{cm}$, normal ionic concentration at 524 $\mu\text{S}/\text{cm}$, and high ionic concentration at 1225 $\mu\text{S}/\text{cm}$.

The changes in ionic concentration or EC were expected to affect the settling behavior of solids by compressing the double-layer and subsequently affecting flocculation. For Big Creek (Fig. 31), when lake-water EC was adjusted to 135 $\mu\text{S}/\text{cm}$ percent optical density reading after 100-min sample reached approximately 85 but at EC of 1004 $\mu\text{S}/\text{cm}$ (high ionic concentration) percent optical density reached approximately 20 for the same settling time, which was a significant change. Lake Laverne water sample (Fig. 32) showed a similar trend. When lake-water sample EC was adjusted to 197 $\mu\text{S}/\text{cm}$ percent optical density reading after 100-min reached approximately 80, but at EC of 1200 $\mu\text{S}/\text{cm}$ (high ionic concentration) percent optical density reached approximately 25 after 100-min settling. This was also a significant change in optical density. However, the other two lakes, Little Wall and Saylorville showed little change with time in percent optical density relationship when EC was changed. For Little Wall lake-water (Fig. 33) when EC was adjusted to 155 $\mu\text{S}/\text{cm}$, percent optical density reading after 100-min reached approximately 60, but at EC

1110 $\mu\text{S}/\text{cm}$ (high ionic concentration), optical density reached approximately 50 % for the same time. This showed very little change in optical density. For Saylorville (Fig. 34), when EC was adjusted to 165 $\mu\text{S}/\text{cm}$, percent optical density reading after 100-min reached approximately 58, but at EC 1225 $\mu\text{S}/\text{cm}$ (high ionic concentration) percent optical density reached approximately 48 for the same time, a relatively small difference. For all the lakes, percent optical density for normal lake-water after 100-min reached 55, 60, 58 and 50 for Big Creek, Laverne, Little Wall and Saylorville, respectively.

The practical implication of the above data is that a very small increase in dissolved solids means a significant change in settling behavior. As predicted, the settling behavior of the suspended particles contained in the four lakes was dependent on ionic concentration (EC) (Evangelou, 1990). The double layer theory states that at high ionic concentration, flocculation will set in, and at low ionic concentration, dispersion will set in. Of the four lakes studied, Big Creek, Laverne and Saylorville obeyed DLVO theory, whereas, Little Wall appeared to show very little change in settling upon changing ionic concentration. Settling appeared to be similar at different ionic concentrations. There could be a number of explanations to this, most probable one being the type of organic matter and content in the sediments and perhaps even the size of dispersed clay colloids. It can be concluded from this experiment that suspended solids in most natural aquatic systems would behave predictably with respect to water chemistry.

CONCLUSIONS

On the basis of the above, the potential of soil colloids to disperse depends on a number of factors. The process itself is complex but predictable. Dispersed colloids are postulated to contribute indirectly to lake eutrophication. When clay particles exhibit a net surface electrical potential any fluctuation in lake-water chemistry due to rainfall, evaporation, or any other natural or anthropogenic factor may have significant influence on the rate of settling of suspended solids in these systems, hence water clarity and quality.

GENERAL CONCLUSIONS

This project was mainly focused on lake-water and lake-sediments with respect to 1) organic and inorganic nitrogen and phosphorus content, 2) sediment flocculation/dispersion behavior, 3) influence of seasonal changes on lake-water chemistry, and 4) lake-water-sediment interactions. The study included four lakes: Big Creek, Laverne, Little Wall, and Saylorville.

In general, lake-water chemistry is expected, to be influenced by land-fertilization practices, natural or human processes (e.g., erosion, road construction, housing development, road de-icing), as well as seasonal variation in temperature and rainfall. Changes in chemical composition of lake-water were observed as seasons progressed from mid-summer to mid-fall. This was attributed to natural variation and to different types and sources of lake inputs. The data also showed that electrical conductivity (EC) and pH of lake-water samples were within Federal and State drinking water quality standards. The EC ranged from 234 to 840 $\mu\text{S}/\text{cm}$ and lake-water pH in all four lakes appeared to be buffered in the alkaline range of 8.2 to 9.4 due to Ca-Mg-CO₃ equilibrium dynamics. Three apparent pKa values were determined for each lake system: One pKa of the solution or lake water was approximately 6.3, representing solution bicarbonate, whereas the other two pKa's, 5.8 and 4.7, represented the sediment components of the lake system, humic substances and aluminum-hydroxide mineral solids, respectively. Moreover, calcite and dolomite were determined to be the dominant components of all four lake-sediment systems, which perhaps were responsible for the alkaline pH range. Computer speciation simulations of the lake-water using GEOCHEM-PC suggested that lake-water chemistry was indeed controlled by alkaline-earth carbonates.

Sediment clays of all four lakes were determined to be smectitic. Generally, smectitic clays are not expected to be associated with fixed K^+ and/or NH_4^+ . However, on-going work in Dr. Evangelou's laboratory and others at Iowa State University showed that smectites associated with Iowa soils fix considerable quantities of K^+ and/or NH_4^+ . Mineral nitrogen in this study was mostly in the NH_4 fixed or 'confined' form and varied from 0.45 to 3.42 meq NH_4 -N/100 g lake sediment. Since fixed NH_4^+ has been shown to be slowly available to microorganisms, it may serve as a nutrient and may contribute to lake eutrophication.

The study also showed that as the seasons progressed from mid-August to mid-October, lake-water chemistry changed. A lake-water index of particular interest was the proportion of monovalent (e.g., Na^+ , K^+) to divalent cations (e.g., Ca^{2+} , Mg^{2+}). This proportion may play a major role in controlling water turbidity, an important water quality indicator. The data revealed that the SAR [$Na/(Ca + Mg)^{1/2}$] and KAR [$K/(Ca + Mg)^{1/2}$] greatly impacted water turbidity or suspended colloidal solids in all four lakes. Lake-water Na^+ may have originated from animal waste (manures) or de-icing salt, whereas lake-water K^+ may have originated from manures and/or chemical fertilizers. Generally, SAR and KAR are related to exchangeable Na^+ and K^+ on the exchanger phase (sediment), respectively. Exchangeable K^+ in the lake sediments was within normal concentration ranges, however exchangeable Na^+ appeared to be very high (~ 4 meq/100 g). This exchangeable Na^+ represented an exchangeable sodium percentage (ESP) in the range of 10 to 45. Literature reveals that an ESP in the range of 10 to 15 will induce sediment dispersion. Adsorbed Na^+ in all four lake-sediments exceeded that of normal Na^+ in Iowa soils (Dr. L. Sonon, unpublished data). The high levels of exchangeable Na^+ in the lake-sediments may be due to NaCl, used as road de-icing agent. Laboratory tests showed that the lake sediments

were indeed sensitive to dispersion. Upon examining this lake-sediment dispersion sensitivity the test revealed that two of the lakes (Big Creek and Laverne) were highly sensitive to dispersion with respect to small changes in total dissolved solids, whereas the other two lakes (Little Wall and Saylorville), were highly insensitive. Although one may hypothesize possible reasons for this difference in dispersion sensitivity, the observation requires additional investigation. Occurrence of suspended solids in lakes maybe attributed to the type of dissolved solids in the lake water and the proportionality of monovalent to divalent cations. High concentration of dispersed solids in lake-water severely impacts water quality by promoting lake eutrophication. Additionally, pH and presence of potentially determining ions (PDI), e.g., H_nPO_4 , may influence dispersion/flocculation behavior of lake sediments.

It is known that when pH in a natural body of water reaches the alkaline range, most sediment colloids are expected to disperse, especially under low EC and/or high monovalent cation ratio. Phosphate (H_nPO_4) may also contribute to sediment-colloid dispersion through chemisorption. Phosphate chemisorption may contribute to the surface charge of sediments if pH of lake-water is buffered in the alkaline range as shown in this study. An increase in lake-sediment surface charge by phosphate chemisorption is justified because the latter has the tendency to lower the point of zero charge (PZC) of mineral surfaces. A second reaction, known as precipitation, allows H_nPO_4 to react with various metals, e.g., Ca, Fe, or Al, and form metal-phosphate precipitates. Depending on type of metal-phosphate formed, dispersion potential of these solids differs because their PZC differs. For example, Ca-phosphate particles exhibit a PZC around 8, hence they would flocculate or settle out at around pH 8. On the other hand, Al-phosphate and Fe-phosphate appear to have a PZC

around 4.5 (Stumm and Morgan, 1981), which suggests that such particles would disperse at around pH 8.

The above information necessitated determination of the quantity and general form of phosphorus in the lake sediments. The data showed that most of the phosphate was in the inorganic form, presumably as metal-phosphate precipitates or chemisorbed by the various inorganic lake-sediment minerals. Phosphate concentration ranged from approximately 700 to 2500 mg P/kg lake sediment. Moreover, the N data showed that release of 'confined' $\text{NH}_4\text{-N}$ was negligible and therefore most of the available N would be of the organic form. Organic N (e.g., amino acids, peptides, glycoproteins, etc.) concentration in lake-sediments ranged from 1200 to 2800 mg N/kg. In order to shed additional light on the quantity-form and potential release or bioavailability of NH_4^+ and PO_4 quantity-intensity (Q/I) studies were carried out. The Q/I plots showed that all four lakes exhibited high dissolved inorganic P. In two of the lakes (Big Creek and Saylorville) a P-adsorption mechanism was operative whereas the other two lakes (Laverne and Little Wall) showed some form of metal-phosphate precipitates. These data suggested that in all four lakes, P would not be a limiting nutrient. However, the colloidal nature (dispersion/flocculation) of the inorganic P would be different. The importance of this is discussed below.

Lake water turbidity, a product of colloid dispersion inhibits light penetration, limits processes such as photosynthesis and aquatic-organism reproduction. The US government regulates suspended solids in natural bodies of water to around 35 mg/L. Epilimnetic suspended solids are exposed to sunlight, which enhances photosynthetic activity and depletes dissolved oxygen on the surface of the lakes. Such condition is generally shown to be detrimental to aquatic life. This study dealt with the potential of lake-bottom sediments to

become suspended, but more information would be needed in the future for quantifying and determining the nature of the suspended solids and their contribution to lake eutrophication.

Two factors control the potential of a given lake to become eutrophic. One factor is the total quantity or 'load' of nutrients and the second factor is the potential of such nutrients to become available to organisms causing lake eutrophication. However, the relationship between total nutrient quantity or 'load' and bioavailable nutrient quantity is very complex and is not easily predictable. Generally, limnologists use the total N (TN) to total P (TP) ratio as means of predicting lake eutrophication. This TN:TP ratio omits the complexity of the relationship between 'load' and availability. Partly because of this omission, TN:TP ratio does not appear to be a sensitive eutrophication index. For example, limnologists point out that a ratio of 21 to 240 predicts mesotrophic lakes but TN:TP ratios of 17 to 96 and 4 to 71 predict eutrophic and hypereutrophic lakes, respectively. Note however, TN:TP ratio of 21 to 240 covers mesotrophic lakes, eutrophic lakes and hypereutrophic lakes. The above suggest that TN:TP ratio alone does not predict lake eutrophism. Additional factors are involved and may include chemical form of nutrients, turbidity, dispersion, quantity-intensity relationships, etc. This study did not prove that these latter factors are involved in lake eutrophication, but the study suggested that they may play a very important role. Extensive lake-water-sediment data are needed to quantify such a role.

The overall study demonstrated that lake water chemistry maybe sensitive to external environmental factors and most likely management and use of the surrounding watershed. Furthermore, the study showed that lake-water chemistry and lake-sediment dispersion/flocculation behavior are interrelated. Dispersion/flocculation behavior of lake sediments may also be related to chemical forms of nutrients and possibly to eutrophication.

Therefore, this study formed the foundation for the need of additional parameters to be investigated in order to improve the prediction of lake-water quality trends and potential lake eutrophication.

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