STRATIGRAPHICAL ANALYSIS OF SEDIMENTARY INORGANICS TO DETERMINE PALEO-PRODUCTIVITY TRENDS IN LAKE TENKILLER

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CHAPTER I

INTRODUCTION

Paleolimnological studies are important for effective ecosystem management. Effective ecosystem management requires long term data so that baseline conditions, natural variability, and the point in time that the system changed can be established. The main sources of data are direct historical measurements, comparisons to similar but unaffected ecosystems, hindcasts using computer models, and paleolimnological reconstructions. However, direct historical measurements are rarely available, continuous data collection on all lakes is not economically feasible, and computer models contain much uncertainty. Thus, paleolimnological studies are important in unraveling lake history archived in the sediments and defining the ecosystem that existed prior to human impact (Smol 1992).

Trace element chemistry in lakes is influenced by biological productivity and the development of an anoxic hypolimnion (Kuhn et al. 1994). As primary productivity increases, hypolimnetic dissolved oxygen consumption increases (Gachter and Meyer 1990). Elevated levels of productivity and organic input can result in the development of anoxic conditions in the hypolimnion during summer thermal stratification. During this critical stage, the redox of the hypolimnion changes dramatically resulting in greater recycling of iron, manganese, and other trace elements (Wetzel 1983). Therefore, the degree of oxygenation of the hypolimnion could reflect the productivity of the lake with less productivity indicated by more hypolimnetic oxygen and increasing productivity indicated by hypolimnetic oxygen depletion. Increasing and decreasing degrees of oxygenation are then manifested in varying redox conditions.

Because changes in organic input results in changes in redox (Horowitz 1991), paleoredox conditions can be useful indicators of historic productivity. Several methods have been developed for determining paleoredox conditions. The precipitation and solubility of iron and manganese can be controlled by redox conditions. Since changes in redox conditions can alter the amounts of iron and manganese flushed from the lake and the amounts retained in the sediments, sedimentary iron and manganese concentrations are useful indicators of the paleoredox conditions in lakes (Engstrom and Wright 1984). Mackereth (1966) used the iron to manganese ratio (Fe:Mn), along with iron and manganese concentration-depth profiles, in sediment cores to determine the paleoredox conditions of several lakes in the English Lakes District. However, Engstrom and Wright (1984) said that the Fe:Mn should be used with caution when reconstructing paleoredox conditions of lakes and suggested that supporting evidence be used when possible.

Hallberg (1972) suggested that the differing mobilities of copper and zinc (i.e. $R=Cu/Zn$) could be used to indicate paleoredox conditions. During reducing conditions metals are precipitated as metal sulfides. The solubility products of metal sulfides indicate that precipitation of copper is more favored than zinc during reducing conditions. During oxidizing conditions the solubilities of zinc and copper are similar. Therefore, R drops under oxidizing conditions and rises under reducing conditions. This paleoredox indicator was later expanded to $RP=(Cu+Mo)/Zn$ by Hallberg to calibrate it to more natural conditions. Frevert and Sollmann (1987) determined the paleoredox conditions of Lake Kinneret (Israel), a regularly stratified and mixed lake, using the paleoredox indicator RP.

Brooks et al. (1969) and Powell and McKirdy (1973) postulated that the pristane to phytane ratios (Pr:Ph) of ancient sediments and oils reflected paleo-environmental conditions. Pristane and phytane are both products of chlorophyll decomposition. Pristane formation is dominant in aerobic environments and phytane formation is dominant in anaerobic environments. Therefore, a high Pr:Ph may indicate an aerobic environment and a low Pr:Ph may indicate an anaerobic environment. Didyk et al. (1978) used the Pr:Ph to determine the paleoredox conditions of the Cariaco Trench and the Black Sea, both of which are presently anoxic. Didyk emphasized, however, that the Pr:Ph should not be regarded as the definitive indicator of paleo-environmental conditions. After further search of the literature, it was concluded that this method did not provide an adequate indicator of paleoredox conditions.

In addition to the paleoredox indicators, other indicators of historical productivity were used. Calcium should provide a good indicator of historic trends in the productivity of Lake Tenkiller. Increased biological productivity generally results in increased calcium carbonate concentrations in the sediments (Hickman and Klarer

1981; Flannery et al. 1982). If CO_2 is removed from a solution where $Ca(HCO_3)_2$, CO_2, H_2CO_3, and CO_3 are in equilibrium, $CaCO_3$ will precipitate until equilibrium is reestablished. When CO_2 is removed from the water by photosynthetic organisms, large amounts of $CaCO_3$ are precipitated (Wetzel 1983). Therefore, increasing productivity should result in increasing calcium concentrations in the sediment.

Phosphorous is an essential nutrient for phytoplankton (Cole 1975). Its concentrations are generally closely related to productivity in natural systems (Engstrom and Wright 1984). Because of this association, it has been used by many researchers to predict trophic state (Leach and Herron 1992). Because phosphorous is generally efficiently fixed in sediments, stratigraphical trends in sedimentary phosphorous may be useful in determining the historical trends in trophic state (Engstrom and Wright 1984).

Sodium was used as an indicator of past erosion (Anderson and Rippey 1988). When erosion occurs, unweathered minerals containing high concentrations of sodium are transported to the lake and sedimented. Because these minerals and their components are rarely altered in aquatic systems, their distribution in sediments is useful for determining weathering and erosion (Engstrom and Wright 1984). Increasing sedimentary sodium concentrations generally indicate increasing erosion (Sekar et al. 1992) while declining sedimentary sodium concentrations indicate decreasing erosion (Hickman and Klarer 1981; Sekar et al. 1992).

Cesium-137, which was analyzed by the USDA-ARS in Durant, Oklahoma, was used to date the sediments and determine the historical sedimentation rate of the lake.

The objectives of this study were to evaluate the potential of trace element concentration-depth profiles and ratios for determining the paleoredox conditions and historical trends in the productivity of Lake Tenkiller. The specific tasks were the following:

1) Measure phosphorous, zinc, copper, molybdenum, calcium, sodium, iron, and manganese concentration-depth profiles from a sediment core taken from Lake Tenkiller and calculate the Fe:Mn ratio, R=Cu/Zn, and RP=(Cu+Mo)/Zn.

2) Date the sediments using Cesium-137.

3) Use the Fe:Mn ratio, R=Cu/Zn, RP=(Cu+Mo)/Zn, iron, manganese, molybdenum, calcium, and phosphorous to determine the historic productivity.

4) Use the sodium profile to determine past erosion intensity.

This paleolimnological study was part of the Clean Water Act (CWA) Section 314 Phase I Clean Lakes project on Lake Tenkiller, Oklahoma, which was conducted by the Oklahoma State University Water Quality Research Laboratory.

CHAPTER II

LITERATURE REVIEW

Trophic Classification Using Hypolimnetic Dissolved Oxygen

Trophic classification based on hypolimnetic dissolved oxygen concentrations is not a new concept. In the early 1900s Thienemann proposed use of hypolimnetic dissolved oxygen depletion as an indicator of trophic state. Later, Hutchinson (1938) and Hutchinson and Mortimer (Hutchinson 1957) expanded on Thienemann's work suggesting that areal hypolimnetic oxygen depletion rates provided a useful indicator. In 1976, Burns suggested that both areal and volummetric hypolimnetic oxygen depletion rates were needed for correct trophic classification. In addition to these researchers, trophic classification based on hypolimnetic oxygen has also been used by Lueschow and others in 1971 as a Trophic Index Number (TIN) in EPA's National Eutrophication Survey (1974), and in Uttormark and Wall's (1975) Lake Classification Index (LCI). Walker (1979) expanded Carlson's (1977) TSI using hypolimnetic oxygen as it applies to trophic state. Chapra and Dobson (1981) observed that measurement of the hypolimnetic dissolved oxygen deficit was essential in trophic classification (Leach and Herron 1992). Models have also been developed for determining volummetric hypolimnetic oxygen depletion (Vollenweider and Janus

1982, Coffey et al. 1989) and the probability of having an oxic hypolimnion (Reckow 1988, Coffey et al. 1989).

Relationship Between Dissolved Oxygen and Redox

According to Wetzel (1983) redox potential in water is affected by oxygen concentrations according to the reaction,

$$H_2O = \frac{1}{2} O_2 + 2H^+ + 2e-.$$

However, clinograde oxygen profiles do not necessarily result in clinograde redox profiles (Hutchinson 1957). Even though a clinograde oxygen profile is present, the redox remains positive and high as long as the water is not near anoxia (Wetzel 1983). However, in most lakes with clinograde oxygen profiles and extreme oxygen deficits, clinograde redox profiles exist (Hutchinson 1957). This is because redox quickly decreases as dissolved oxygen nears zero and anoxia occurs in the lower hypolimnion and sediments (Wetzel 1983). In most cases, measurement of dissolved oxygen is sufficient to estimate redox (Goldman and Horne 1983).

Organisms act as redox catalysts by mediating redox reactions and the transfer of electrons (Wetzel 1983). The balance between photosynthesis and respiration is primarily responsible for regulating lake redox conditions. Products of photosynthesis settling into the hypolimnion and sediment act as reductants by supplying electrons. Most redox reactions are carried out by bacteria (Goldman and Horne 1983).

Iron and Manganese Cycling in Aquatic Systems

Much research has been conducted on the cycling of iron and manganese in aquatic environments. Iron and manganese are closely associated (Hsiung and Tisue 1994). Most iron and manganese transported into lakes is associated with mineral particles resulting from erosion or resulted from rock or soil weathering (Mackereth 1966). Acid rain can increase transport of iron and manganese. In addition, organic acids can vastly increase the mobility of iron and manganese in water by lowering the pH, enhancing reducing conditions, and forming organometallic complexes. Correlations between iron and manganese and sedimentary organics have been noted in lake sediments. Anoxic groundwater may also be important in transporting iron and manganese to lakes.

Iron and manganese compounds are generally insoluble under oxidizing conditions (Engstrom and Wright 1984). In oxygenated waters, iron is primarily found as insoluble iron hydroxide [$Fe(OH)_3$] or associated with colloidal or suspended particles, with only low concentrations found in ionic form (Engstrom and Wright 1984, Vuorinen et al. 1986). Manganese is more soluble than iron, however, it is more complexed with sulfates, carbonates, and organic acids (Engstrom and Wright 1984). In natural waters, manganese can be reduced by reaction with Fe^{2+}, readily oxidizable organics, and reduced sulfur compounds. In addition, manganese reduction by organic matter is promoted by sunlight. Microbial mediations dominate manganese biogeochemistry (Hsuing and Tisue 1994).

Most iron and manganese flowing into lakes is transported to the sediments

(Davison et al. 1982). In oxic waters, iron and manganese are deposited as hydrated oxides and with coagulates of humic organics. Manganese may also be precipitated by sorbing onto iron oxides (Engstrom and Wright 1984). Because iron and manganese oxide precipitates are fine (Engstrom and Wright 1984, Horowitz 1991), wave and current action transports them to more protected areas. Therefore, iron and manganese concentrations generally increase with depth of water (Engstrom and Wright 1984).

In oxic environments, iron and manganese become enriched in the sediments because of the efficient precipitation mechanisms (Mackereth 1966). Once in the sediments, microbial degradation of organic matter releases iron and manganese which are subsequently transformed to immobile hydrous oxides. Most iron and manganese in oxygenated surface sediments exists as immobile hydrous oxides. However, large concentrations of iron and manganese in sediments are also bound to humic acids or in ferromanganese nodules and crusts. The stability of iron and manganese is increased by interaction with organic and sulfur compounds as well as with equilibrium with enriched interstitial waters (Engstrom and Wright 1984). Kjensmo (1988) found that the redox sensitive elements (iron and manganese) accumulate in organic sediments. The concentrations of iron and manganese oxides in sediment are important, because they contribute to the metal-sorption potential of sediment and greatly influence the quantities of other trace metals present (Jenne and Zachara 1987).

In most lake sediments, only a thin layer at the surface of the sediments is oxygenated. Below this layer, microbial activity and diagenesis of inorganic chemicals deplete the sediments of oxygen and cause reducing conditions (Engstrom and Wright

1984). Most redox reactions do not occur at significant rates unless they are microbially mediated (Kuhn et al. 1994). Degradation of organic compounds by microorganisms results in the sequential consumption of oxygen, Mn^{4+}, nitrate, Fe^{3+}, sulfate, and bicarbonate (Carlton and Klug 1990, Adams et al. 1990). This consumption of oxygen causes a sharp separation between the oxidizing and reducing environments (Peiffer 1994), which is known as the redoxcline.

As sediments are moved across the redoxcline due to progressive burial, iron and manganese are reduced causing them to enter the interstitial water (Engstrom and Wright 1984). Reduction of oxidized manganese occurs more rapidly than the reduction of oxidized iron (Hsuing and Tisue 1994) to its ionic form Fe^{2+} (Vuorinen et al. 1986). Upward diffusion may occur until the iron and manganese are reprecipitated at the redoxcline as ferric and manganic compounds (Engstrom and Wright 1984, Sakata 1985, Anderson and Rippey 1988, Peiffer 1994). This can produce iron and manganese concentration peaks at the top of the sediment profile. However, surface enrichment of iron usually can not be recognized, because the sedimentary flux is greater than the diffusive flux (Sakata 1985). Because of this post-depositional migration, trends at the top of cores must be carefully interpreted.

If surface sediments remain oxidized, then iron and manganese remain relatively immobile even below the redoxcline (Engstrom and Wright 1984). Iron is generally retained by the sediments with minimal loss (Davison et al. 1982), however, it alternates between mobile and immobile states (Cole 1975).

Diagenetic effects on iron and manganese in lake sediments are pronounced in eutrophic systems, where seasonal anoxia, organic accumulation, and changes in redox are substantial (Anderson and Rippey 1988). In the hypolimnion of eutrophic lakes, microorganisms remove oxygen and reduce iron and manganese hydroxides (Kuhn et al. 1994). When the hypolimnion becomes anoxic, iron and manganese are reduced and released from the sediments into the hypolimnion (Engstrom and Wright 1984, Sakata 1985, Anderson and Rippey 1988, Kuhn et al. 1994). However, iron and manganese may begin dissolving before complete deoxygenation of the hypolimnion (Davison et al. 1982).

Iron and manganese diffuse into anoxic water from sediments when the redox potential drops to 0.20 isovolts (Eh) above the sediment interface. Manganese is released from the sediment before iron because of its greater solubility and can be selectively depleted under a moderately anaerobic hypolimnion (Engstrom and Wright 1984). Loss of iron from sediments results mainly from microbial reduction of ferric oxides (Peiffer 1994, Kuhn et al. 1994) and occurs with low redox and extreme hypolimnetic anoxia (Anderson and Rippey 1988). Therefore, if anoxia becomes severe, both iron and manganese will be removed from the sediment. Continued loss of iron and manganese from the sediments occurs as iron and manganese are desorbed from the solid phases and as hydrous oxides dissolve (Engstrom and Wright 1984).

The release of metals from the sediment results in increased metal concentrations in the hypolimnion. High concentrations of dissolved iron accumulates in the hypolimnion during summer anoxia (Davison et al. 1982). The sedimentation of phytoplankton from the epilimnion also carries metals associated with the algae into the hypolimnion and sediments (Kuhn et al. 1994). Substantial dissolution of manganese and some dissolution of iron occurs in lower anoxic water of lakes (Davison et al. 1982). Davison (1981) found that most iron accumulated in an anoxic hypolimnion was derived from the sediment, while most manganese was supplied by dissolution from particulate matter sedimenting through the water column. This contradicts previous studies which attribute the hypolimnetic manganese to diffusion from sediment alone. Regardless of whether manganese diffuses from the sediments, dissolves from particulates, or both, the result will be less manganese in the sediment.

Manganese is generally rapidly reduced even when the hypolimnion is oxic. Most manganese entering a seasonally anoxic lake is washed out, generally following one redox cycle so that less than 10% is retained by the sediments. The residence time of manganese is generally less than 1 year (Davison et al. 1982). A recent study by Hsuing and Tisue (1994) indicates that more manganese is released from sediments when the hypolimnion is oxygenated then when it is anoxic. The mobilization and accumulation of manganese in the hypolimnion was linked to degradation of organic matter, which occurred more rapidly under aerobic conditions. Anoxia may inhibit the release of manganese associated with organic matter from the sediments, because degradation is decreased. Therefore, aerobic degradation of organic matter by microorganisms may be more important in releasing manganese from sediments than dissolution of manganese oxides during anoxia (Hsuing and Tisue 1994).

When the redox potential goes below 100 mv, H_2S is formed through SO_4 reduction. Since iron is released before hydrogen sulfide (200-300 mv), iron and hydrogen sulfide will quickly form insoluble iron sulfide (FeS) when the redox potential goes below 100 mv (Engstrom and Wright 1984). In eutrophic lakes, reoxidation of Fe^{2+} and sulfide does not occur causing an accumulation of iron sulfide in the sediments (Peiffer 1994). However, this recycling of iron between sediment and water through dissolution and precipitation as FeS is generally small compared with other iron fluxes (Davison et al. 1982). Manganese sulfide (MnS) is more soluble than iron sulfide (FeS), therefore, hydrogen sulfide does not inhibit the release of manganese from the sediments. Iron sulfide may also form below the redoxcline in sediments under oxic waters (Engstrom and Wright 1984).

Precipitation and sedimentation of iron and manganese occurs at fall mixing (Davison et al. 1982). The reoxidation of Fe^{2+} is rapid while reoxidation of Mn^{2+} is slow (Kuhn et al. 1994, Hsiung and Tisue 1994, Peiffer 1994). The oxidation of manganese is catalyzed by adsorption onto oxide surfaces. However, most manganese oxidation is microbially mediated (Kuhn et al. 1994). The oxidation of Mn^{2+} is initiated by bacteria after which abiotic processes complete the oxidation (Hsiung and Tisue 1994). Precipitation of iron and manganese oxides at overturn carry significant amounts of trace metals to the sediments (Horowitz 1991, Kuhn et al. 1994).

The precipitation and solubility of iron and manganese is primarily controlled by the ionic composition, pH, and redox. Since long-term changes in redox conditions could alter the amount of iron and manganese being flushed from the lake and the amount being retained in the sediments, iron and manganese concentrations in the sediments can be used to determine the paleoredox conditions in lakes (Engstrom and then precipitated to the sediments in oxic lake environments.

When iron maxima corresponds with Fe:Mn maxima, the iron concentration in the sediment is produced by varying rates of supply from the watershed. If the Fe:Mn is consistent throughout the sediment profile, then it can be concluded that redox conditions have remained at constant levels.

When an anoxic hypolimnion develops, a significant decrease in sedimentary manganese can be observed in the manganese profile (Mackereth 1966). Loss of manganese from lake sediment by diffusion and its subsequent washout at overturn is indicated by a decrease in sediment concentration and reflects the onset of eutrophication (Anderson and Rippey 1988). The position of the marked fall in the manganese concentration-depth profile indicates the development of the anoxic hypolimnion and eutrophic conditions (Mackereth 1966). The drop in sedimentary manganese concentration is an indicator of redox related cycling (Anderson and Rippey 1988). This release of manganese causes the Fe:Mn to increase. Therefore, increasing Fe:Mn can indicate a change from oxidizing to reducing environments (Cole 1975). If a peak in the Fe:Mn correlates with a minima in the iron concentration, then its caused by changes in the hypolimnetic redox conditions (Engstrom and Wright 1984).

Maximum oxidation results in the correspondence of a iron maxima with a Fe:Mn minima which is preceded and followed by a Fe:Mn maxima (Mackereth 1966). The final stages of anoxia are characterized by increased iron and sulfide content in the sediment and an increased Fe:Mn (Engstrom and Wright 1984). However, overturn of many eutrophic lakes terminates stratification before this stage occurs (Cole 1975).

If watershed soils are reduced and the hypolimnion is anoxic, the sedimentary manganese concentration will be low and Fe:Mn will be high (Mackereth 1966).

The Fe:Mn may vary spatially due to the greater solubility of manganese. The Fe:Mn decreases with distance from a source such as a river. However, such variations are minor relative to changes in overall inputs and preservation.

Post-depositional migration below the redoxcline may alter the initial Fe:Mn and result in poor correspondence between the Fe:Mn and other evidence for hypolimnetic oxygen conditions (Engstrom and Wright 1984). Mechanical disturbance of sediments can also alter original sediment profiles (Mackereth 1966). Because several factors control the flux of iron and manganese from the sediments, interpretation of profiles for paleolimnological purposes should be done with caution, and supporting evidence should be used when possible (Engstrom and Wright 1984).

Cycling of Zinc, Molybdenum, and Copper

While redox is significant in iron and manganese cycling, living organisms are chiefly responsible for the cycling of zinc, copper, and molybdenum. Whereas iron and manganese are easily released from anoxic sediment, zinc, molybdenum, and copper are less mobile (Goldman and Horne 1983). The cycling of zinc, copper, and molybdenum is primarily controlled by uptake by organisms and subsequent release by decay from the sediments (Mackereth 1966, Goldman and Horne 1983).

In most lakes, zinc is supplied by anthropogenic sources and the flow of trace element loaded sediment caused by erosion (Goldman and Horne 1983). Acid rain can also result in high rates of leaching of zinc from poorly buffered soils (Wetzel 1983).

In freshwater, zinc is present in the following forms: in its ionic form as a divalent cation; bound to siliceous matter, iron oxyhydroxides, diatoms, and sulfate; complexed in organic materials; absorbed on solids; and incorporated in crystalline structures (Wetzel 1983, Vuorinen et al. 1986). Most zinc is transported as crystalline solids or absorbed on solids with little zinc present in its ionic form (Wetzel 1983). In basic waters, zinc is primarily absorbed on colloidal particles. High zinc concentrations are associated with low pH. In acidic waters, approximately 50% of the zinc is present in its noncolloidal inorganic form (Nriagu 1980).

During summer stratification, algal uptake and sedimenting detritus are important in the cycling of zinc (Wetzel 1983). Zinc is also removed from water by precipitation with clay, hydrous iron and manganese oxides, and calcium carbonate (Mackereth 1966, Cole 1975, Nriagu 1980). The zinc bound to biomass or manganese oxides is then transported to the sediments (Kuhn et al. 1994). Zinc is insoluble in oxidized states and in intensely reducing environments where sulfides are formed (Cole 1975). Zinc also precipitates at high alkalinities (Nriagu 1980). Sulfide increases the precipitation and sedimentation rate of zinc (Cole 1975, Kuhn et al. 1994).

Sedimentary zinc concentrations are indirectly influenced by redox conditions, because anoxic conditions favor its retention. Zinc is generally efficiently retained by sediments (Mackereth 1966, Kuhn et al. 1994). In reducing sediments, zinc is held as an insoluble sulfide (Mackereth 1966). Degradation of sedimentary organic detritus is the primary source of hypolimnetic zinc (Wetzel 1983).

Molybdenum occurs in seven stable and five radioactive isotopes. The molybdenum cycle is similar to iron's. Because molybdenum is a micronutrient, it is concentrated in plankton and eventually carried to the sediments. Molybdenum concentrations in water are generally low while the sediments are oxidized. However, during summer thermal stratification, molybdenum may accumulate in the hypolimnion. Molybdenum is most abundant in water when phosphorous is released from the sediments. However, molybdenum concentrations decrease when $Fe(OH)_3$ and FeS precipitate (Cole 1975).

Copper exists in ionic, organic, and sestonic forms in water. Most copper is associated with colloidal organic matter. In aquatic systems, copper is virtually immobile. Copper uptake by plants and its subsequent release from decaying plants is responsible for most of its cycling (Hutchinson 1957).

Copper is insoluble in oxic environments and intensely reducing environments where sulfides are formed (Cole 1975). At normal pH, most copper is lost from solution by precipitation, sorption, or chelation by organic matter (Goldman and Horne 1983). Copper also coprecipitates with iron and manganese (Mackereth 1966).

Once in the sediment, copper is firmly bound by sulfides (Mackereth 1966, Vuorinen et al. 1986) and organic matter (Vuorinen et al. 1986). Some copper is released under anoxic conditions from the sediments by dissolution of ferromanganese oxides and hydroxides, and organic degradation. However, copper is usually not released in appreciable amounts indicating that diagenetic remobilization is negligible (Sakata 1985). Bacterial decomposition of organic matter is primarily responsible for the release of copper. Increasing copper concentrations near the bottom may be observed because of the decomposition of copper containing seston or diffusion of copper containing organic compounds from the sediments. When the surface sediments are reduced, copper is generally present as CuS and immobile. Copper is more mobile when oxidizing conditions are present (Hutchinson 1957).

Copper, Molybdenum, and Zinc as Paleoredox Indicators

After sedimentation, debris is attacked by chemical and biochemical processes. However, these processes differ depending on redox conditions. Reducing environments created in the absence of oxygen are characterized by hydrogen sulfide (H_2S) production. Hydrogen sulfide causes metals to precipitate in quantities dependent on their sulfide solubility product. Therefore, sulfide solubility products are important for metal precipitation in reducing environments.

In sediments, microbial decomposition produces intermediate compounds which act as metal chelators. As a result, competition occurs between H_2S and the chelating compounds for metals. However, chelating ability differs for different metals. Chelated metals can not be trapped in the sediment and fixed as sulfides. Thus, metals are generally either fixed in the sediment as sulfides, or in solution as metal chelates.

Chelated metals are located above the redoxcline, and sulfides are located below. If the redoxcline is above the sediment surface, the metal chelates are released from the sediment. Conversely, little metal is released when the redoxcline is in the sediment. Metal sulfides are stable and remain in the sediment.

Differences between copper and zinc concentrations in oxic environments is primarily a factor of chelating ability (Hallberg 1972). In oxic environments, changes from oxic to anoxic conditions during diagenesis in the sediment leads to copper chelation and higher mobility of copper than zinc (Frevert and Sollmann 1987). Copper has a higher chelating ability than zinc and is not as readily fixed as a sulfide in the sediments relative to zinc when the redoxcline is below the sediment surface (oxic environment). Copper has a greater tendency to chelate than to form a sulfide in oxic sediments. Zinc is fixed in oxic sediments and chelating compounds have little effect on its sedimentary concentrations.

If copper is precipitated directly as a sulfide in a reducing environment, it may become more enriched in the sediment than if it is precipitated in an oxic environment. This is due to CuS being less soluble than oxidized or chelated copper (Hallberg 1972). The formation of copper sulfides is more favored than zinc sulfide formation in reducing environments. Therefore, Cu/Zn decreases under oxidizing conditions and increases under reducing conditions (Hallberg 1972, Frevert and Sollmann 1987).

The paleoredox variable $R = Cu/Zn$ was later expanded to $RP = (Cu+Mo)/Zn$ by Hallberg. Molybdenum, like copper, is more abundant in the sediment in strictly reducing environments. However, copper is generally high in areas which are chemically reduced, while molybdenum is generally high in areas with high H_2S levels.

The paleoredox variable RP is also applicable to lakes which experience seasonal anoxia if copper and zinc inputs are similar and constant, sedimentation rate is greater than or equal to the penetration of dissolved oxygen into the sediment, no resuspension of sediment occurs, sulfate is sufficient for microbial hydrogen sulfide reduction, and chelating mobilization of copper is negligible.

In Lake Kinneret, RP indicated the length of reducing and oxidizing periods in the hypolimnion during seasonal anoxia. Periods of increasing oxygen (shorter periods of anoxia) resulted in lower RP values. In contrast, periods of decreasing oxygen (longer periods of anoxia) resulted in a higher RP variable. Therefore, RP may provide a useful indicator of the relative duration of annual reducing and oxidizing periods if the five assumptions are true (Frevert and Sollmann 1987).

Pristane:Phytane as Paleoredox Indicators

Terpenoid hydrocarbons, also known as isoprenoid hydrocarbons, are some of the most ubiquitous natural products (Blumer and Snyder 1965) and have attracted much attention from petroleum chemists since pristane was first isolated by Bendoraitis and others in 1962 (Trusell 1979). Isoprenoid hydrocarbons, such as phytane (2,6,10,14-tetramethylhexadecane) and pristane (2,6,10,14-tetramethylpentadecane), are naturally occurring compounds considered to be derived from the isoprene (2-methyl-1, 3-butadiene) molecule (Adlard 1979). Pristane and phytane are considered to originate from phytol the esterified side-chain of chlorophyll a (Didyk et al. 1978).

Pristane occurs in some terrestrial plants and animals and is also abundant in marine copepods which derive pristane from phytol in their food (Blumer and Snyder 1965). Both pristane and phytane are found in crude oil, oil shale, coal, and ancient sediments (Blumer and Snyder 1965, Brooks et al. 1969, Powell and McKirdy 1973).

In recent sediments, pristane alone is generally found suggesting that phytane is a post-depositional product (Blumer and Snyder 1965, Brooks et al. 1969). Phytane is likely formed by conversion of sedimentary phytol, which is too slow to generate detectable quantities of phytane in the uppermost sediments (Blumer and Snyder 1965).

Pristane appears at the brown coal stage of diagenesis suggesting that isoprenoid hydrocarbons could be derived from esters or by similar reaction routes. Because pristane is always the major isoprenoid hydrocarbon in coal extracts or in artificial diagenesis, phytol cannot be the principal precursor. The dominance of pristane suggests that it is formed by the decarboxylation of a C_{20} isoprenoid acid, such as phytanic acid (Brooks et al. 1969, Powell and McKirdy 1973). Phytane is formed by dehydration and hydrogenation of phytol (Powell and McKirdy 1973). Phytanic acid (precursor of pristane) formation is less likely in the more anaerobic conditions of aquatic environments than it is in the more aerobic conditions on land during the decay of plant material. Therefore, a pristane:phytane ratio (Pr:Ph) may reflect the amount of oxygen present during the early stages of chlorophyll decomposition, with a low Pr:Ph indicating origination from an aquatic environment and a high Pr:Ph indicating land plant origin (Brooks et al. 1969, Powell and McKirdy 1973).

Pristane and phytane can be useful in paleoredox determinations, because they resist diagenesis and their abundance patterns often reflect the conditions of the environment in which they were deposited (Didyk et al. 1978). The relative abundance of pristane and phytane depend on the redox conditions and the acidity of the environment in which they are formed. Phytane is the principle product during anoxic conditions, while pristane is the main product during oxic conditions (Wakeham 1993).

The Pr:Ph of sediment can reflect paleo-environmental conditions. Sediment deposited during anoxic conditions has low Pr:Ph values. Sediment deposited during alternating anoxic/oxic conditions has Pr:Ph values near 1. Oxic conditions produce sediment Pr:Ph values greater than 1 (Didyk et al. 1978).

Several organic geochemistry studies and geological constraints suggest that the Pr:Ph is not a valid indicator of paleoredox conditions (ten Haven et al. 1987).

1. Terpenoid hydrocarbons are among the most ubiquitous natural products and reenter the present-day environment from petroleum and derived products (Blumer and Snyder 1965, ten Haven et al. 1987).
2. Partly decomposed terrestrial matter washed into lakes skew results, because early decomposition occurred in an oxic environment (Brooks et al. 1969).
3. Archaebacterial lipids and pristane originating from tocopherols can provide additional sources of these isoprenoids.
4. Pristane and pristenes have been detected in zooplankton.
5. An analytical problem of precise determination of Pr:Ph arises from the identification of 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane in sediments, which coelutes with pristane on most capillary columns. This raises doubt about the validity of Pr:Ph previously published.
6. All sediments are anoxic below a surface oxic layer.
7. Extraction of organic rich sediments from the eastern Mediterranean revealed that most phytol (>95%) was present in an esterified form, while

pristane and phytane were absent or present in low concentrations. When phytol eventually degrades in sediments, it takes place under reducing conditions, giving rise to low Pr:Ph. Therefore, Pr:Ph reflects the result of reactions taking place well after reducing conditions have been established, not the oxicity of the environment of deposition.

It is virtually impossible to draw valid conclusions from Pr:Ph with respect to the oxicity of the environment of deposition (ten Haven et al. 1987).

Calcium as a Paleolimnological Indicator

Calcium is generally considered an essential nutrient for most algae (Cole 1975, Wetzel 1983, Goldman and Horne 1983). However, in aquatic environments it is rarely deficient, because typical inland waters are basically a solution of $CaCO_3$. Calcium is abundant in the earth's crust. Calcium carbonate is found in nature as calcite and aragonite. Calcium carbonate is also abundant in soils; however, it is only weakly soluble (Cole 1975). Other sources of calcium are gypsum, dolomite, anhydrite, fluorite, plagioclase, paraoxon, and amphibole (Hounslow 1993). Calcium carbonate is generally insoluble in water, except in the presence of acid (specifically carbonic acid), where it becomes $Ca(HCO_3)_2$ (Cole 1975). Calcium bicarbonate is relatively soluble in water (Wetzel 1983).

Calcium is present in aquatic systems as suspended particulates (mainly $CaCO_3$) and in its ionic form. Calcium levels, bicarbonate, pH, and conductivity are all correlated in lake water (Goldman and Horne 1983). In many lakes, specific conductance follows changes in Ca^{2+} and HCO_3^- concentrations in lake water (Wetzel 1983). Calcium carbonate solubility is also temperature dependent and decreases as temperature rises from O° to 35° C (Cole 1975). The concentration of calcium in lakes is primarily controlled by precipitation of $CaCO_3$ during photosynthesis and the solution of calcium by rainwater in the watershed (Goldman and Horne 1983).

The most common sinks for calcium in aquatic systems are as calcite and gypsum (Hounslow 1993). If CO_2 is removed from a solution where $Ca(HCO_3)_2$, CO_2, H_2CO_3, and CO_3 are in equilibrium, $CaCO_3$ will precipitate until equilibrium is reestablished. The general equation (Wetzel 1983) for this process is the following:

$$Ca(HCO_3)_2 <\text{---}> CaCO_3 + H_2O + CO_2$$

Loss of CO_2 results in massive precipitation of calcium carbonate (Cole 1975, Wetzel 1983). The rate of calcium carbonate precipitation is slow unless induced by metabolic reactions, such as photosynthesis (Wetzel 1983). Photosynthetic organisms trigger this precipitation by absorbing CO_2 (Cole 1975, Goldman and Horne 1983). Plant cells serve as centers for the formation of particulate calcium carbonate (Wetzel 1983). The reaction to $CaCO_3$ is basically irreversible in lakes, because carbonic acid is generally lost soon after CO_2 uptake by plants (Goldman and Horne 1983).

During photosynthesis, large amounts of calcium carbonate are precipitated by algae and macrophytes. Decreasing epilimnetic and metalimnetic calcium concentrations have been directly related to increased photosynthetic utilization of CO_2. The precipitation of $CaCO_3$ is also responsible for the removal of nutrients from the water column, because phosphates coprecipitate with carbonates (Wetzel 1983).

Calcium is also abundantly sedimented during intense erosion. However, in productive lakes, calcium is associated more with organic matter than erosion products, except for during periods of intense erosion (Mackereth 1966).

Carbon dioxide released from decaying organic matter may hinder $CaCO_3$ deposition (Cole 1975). Some of the precipitating $CaCO_3$ moving through the hypolimnion is resolubilized; however, most is permanently fixed in the sediments. Under oxic conditions, Ca^{2+} is incorporated into the sediments. Association with organic detritus also reduces the dissolution rate of sedimenting $CaCO_3$ allowing it to become incorporated permanently into the sediments. However, when the hypolimnion becomes anoxic, some Ca^{2+} is released from the sediments (Wetzel 1983).

Calcium concentrations generally followed carbonate concentrations in a sediment profile from Lake Isle indicating that most calcium was deposited as calcium carbonate (Hickman and Klarer 1981). Sedimentary calcium concentrations are also closely associated with organic matter (Mackereth 1966, Flannery et al. 1982). High calcium concentrations in surface sediments were observed in Florida lakes with high TSI values. This sedimentary calcium enrichment was attributed to increased biogenic calcium sedimentation resulting from increased primary productivity (Flannery et al. 1982). Therefore, stratigraphical analysis of calcium concentration-depth profiles should provide an accurate assessment of historical productivity, because increased biological productivity generally results in increased $CaCO_3$ concentrations in the sediments (Hickman and Klarer 1981).

Phosphorous as a Paleolimnological Indicator

Phosphorous is an essential nutrient (Cole 1975), therefore, a close relation exists between its concentration and primary productivity (Engstrom and Wright 1984). Because of this, it has been used to predict algal biomass and trophic state. Phosphorous has been used to predict trophic state by Carlson (1977), Vollenweider (1968), the EPA (1974), and many others. Hakanson (1984) used sedimentary nitrogen, phosphorous, carbon, and loss on ignition to indicate trophic state (Leach and Herron 1992). Phosphorous may also provide a possible indicator of paleo-productivity. However, deviations are possible due to limnological factors controlling phosphorous incorporation in the sediments (Engstrom and Wright 1984).

Igneous rock was the original source of phosphorous. However, now it is mined and used extensively by industry and agricultural (Cole 1975). Most phosphorous in fresh water is bound in organic phosphates, cellular constituents of organisms, and adsorbed to organic colloids. Orthophosphate, which is directly used by organisms, is generally present in small concentrations due to rapid uptake and sedimentation (Wetzel 1983).

Phosphorous is sedimented by biological uptake and subsequent deposition (Mackereth 1966, Cole 1975, Engstrom and Wright 1984), sorption by humic complexes and iron oxides (Mackereth 1966, Engstrom and Wright 1984), precipitation as iron phosphates, and coprecipitation with carbonates (Engstrom and Wright 1984) and calcium (Cole 1975, Goldman and Horne 1983). Dissolved phosphorous is removed from the water so rapidly that generally the water is depleted and the sediment is enriched with phosphorous (Engstrom and Wright 1984).

Sedimenting organic phosphorous is incorporated into the sediments or degraded in the hypolimnion or surface sediment by microbes and released as orthophosphate or soluble organic compounds (Cole 1975, Engstrom and Wright 1984).

The sedimentary phosphorous concentration depends on rate of supply, efficiency of precipitation mechanisms (biological and chemical), sedimentation rate, and rate of loss from sediment. Biological precipitation of phosphorous, which operates only part of the year, is inefficient compared to the more continuous coprecipitation of phosphorous with iron and manganese. However, high efficiency of phosphorous sedimentation is achieved by the combined mechanisms of biological precipitation and coprecipitation with iron and manganese (Mackereth 1966).

Sediments provide an effective sink for phosphorous (Engstrom and Wright 1984). In oligotrophic lakes, where productivity and nutrients are low and hypolimnetic dissolved oxygen is high, most phosphorous is permanently buried in the sediments (Gachter and Meyer 1990). This is because phosphorous is efficiently retained in oxidized sediments (Engstrom and Wright 1984). However, when the sediment surface becomes anoxic, phosphorous is released leading to accelerated eutrophication (Mackereth 1966, Cole 1975, Wetzel 1983, Engstrom and Wright 1984, Gachter and Meyer 1990).

Phosphorous is fixed in the sediments primarily by sorption to hydrated ferric oxides or complexation with organics. Variations in iron content and redox influence phosphorous concentrations in the sediment (Engstrom and Wright 1984). When iron is lost from the sediment, phosphorous is also lost (Mackereth 1966). Therefore, changes in phosphorous retention may be responsible for sediment stratigraphy. Because of this, interpretation of past trophic state is possible only if redox remains constant over time. If redox is not constant, then sedimentary phosphorous concentrations may not reflect the actual phosphorous deposition. Although sedimentary phosphorous is generally uncorrelated with measures of lake productivity, several studies found good agreement between sedimentary phosphorous and historic trophic development (Engstrom and Wright 1984). High phosphorous indicated high organic material and high productivity (high TSI) in the deep water sediments of Florida lakes. Phosphorous abundance was unrelated to iron ($r^2=0.024$). Therefore, biogenic sedimentation was considered the main process for the phosphorous sedimentation (Flannery et al. 1982).

If iron and other sedimentological conditions remain constant, changing phosphorous levels may be preserved in the sediments. However, comparisons of sedimentary phosphorous trends with historical phosphorous loading data is beneficial (Engstrom and Wright 1984).

Sodium as an Indicator of Erosion

Sodium is the sixth most abundant element. When leached from rocks, it stays in solution because it is reactive and soluble. Thus, it is at least the third most abundant element in lakes and streams (Cole 1975). The main sodium sources are halite, silicates, and natural ion exchange. The only common sink for sodium is reverse ion exchange which occurs only in highly saline waters (Hounslow 1993).

Sodium is conservative in aquatic systems. In most lakes, sodium is uniformally distributed throughout and experiences only small seasonal fluctuations (Wetzel 1983). Sodium is also unaffected by redox conditions (Moore 1994).

Sodium provides a geochemical indicator of erosion (Anderson and Rippey 1988). Sodium is generally associated with the mineral fraction of the sediment (Mackereth 1966, Vuorinen et al. 1986). Variations in the sediment mineral content are primarily brought about by variations in erosion. Therefore, variations in sodium should represent erosion intensity, because when erosion occurs, unweathered minerals carrying sodium are transported to the lake and sedimented. Because these minerals and their components are rarely altered in aquatic systems, their distribution in sediments is useful for assessing weathering and erosion in the watershed. In contrast, dissolved sodium from areas which are not actively eroding is not appreciably sedimented (Engstrom and Wright 1984). Therefore, increasing sodium concentrations in sediment profiles indicate decreasing soil stabilization and increasing erosion (Sekar et al. 1992) and declining sodium concentrations indicate soil stabilization and decreased erosion (Hickman and Klarer 1981, Sekar et al. 1992). However, dilution of minerals in sediment by organic matter can be responsible for sodium trends instead of erosion (Engstrom and Wright 1984).

Cesium-137 Dating

Cesium-137 has been present in the atmosphere since 1954 due to atomic bomb testing (Engstrom and Wright 1984). Between 1958 and 1967, nuclear testing created significant quantities of cesium-137 which was deposited as fallout. The annual deposition of cesium-137 follows the frequency of the nuclear testing. The maximum deposition of cesium-137 occurred in the northern hemisphere between 30° and 60° latitude. The peak fallout rate occurred between 1962 and 1964. Cesium-137 was distributed throughout the northern hemisphere after atmospheric testing and is now used to estimate the age of sediments deposited since 1958 within plus or minus 2 years (Vuorinen et al. 1986).

The method assumes that cesium-137 fallout with rain becomes attached to particles which are quickly (<1 year) transported from the drainage basin to lake sediments. Cesium-137 falling directly upon the lake surface is adsorbed onto suspended particulate matter and sedimented. It is also assumed that disturbance of the sediment stratigraphy is small. In some cases, disturbance by water movements and redistribution of sediments by benthic macroinvertebrates can obscure dating chronology. However, careful interpretation of cesium-137 dating results, combined with other paleolimnological data, provides much insight into the reconstruction of recent lake events (Wetzel 1983).

CHAPTER III

MATERIALS AND METHODS

Study Site

Lake Tenkiller is located on the Illinois River in Cherokee and Sequoyah counties approximately 16 km south of Tahlequah and 88 km southeast of Tulsa, Oklahoma. The reservoir, which receives drainage from the Illinois River basin, has been recognized as one of the clearest lakes in Oklahoma since its impoundment in 1953. However, data indicate eutrophication of the lake, decreasing water clarity, and development of an anoxic hypolimnion during summer thermal stratification. Between 1975 and 1985, phosphorous and chlorophyll a concentrations increased 2 to 3 fold, while secchi disc transparency decreased 25 percent (Nolen 1988). Presently, trophic status ranges from eutrophic in its headwaters to mesotrophic at the dam.

The dam is located on the Illinois River at Section 14, T13N, R21E, in Sequoyah County. Table 1 lists the morphological characteristics of Lake Tenkiller. Lake Tenkiller was built to provide flood control, hydroelectric power, water supply, and recreation. The major tributaries to Lake Tenkiller are the Illinois River, Barren Fork, Muddy Fork, Osage Creek, Flint Creek, and Caney Creek (OWRB 1984).

Table 1. Morphological characteristics of Lake Tenkiller

Parameter	Units
Shoreline	209 km
Drainage Area	4170 km^2
Shoreline Development	8.2
Mean Depth	15 m
Maximum Depth	46 m

Station 5 of the EPA Phase I Clean Lakes project (Figure 1) was located at 35° 43.57 minutes North, 94° 57.21 minutes West, at an altitude of 242 m. The samples were taken in 21.6 m of water. High chlorophyll density has been observed in this area and eutrophication is pronounced. The sediments are always located below the thermocline. It correlates with a preexisting sampling station; therefore, historical data can be referenced. It is not influenced dramatically by conditions of the Illinois River.

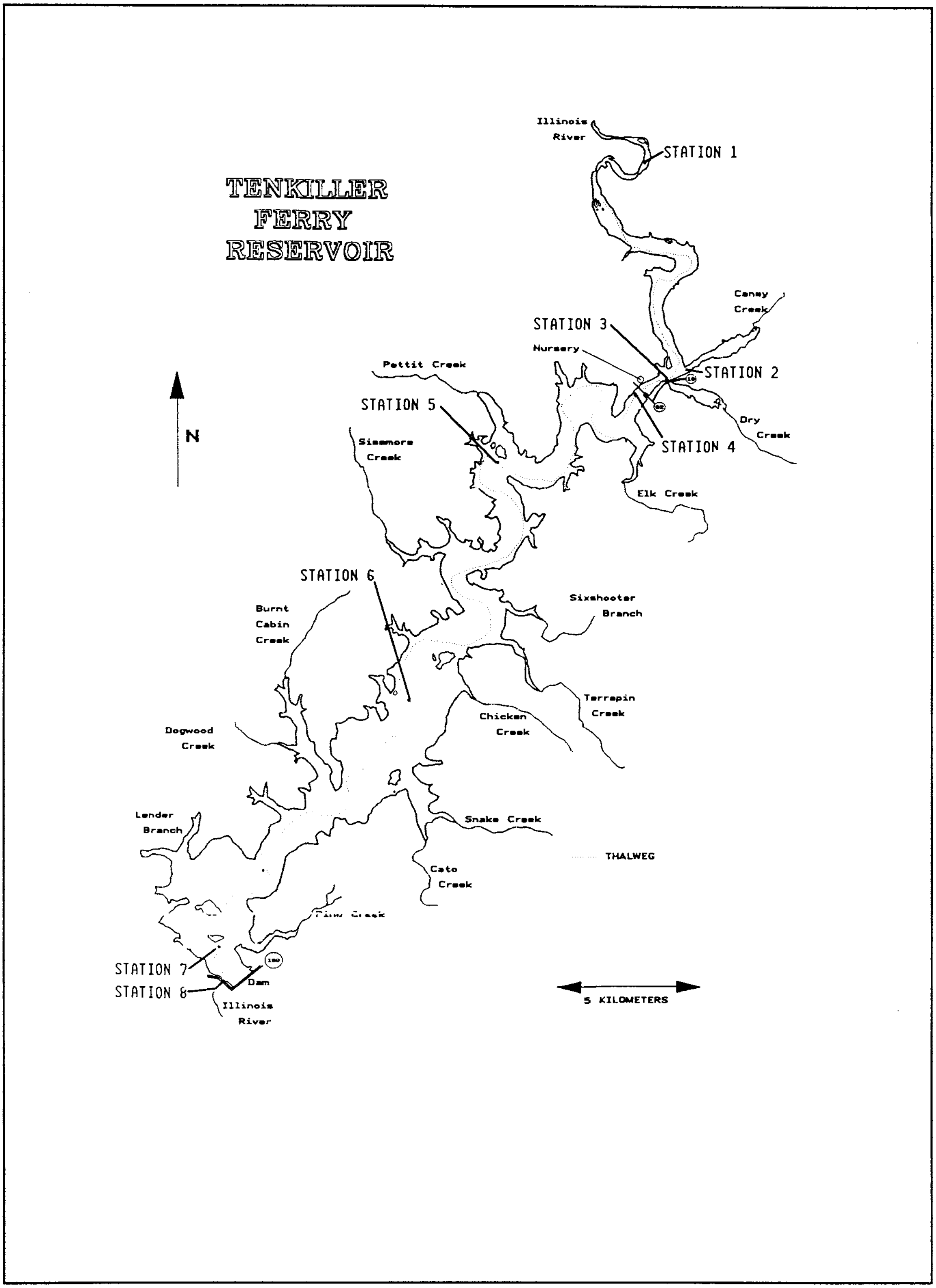
Review of Historical Data

Historical data from USGS were reviewed to determine historical discharge to Lake Tenkiller. The National Eutrophication Survey and other limnological studies on Lake Tenkiller were also reviewed to determine the historic trophic state and hypolimnetic oxygen conditions of the lake.

Limnological Methods

At Station 5, dissolved oxygen, temperature, conductivity, and pH, were measured *in situ*. Dissolved oxygen and temperature profiles were determined using a

Figure 1. Map of Lake Tenkiller and Phase I Clean Lakes Project sampling stations, 1992-93



YSI Dissolved Oxygen/Temperature meter. Conductivity profiles were determined using a YSI Combination Salinity-Conductivity-Temperature meter. The pH was determined using an Orion pH meter in samples collected at 0.5 m from the surface and bottom using a van Dorm sampler.

Metals Analyses (Water)

Metals were analyzed in the water on 4 June 1992, 18 April 1993, 26 May 1993, and 19 August 1993. The samples (100 ml) were collected at 0.5 m from the surface and 0.5 m from the bottom using a van Dorm sampler. The water samples were then acidified with 3 ml of concentrated nitric acid and returned to the lab. In the lab, the water samples were digested and then refluxed with concentrated nitric acid. Finally, the samples were decanted into a 100 ml graduated flask and diluted to 100 ml with Type II water (EPA 1987). Metals were analyzed with a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer using the settings listed in Table 2. Metals concentrations (mg/l) were then determined from a standard curve.

Table 2. Atomic absorption spectrophotometer settings for analysis of metals from Lake Tenkiller water

Metal	Wavelength	Slit Width	FAA or HGA
Iron	248.3	0.2 High	FAA
Manganese	279.5	0.2 Low	HGA
Copper	324.8	0.7 Low	HGA
Zinc	213.9	0.7 High	FAA
Calcium	422.7	0.7 High	FAA

Sediment Collection and Preservation

Sampling was completed on 18 October 1993. Sediment cores were collected using a Ballchek sediment corer holding liner tubes two inches in diameter and thirty inches long. The liner tubes containing the sediment were removed from the corer after each sampling and were capped on both ends. The capped liner tubes were stored in an upright position and kept cool until returned to the lab. Upon arrival at the lab, the liner tubes containing the sediments were drained of excess water and frozen until analysis. Before analysis the sediment cores were sectioned while frozen. The top 10 cm of the sediment core was cut into 1 cm sections, and the rest was cut into 2.5 cm sections. Each section was then placed in a labeled glass sample bottle for storage until analysis. Each section was allowed to melt and then was mixed thoroughly before subsamples were taken for the individual digestions and analyses.

Metals Analyses (Sediment)

The tare weight of beakers were obtained by drying and weighing until two consistent weights were recorded. Three 1 to 2 g (wet weight) subsamples were then taken from each section of the sediment core and placed into the tared beakers. The samples were then dried until two consistent weights were recorded. The dry weight of the sample was determined by subtracting the weight of the tared beaker from the weight of the dried sample and beaker.

Sediment samples were prepared for metals analyses using the digestion procedure described in EPA Method 3050. The sediment samples were digested in nitric acid and hydrogen peroxide. The digestates were then refluxed with hydrochloric acid. Finally, the samples were decanted into 100 ml graduated flasks and diluted to 100 ml with Type II water (EPA 1986). Metals were analyzed with a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer using the settings listed in Table 3. Metal concentrations (mg/l) were then determined from a standard curve. These concentrations (mg/l) were then converted to mg/g of dried sediment.

Table 3. Atomic absorption spectrophotometer settings for analyses of metals from Lake Tenkiller sediment

Metal	Wavelength	Slit Width	FAA or HGA
Iron	248.3	0.2 High	FAA
Manganese	279.5	0.2 High	FAA
Copper	324.8	0.7 Low	HGA
Molybdenum	313.3	0.7 Low	HGA
Zinc	213.9	0.7 High	FAA
Calcium	422.7	0.7 High	FAA
Sodium	589.0	0.4 High	FAA

Sedimentary Phosphorous Analysis

After the sediment cores were sectioned and thawed, they were mixed thoroughly. An aliquot of mixed sediment was taken from each section and dried. After the sediment was dried, duplicate subsamples weighing between 0.0123 and 0.03924 g were taken from each section and placed into 250 ml Erlenmeyer flasks. To each subsample, 50 ml of water and 8 ml of 5% potassium persulfate were added. The samples were then capped with aluminum foil and digested in an autoclave at 15 psi for 30 min at 121°C. Then, 8 ml of mixed reagent were added to each digested sample.

After 10 min, the absorbance of each sample was measured at 880 and 690 nm in a spectrophotometer. The phosphorous concentrations (mg/l) were then determined from a standard phosphorous calibration curve (Lind 1985). These concentrations (mg/l) were then converted to mg/g of oven dried sediment.

Sediment Dating

Sediment cores were also collected by the USDA on October 18, 1993 for use in dating of the sediments. The sediment cores were dated in conjunction with the USDA-ARS lab in Durant, Oklahoma using the cesium-137 dating method. The sediment cores were divided into 5 cm sections beginning at the sediment surface. Core sections of like depth were composited and placed into labeled plastic bags for transporting to the laboratory. In the laboratory, sediment samples were oven dried at 105°C and then ground with a mortar and pestle until they passed a 6 mm screen. Samples were then analyzed for cesium-137 with a multichannel analyzer using a lithium-drifted germanium detector (McHenry et al. 1980). Cesium-137 activity from each sample was counted twice and then averaged.

Quality Assurance

Accuracy was assessed by using EPA reference standards and percent recoveries. A universal blank matrix does not exist for solid samples; therefore, no matrix blank was used (EPA 1987). A duplicate sample from each batch of samples was spiked with a predetermined quantity of stock solution prior to digestion and analyzed. Percent recoveries, calculated from these spikes, were used to determine accuracy and matrix effects. Precision was assessed by analyzing triplicate samples. The standard deviations of the triplicates were used to determine precision (Horowitz 1991). Standard curves were used to determine the concentrations of the samples. The standard curves were verified using an initial calibration verification standard (an EPA reference standard) before analysis of any samples. After initial verification, one EPA reference standard was run for every ten samples and if results were beyond the EPA predetermined acceptable limits, corrective action was taken. All important dates, such as collection, digestion, and analysis dates, were documented. Holding times were no longer than 6 months after digestion (EPA 1987).

Data Analysis

The concentrations at each depth were averaged. In addition, standard deviations were determined for each depth. The raw data, averages, and standard deviations for all parameters measured can be found in the Appendixes. Depths were converted to years using the sedimentation rate of 1.9 cm/year. Concentration-year profiles were then produced and analyzed to determine paleolimnological significance. Large shifts in the chemical concentrations of each element's profile were interpreted to determine its paleolimnological significance. Standard deviations of the average concentrations at each depth were used to determine if changes in the chemical concentrations were significant.

Correlation coefficients among each sedimentary trace element profile were also determined. The significance of the correlations were determined using the following test statistic:

$$t\ calc = r/[(1-r^2)/(n-2)]^{0.5} \qquad df = n-2 \qquad \alpha = 0.01$$

Correlation coefficients greater than or equal to 0.48 were found to be significant (Steel and Torrie 1960).

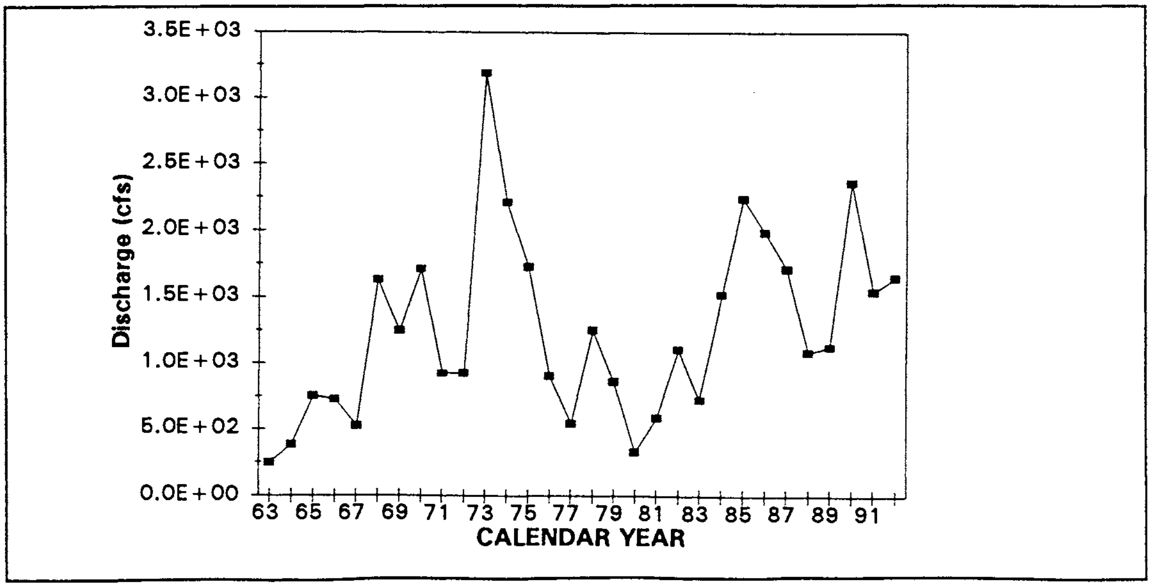
CHAPTER IV

RESULTS AND DISCUSSION

Historical Conditions of the Basin

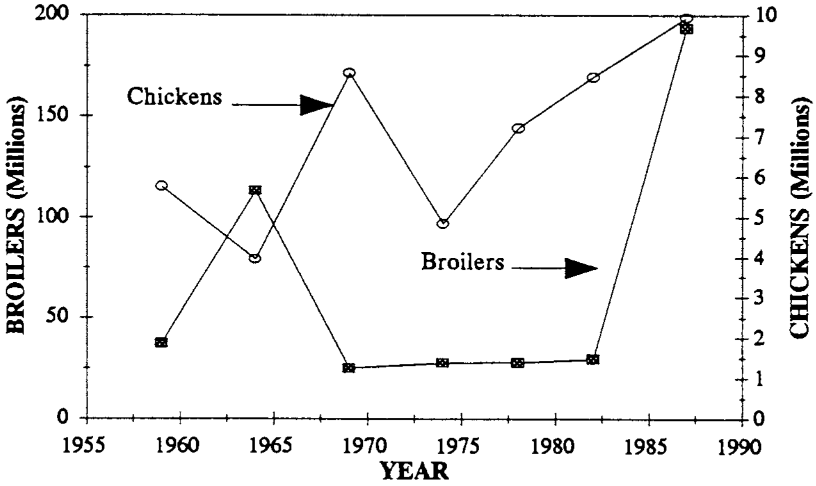
The combined mean daily discharge from the Illinois River (USGS Station 07196500) and Baron Fork (USGS Station 07197000) averaged 1257 cubic feet per second (cfs) (standard deviation 695 cfs). Above average flows (Figure 2) occurred from 1973-74, 1985-86, and 1990. Below average flows occurred from 1963-64, 1967, 1977, and 1980-81 (USGS 1965-1993). An upward trend in discharge has occurred (Gade 1990).

Figure 2. Mean daily discharge from 1963-92 based on the combined discharge of the Baron Fork (07197000) and the Illinois River (07196500)



This area of Oklahoma has experienced major growth in agriculture. The number of chickens raised in the Illinois River Basin (Figure 3) peaked in the late 1960s and has increased since the mid-1970s. The number of broilers in the basin (Figure 3) peaked in the mid-1960s and has experienced phenomenal growth since the early-1980s.

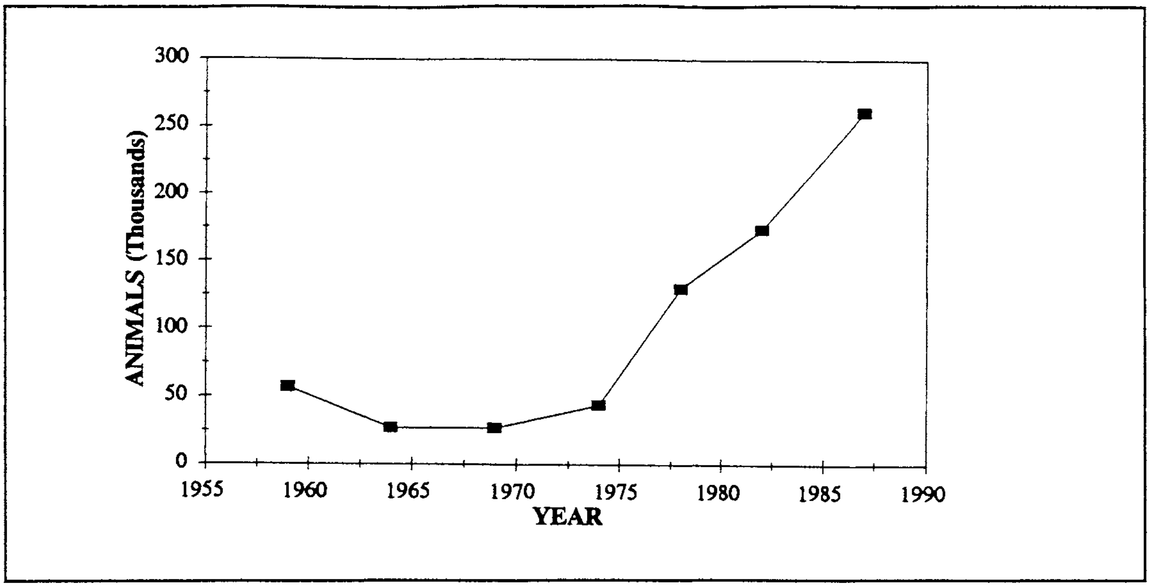
Figure 3. Number of broilers and three month old or older chickens in the Illinois River Basin



The number of hogs (Figure 4) raised in the Illinois River Basin has increased continuously since the mid-1970s. These growing industries have surely impacted Lake Tenkiller due to the additional nutrient sources present in the basin.

Nutrient levels in the Illinois River have increased with time. This increase in nutrient loading to Lake Tenkiller resulted in an increasing rate of eutrophication (Gade 1990).

Figure 4. Number of hogs in the Illinois River Basin



Historical Conditions of the Lake

Numerous studies have been conducted on Lake Tenkiller since its impoundment began in 1952. Jenkins (1953) studied fish of Lake Tenkiller during its first year of impoundment. Temperature and dissolved oxygen profiles were measured. A thermocline was present at the dam at a depth of 6 to 12 m throughout the summer. Dissolved oxygen was negligible below the thermocline. Dissolved oxygen ranged from 8.1 mg/l at the surface to zero at the bottom. Dissolved oxygen was generally less than 1.5 mg/l below 11 m. The thermocline at Standing Rock Bridge (near the Phase I study's station 4) was present at a depth of 6 to 9 m (Jenkins 1953). Finnell (1953) also studied Lake Tenkiller from 16 June to 22 July 1953 to determine if its tailwaters provided suitable temperatures and dissolved oxygen concentrations to sustain a rainbow trout fishery. Dissolved oxygen levels at the dam were generally less than 1.5 mg/l below 11 m and were zero at the bottom. The dissolved oxygen concentration at the bottom of Station II (near Phase I study's station 4) was 1.2 mg/l (Finnell 1953). However, the cause of hypolimnetic anoxia was not determined. Hypolimnetic anoxia often occurs in newly constructed reservoirs due to the decomposition of the terrestrial biomass left in the lake. This could have resulted in the clinograde oxygen profile.

From February 1960 to January 1961, the Oklahoma Department of Wildlife Conservation (ODWC) studied Lake Tenkiller to determine the success of walleye stocking proposed for the spring of 1961. The lake was thermally stratified during summer. During stratification, hypolimnetic dissolved oxygen concentrations ranged from zero to 3.5 mg/l. The trophic state was not determined (Summers 1961).

In 1974, four sites on Lake Tenkiller were sampled quarterly as a part of EPA's National Eutrophication Survey (NES). On 30 August 1974 the hypolimnetic dissolved oxygen at three stations was zero. The NES classified Lake Tenkiller as eutrophic (EPA 1978). Trophic state ranged from eutrophic (TSI=56.8) in the headwaters of the lake (near Phase I Station #3) to mesotrophic (TSI=46.8) near the dam (Phase I Station #7) according to Carlson's TSI-chlorophyll a (Carlson 1977). Station #5 was also eutrophic. However, due to the small sample size, much uncertainty exists.

The Oklahoma State Department of Health (OSDH) studied Lake Tenkiller from June to November 1975. The lake was thermally stratified from June to October between 5-7 m in the headwaters of the lake, and between 11-16 m in the lower regions. Dissolved oxygen in the hypolimnion was generally less than 3 mg/l. At one station , the dissolved oxygen concentration was near zero at the bottom on 18 June 1975. The lake was classified as mesotrophic (OSDH 1977). However, based on surface phosphorous concentrations the trophic status of the lake ranged from eutrophic near Phase I Station #3 to mesotrophic near the dam (Carlson 1977). However, due to the small sample size, much uncertainty exists.

Temperature and dissolved oxygen near Lake Tenkiller's dam on 9, 15, 28 August and 5 September 1979 indicated the lake was thermally stratified and hypolimnetic dissolved oxygen levels were less than 1 mg/l (Morris 1979).

From October 1985 to November 1986, the U.S. Army Corps of Engineers studied Lake Tenkiller. The lake was stratified from May 1986 till late September. Lake Tenkiller exhibited a clinograde dissolved oxygen profile, and dissolved oxygen was generally depleted below 10 m. Based on TSI-chlorophyll a (Carlson 1977), Lake Tenkiller was classified as eutrophic. Total manganese concentrations in the hypolimnion were approximately twice those found in the epilimnion. However, total iron was greatest in epilimnetic samples (Nolen et al. 1988). Harton (1989) found that nonpoint source phosphorous loading was the cause of the eutrophication in the lake.

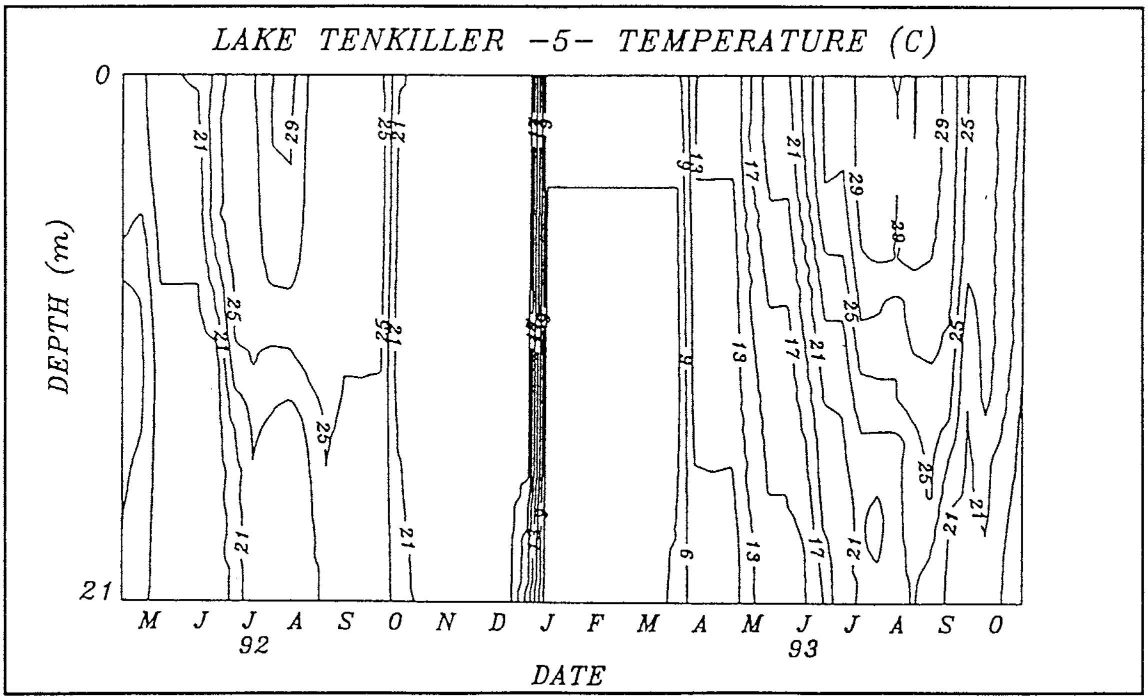
In conclusion, the studies showed that the hypolimnion of Lake Tenkiller experienced dissolved oxygen depletions in 1953, 1961, 1974, 1975, 1979, 1985, and 1986. It can be assumed that the hypolimnion has experienced dissolved oxygen depletion during thermal stratification since impoundment. The studies also showed that Lake Tenkiller has experienced eutrophic conditions in its headwaters since the mid-1970s. Chlorophyll a concentrations had at least doubled between 1975 and 1985.

In addition, manganese accumulated in the hypolimnion in 1986, indicating its release from the anoxic sediments or dissolution from particulate matter falling through the anoxic hypolimnion. Nonpoint source phosphorous loading was the cause of the eutrophication of Lake Tenkiller.

Limnological Results

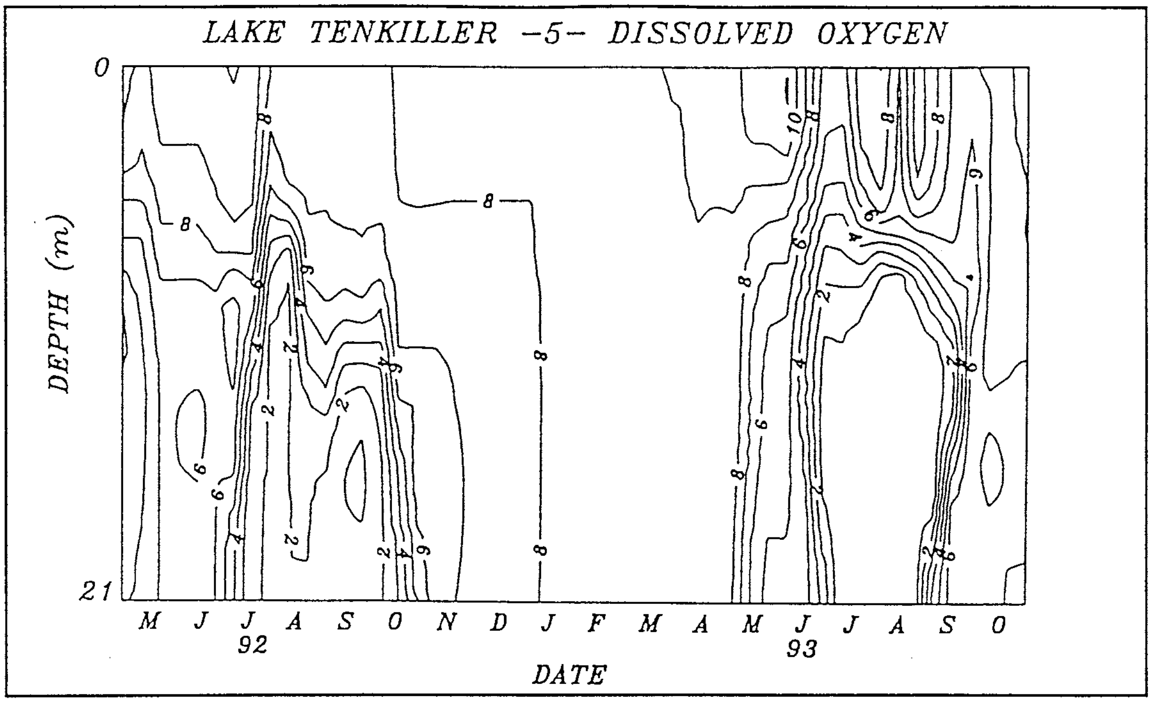
During the Phase I study (1992-93), Station 5 was thermally stratified from mid-June to late-September in 1992, and from July to September in 1993 (Figure 5).

Figure 5. Isopleth of temperature (°C) at Station 5 in Lake Tenkiller, 1992-93



During thermal stratification, a clinograde dissolved oxygen profile was exhibited. In 1992, hypolimnetic dissolved oxygen (DO) concentrations were generally less than 2 mg/l from July through September (Figure 6). In 1993, hypolimnetic dissolved oxygen concentrations were generally less than 1 mg/l from late June to mid-August.

Figure 6. Isopleth of dissolved oxygen concentration (mg/l) at Station 5 in Lake Tenkiller, 1992-93



Metals in the Water Column

Iron and manganese concentrations were consistently higher in the hypolimnion than in the epilimnion. All measurements of iron and manganese were completed between April and August. The increase of hypolimnetic manganese (Figure 7) in Lake Tenkiller shows that manganese is being released from sediments and/or dissolved from particulate matter falling through the hypolimnion. Highest manganese concentrations occurred at the end of summer indicating that it was accumulating and not precipitating. Increased iron concentrations in the hypolimnion (Figure 8) indicated that it was being released from the sediment.

Figure 7. Epilimnetic and hypolimnetic manganese concentrations measured at Station 5 in Lake Tenkiller, 1992-93

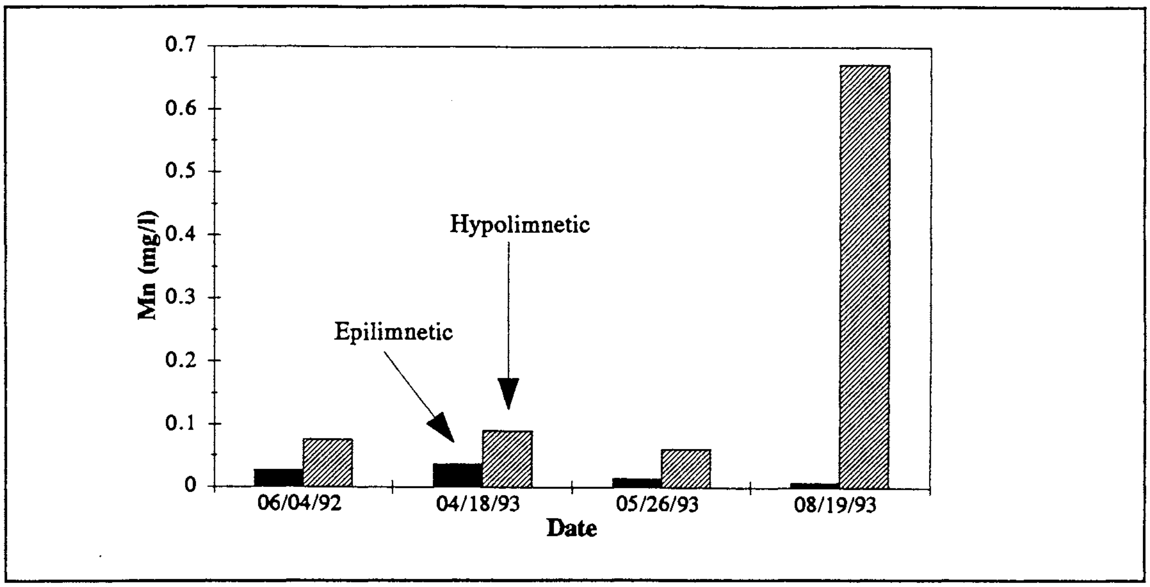
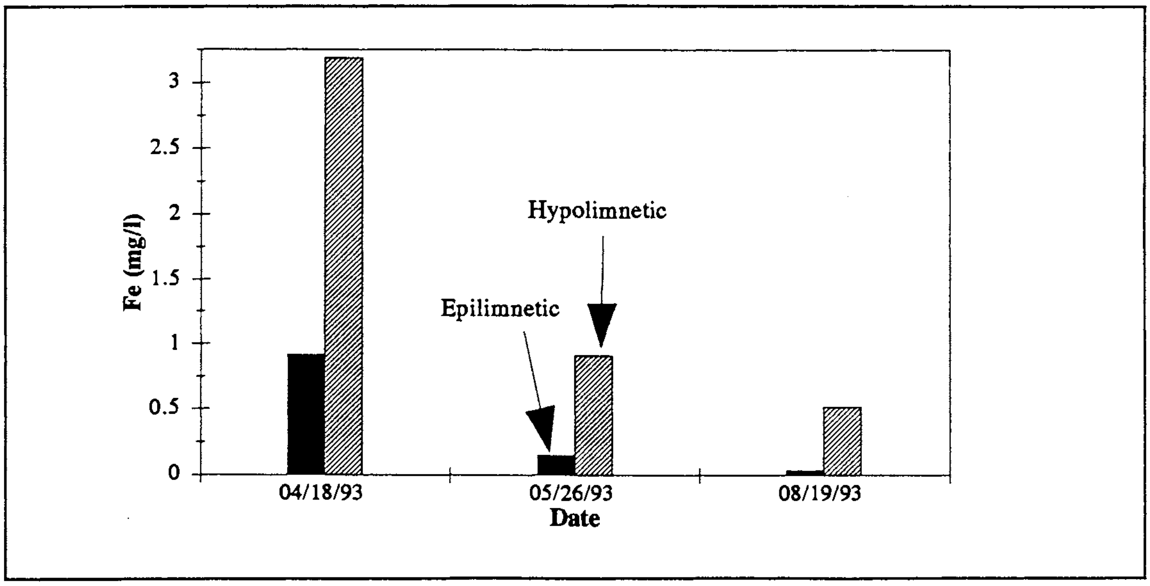


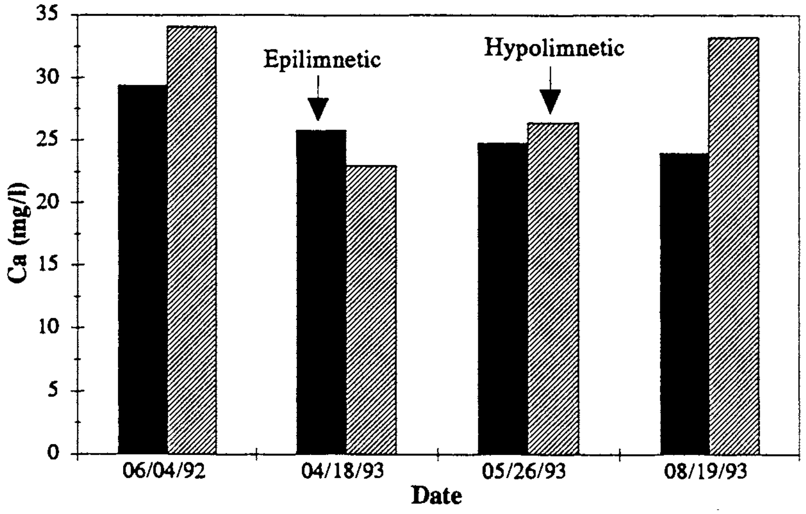
Figure 8. Epilimnetic and hypolimnetic iron concentrations measured at Station 5 in Lake Tenkiller, 1992-93



However, hypolimnetic iron concentrations decreased as summer progressed which was likely due to FeS precipitation. Sodium and molybdenum were not measured in the water. Copper and zinc concentrations were below detection limit.

Hypolimnetic calcium concentrations corresponding with periods of stratification were higher than epilimnetic concentrations (Figure 9) indicating that calcium was precipitating out of the epilimnion and accumulating in the hypolimnion. In contrast, the sample taken prior to stratification had higher epilimnetic calcium concentrations than hypolimnetic concentrations.

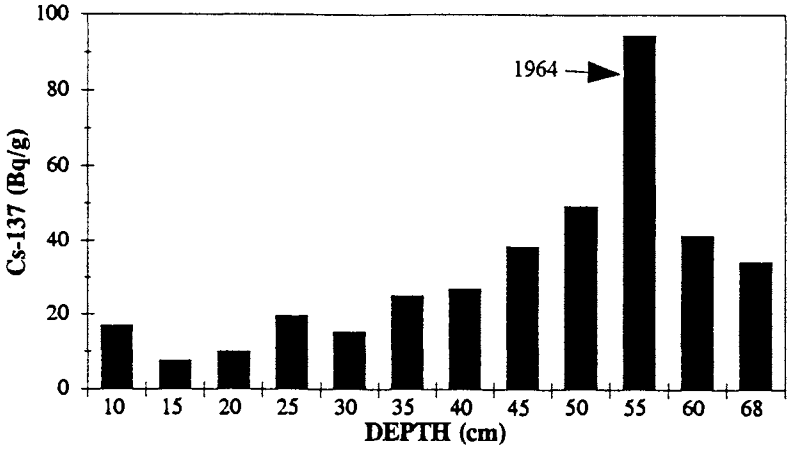
Figure 9. Epilimnetic and hypolimnetic calcium concentration measured at Station 5 in Lake Tenkiller, 1992-93



Sediment Dating

The cesium-137 dating (Figure 10) indicated that the average annual sedimentation rate at Station 5 was approximately 1.5 cm/year from 1954 to 1963 and 1.9 cm/year from 1964 to 1993. However, during high flow years, the sedimentation rate exceeds this average, while during low flow years the sedimentation rate is greatly reduced. The depth of 55 cm corresponded with 1964. Sedimentation rate has remained low throughout the lake's history but has increased slightly since 1964.

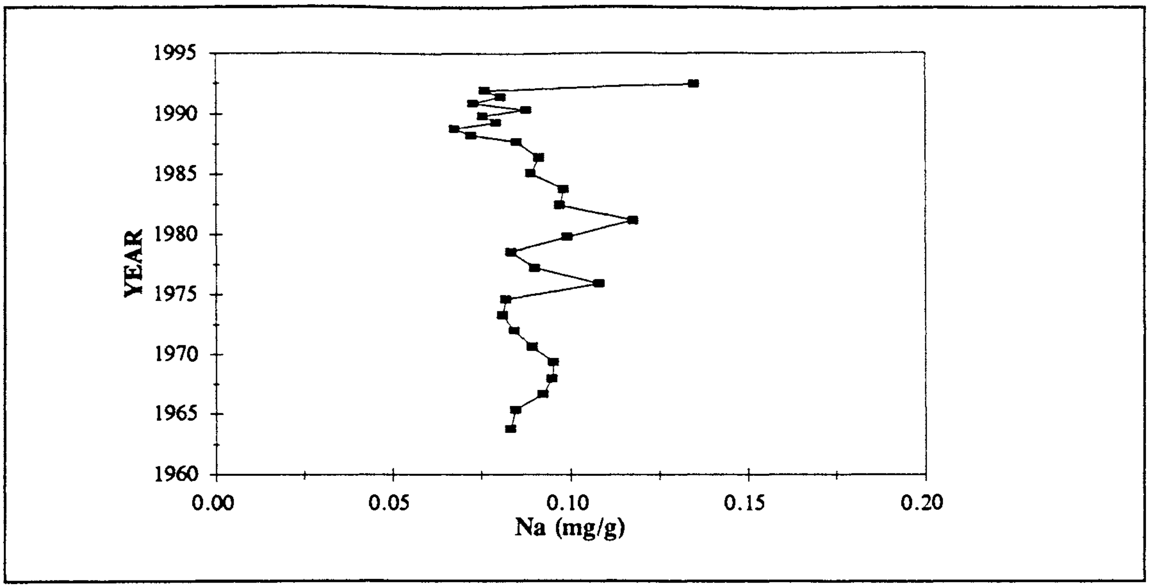
Figure 10. Cesium-137 activity measured in Lake Tenkiller sediment collected from Station 5 in October 1993



Sedimentary Sodium

Sedimentary sodium concentrations (Appendix A) ranged from 0.07 to 0.13 mg/g. Significant changes in the sodium profile (Figure 11) occurred in 1993 (1 cm) and 1980 (25 cm). The peak in 1993 (1 cm) resulted from above average flow of the Illinois River, while the lower concentration in 1980 (25 cm) resulted from below average flow of the Illinois River. This agreed with the discharge data (Figure 2). Excluding these two points, sodium concentrations varied little with depth (year) indicating a stable rate of erosion. However, the sodium profile may not provide an adequate indicator of erosion. The digestion method used did not break down the mineral matrix completely; therefore, the true sodium profile was not measured. Other elements, which are more abundant in soil and more easily extracted from sediment and mineral matrix (i.e. calcium) than sodium, may provide better indicators of erosion.

Figure 11. Concentration-depth profile of sodium measured in Lake Tenkiller sediment collected from Station 5 in October 1993

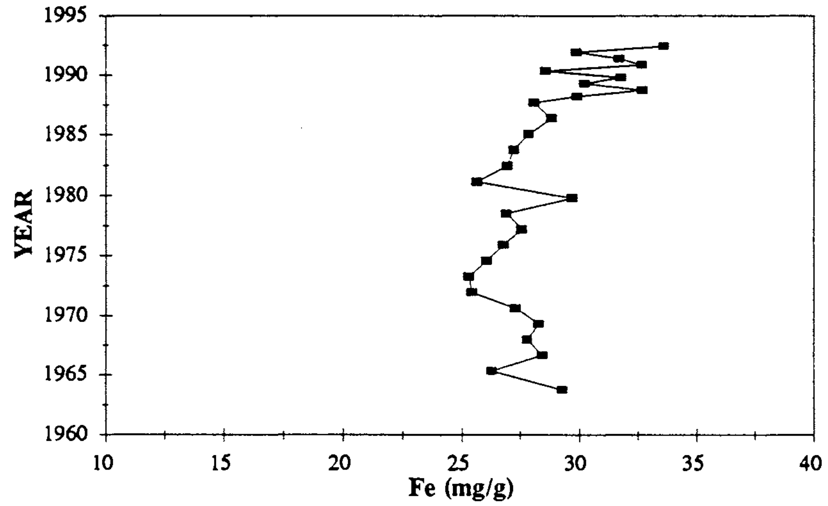


Sedimentary Iron and Manganese

Lake Tenkiller has experienced seasonal anoxia since impoundment as evidenced by previous studies. Therefore, sedimentary iron (Appendix B) and manganese (Appendix C) concentrations in Lake Tenkiller were controlled by changes in supply, variations in hypolimnetic redox, and post-depositional migration.

Sedimentary iron concentrations ranged from 25.3 to 33.6 mg/g. Because Lake Tenkiller discharges from its hypolimnion, release of iron from the sediments should result in an obvious decrease in its sediment concentration-depth profile. However, the iron profile (Figure 12) exhibited no significant variation. Post-depositional migration of iron below the sediment redoxcline can result in poor correlation between the iron profile and other paleoredox indicators (Engstrom and Wright 1984). The highest iron concentrations occurred near the sediment surface. However, the multiple iron peaks near the sediment surface indicated that post-depositional migration was insignificant. Iron maxima, with the exception of the maxima at 25 cm, did not correspond with Fe:Mn maxima indicating that iron concentrations in the sediment were not produced by varying rates of supply from the watershed (Mackereth 1966). The correspondence of the iron and Fe:Mn maxima at 25 cm indicate that it was produced by increased supply (erosion) from the watershed.

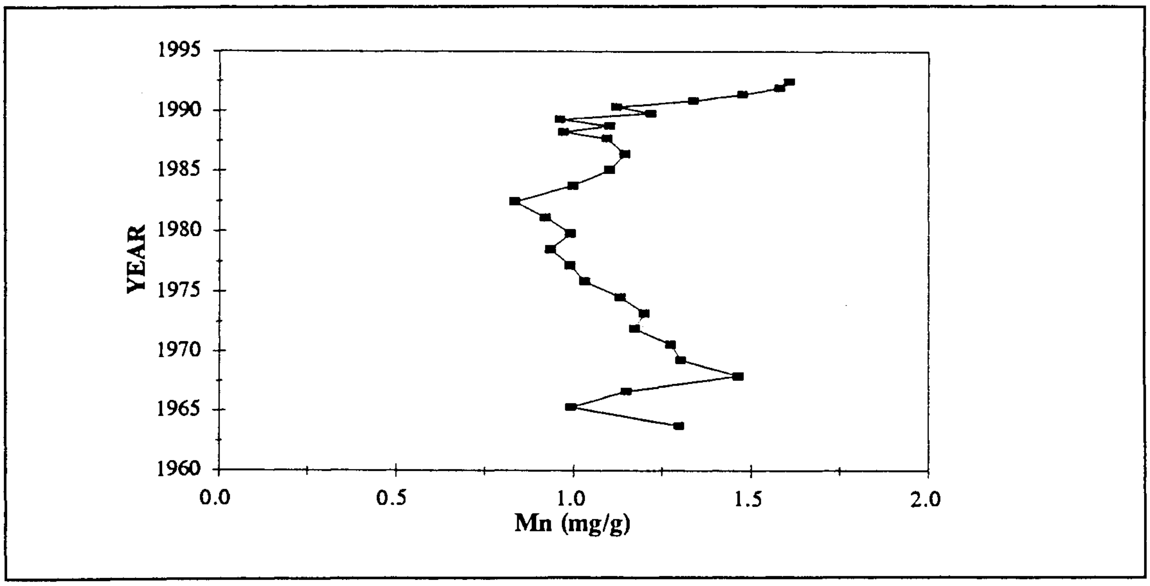
Figure 12. Concentration-depth profile of iron measured in Lake Tenkiller sediment collected from Station 5 in October 1993



The iron profile was correlated with molybdenum, calcium, phosphorous, and manganese (Appendix I). The correlation of molybdenum with iron is due to the fact that the molybdenum cycle in freshwater is similar to the iron cycle (Cole 1975). The correlation of phosphorous and manganese with iron is due to their coprecipitation with iron (Mackereth 1966; Engstrom and Wright 1984; Jones et al. 1993). Because no significant changes occurred in the iron concentration-depth profile, it was not useful in determining the paleoredox conditions or the paleo-productivity of Lake Tenkiller.

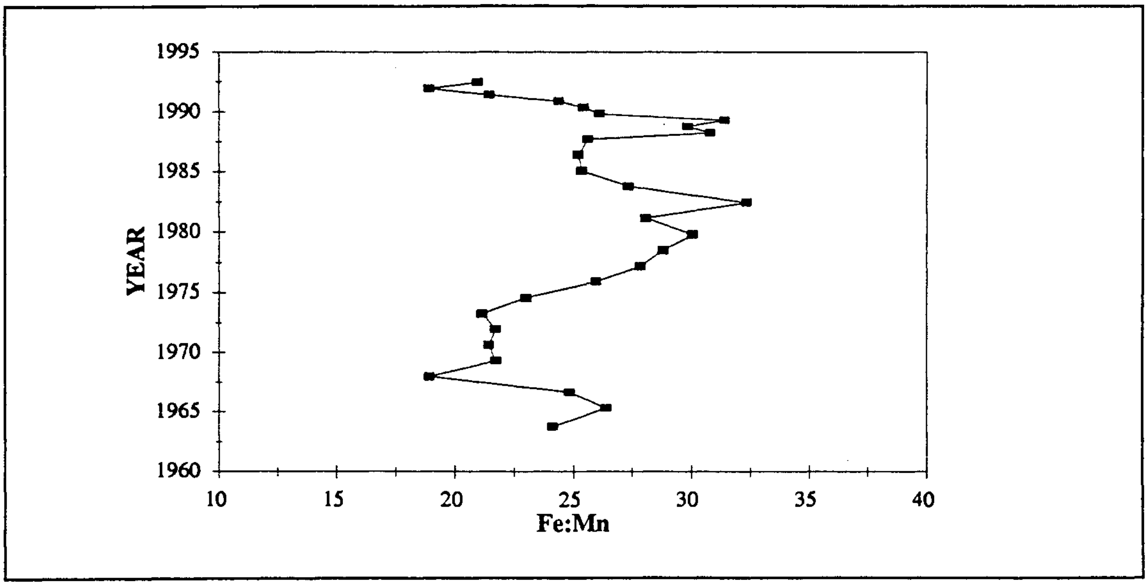
Sedimentary manganese concentrations ranged from 0.8 to 1.6 mg/g. Because Lake Tenkiller discharges from its hypolimnion, release of manganese from the sediments should result in an obvious decrease in its sediment concentration-depth profile. However, this was not the case in the manganese profile (Figure 13). The manganese concentrations decreased from 1968 (47.5 cm) to 1982 (20 cm); however, they increased from 1982 to 1993. Decreasing manganese concentrations from 1968 to 1982 were typical a lake experiencing eutrophication. However, increasing manganese concentrations from 1982 to 1993 were not typical of a lake undergoing eutrophication.

Figure 13. Concentration-depth profile of manganese measured in Lake Tenkiller sediment collected from Station 5 in October 1993



Post-depositional migration of manganese below the sediment redoxcline can result in poor correlation between the manganese profile and other paleoredox indicators (Engstrom and Wright 1984). Sedimentary manganese concentrations steadily increased from 5 cm (1990) to the sediment surface indicating that post-depositional migration of manganese had likely occurred. The manganese profile was correlated with the iron profile only. This correlation was likely due to both iron and manganese being redox sensitive. The validity of the manganese and therefore Fe:Mn as paleoredox indicators is questionable. The manganese profile indicated that post-depositional migration had occurred which changed the original profile lain down in the sediment and resulted in decreasing Fe:Mn values (Figure 14) from 5 cm to the surface of the sediment core.

Figure 14. Fe:Mn profile calculated from Fe and Mn concentrations measured in Lake Tenkiller sediment collected from Station 5 in October 1993

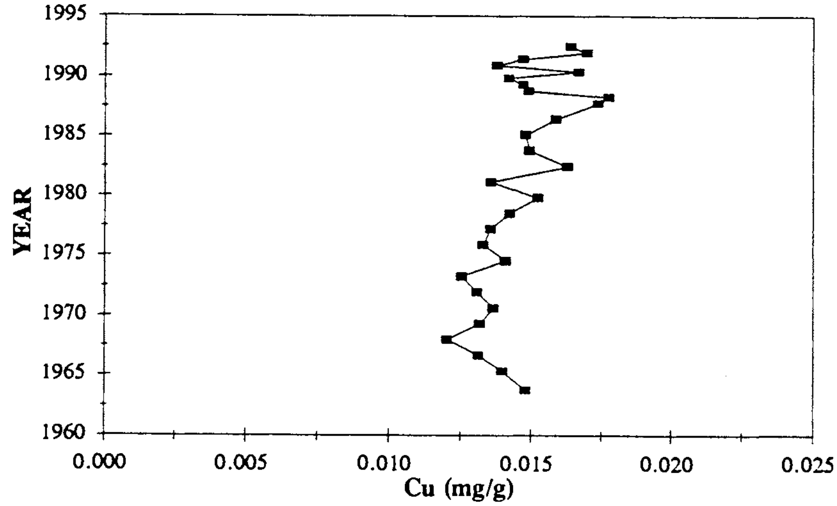


The recent study by Hsuing and Tisue (1994) indicating that more manganese is released during oxic than anoxic periods adds further doubt to its usage. They also concluded that anoxia may inhibit the release of manganese from sediments (Hsuing and Tisue 1994). However, this is unlikely in Lake Tenkiller. In Lake Tenkiller, hypolimnetic manganese concentrations were much greater than the epilimnetic manganese concentration during stratification indicating that manganese was being released from particulate matter in the hypolimnion or sediments. Because manganese experiences post-depositional migration, can be rapidly reduced even when the hypolimnion is oxic (Davison et al. 1982), and is released under both oxic and anoxic conditions, it should not be used as an indicator of paleoredox or paleo-productivity. Because manganese is not a valid indicator, the Fe:Mn is also invalid. Based on recent developments and investigations, manganese and the Fe:Mn should not be used as paleolimnological indicators.

Cu/Zn and (Cu+Mo)/Zn as Paleoredox Indices

Copper concentrations ranged from 0.012 to 0.018 mg/g (Appendix D). The copper profile (Figure 15) exhibited no significant variation. Copper was significantly correlated with only the calcium profile. The correlation between calcium and copper was likely caused by both being associated with primary productivity. Copper uptake and subsequent deposition by algae is responsible for most sedimentation of copper

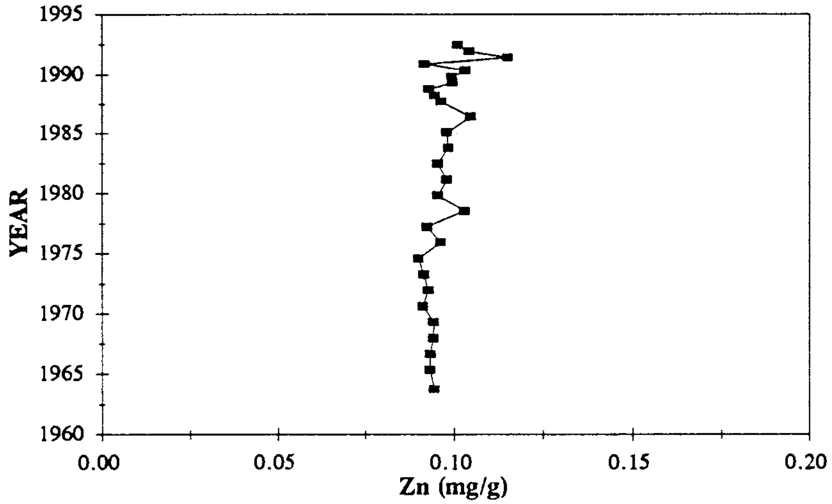
Figure 15. Concentration-depth profile of copper measured in Lake Tenkiller sediment collected from Station 5 in October 1993



(Hutchinson 1957). Calcium precipitates as productivity increases due to the uptake of carbon dioxide (Goldman and Horne 1983).

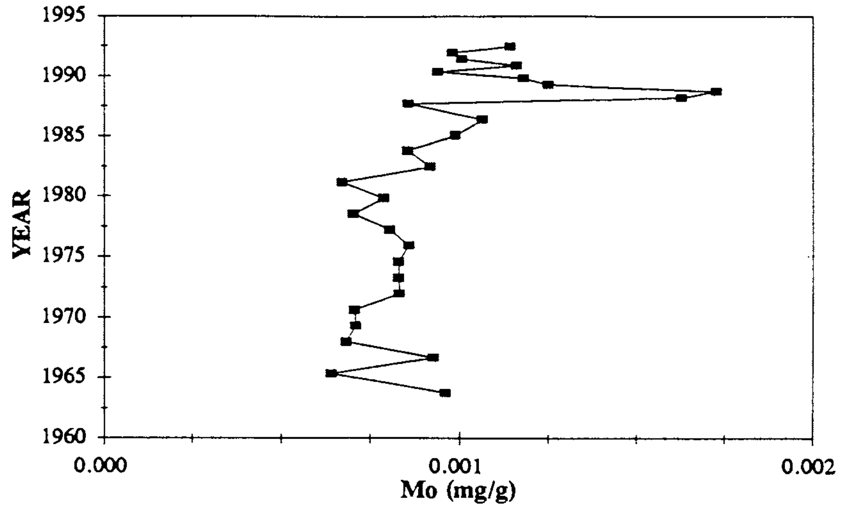
Zinc concentrations ranged from 0.09 to 0.12 mg/g (Appendix E). The zinc profile (Figure 16) profile exhibited no significant variation. The zinc profile was not significantly correlated with any of the parameters measured.

Figure 16. Concentration-depth profile of zinc measured in Lake Tenkiller sediment collected from Station 5 in October 1993



Molybdenum concentrations ranged from 0.0006 to 0.0017 mg/g (Appendix F). No significant variation occurred in the molybdenum profile (Figure 17) with the exception of the molybdenum minima in 1965. Molybdenum was significantly correlated with the iron, calcium, and phosphorous profiles. The correlation of molybdenum and iron were discussed in the previous section. The correlation between molybdenum and phosphorous is likely due to molybdenum being released from the sediments when phosphorous is released (Cole 1975).

Figure 17. Concentration-depth profile of molybdenum measured in Lake Tenkiller sediment collected from Station 5 in October 1993



No significant variation occurred in the Cu/Zn (Figure 18) and (Cu+Mo)/Zn (Figure 19) profiles. Fluctuations in the Cu/Zn and (Cu+Mo)/Zn profiles correspond with fluctuations in the copper profile indicating that the Cu/Zn and (Cu+Mo)Zn were primarily controlled by copper. The (Cu+Mo)/Zn profile followed the Cu/Zn profile closely and provided no additional distinction. The Cu/Zn profile was correlated with the calcium profile. The (Cu+Mo)/Zn profile was correlated with the calcium and Fe:Mn profile. Because the Cu/Zn and (Cu+Mo)/Zn profiles changed little, they were not useful in determining the paleo-productivity of Lake Tenkiller.

These indicators may not apply due to infringement of several assumptions. The sedimentation rate (1.9 cm/yr) may not exceed the penetration of dissolved oxygen into the sediment. Cesium-137 dating of some cores indicated possible resuspension of sediment. No quantitative data that sufficient SO_4 is present for microbial H_2S reduction exists; however, the smell of H_2S in the tailwaters provides qualitative proof.

Figure 18. Cu/Zn profile calculated from copper and zinc concentrations measured in Lake Tenkiller sediment collected from Station 5 in October 1993

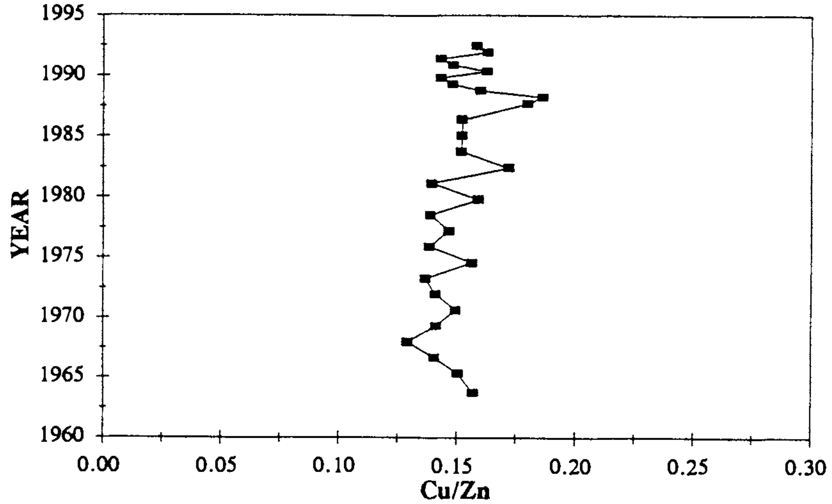
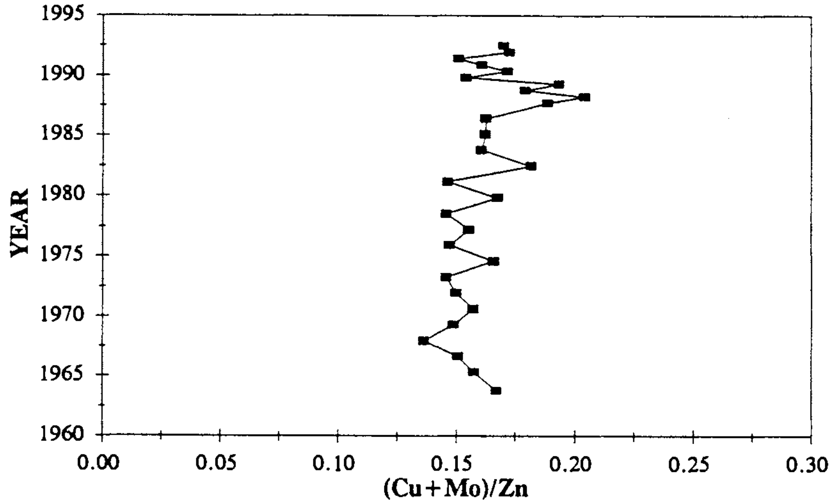


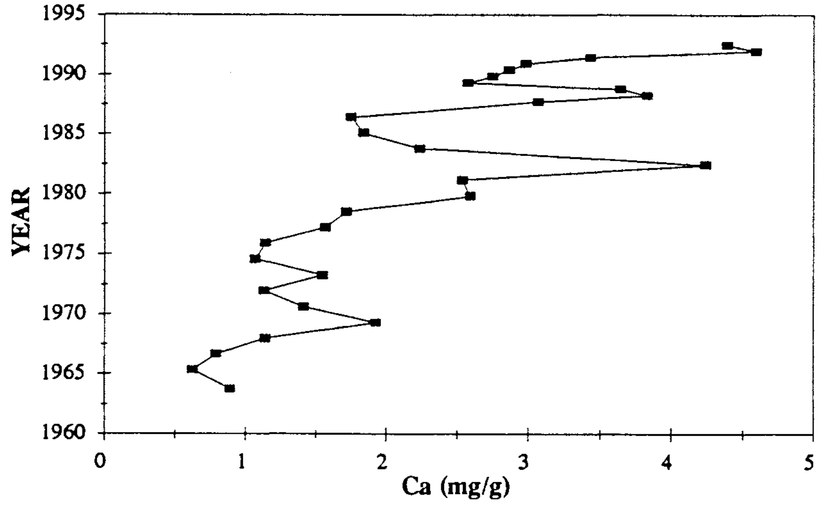
Figure 19. (Cu+Mo)/Zn profile calculated from copper, molybdenum, and zinc concentrations measured in Lake Tenkiller sediment collected from Station 5 in October 1993



Sedimentary Calcium

Calcium concentrations (Appendix G) increased from less than 1 mg/g at the bottom of the sediment profile (1964) to greater than 4 mg/g at the top (1993) of the profile (Figure 20). Significant calcium peaks occurred in 1969 (45 cm), 1982 (20 cm), 1988 (9 cm), and 1992 (2 cm). However, none of the calcium peaks corresponded with years with above average discharges.

Figure 20. Concentration-depth profile of calcium measured in Lake Tenkiller sediment collected from Station 5 in October 1993



A significant trend of increasing concentrations with time can be observed in the calcium profile. This trend of increasing calcium is likely due to the increasing discharge in the Illinois River reported by Gade (1990) and the resulting increased sedimentation rate.

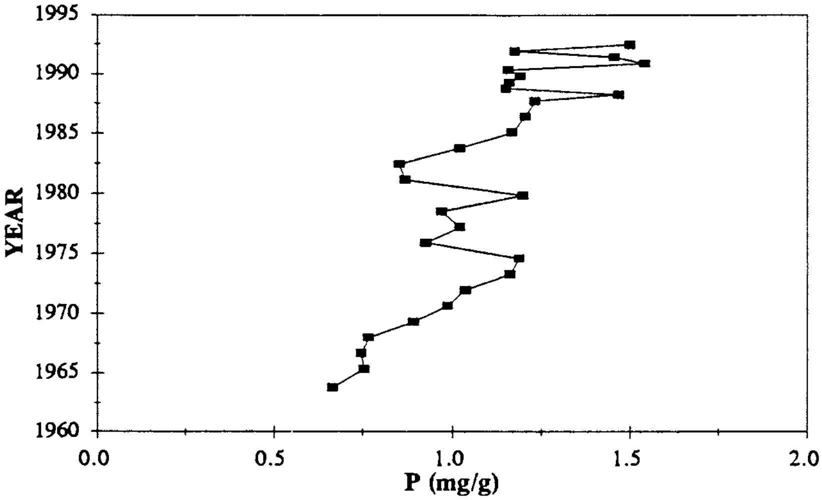
Several factors indicate that the calcium profile in Lake Tenkiller was controlled by increased sedimentation rate instead of increased productivity. More calcium is present in soil than sodium. In addition, calcium is more easily extractable than sodium from sediment and the mineral matrix with the digestion method used. Calcium precipitation occurs in only highly productive hard water lakes. Lake Tenkiller is not a hard water lake; therefore, calcium precipitation due to increased productivity is unlikely. Thus, the increasing concentrations in the calcium profile of Lake Tenkiller were caused primarily by increased input from the watershed and the resulting increased sedimentation rate.

Calcium was correlated with iron, phosphorous, copper, Cu/Zn, (Cu+Mo)/Zn, and molybdenum. Calcium's correlations with iron and copper were discussed in a previous section. The correlation of calcium and phosphorous is discussed in the next section.

Sedimentary Phosphorous

Phosphorous concentrations (Appendix H) increased from 0.67 mg/g at the bottom of the sediment profile (1964) to 1.5 mg/g at the top (1993). This increase (Figure 21) agreed with the two to three fold increase found by Nolen (1988). Significant peaks in the phosphorous profile occurred in 1974 (35 cm), 1980 (25 cm), 1988 (9 cm), 1991 (4 cm), and 1993 (1cm). The phosphorous peaks in 1974 and 1993 were likely caused by floods. The phosphorous peak in 1980 (25 cm) corresponds with a similar peak in the iron profile. The phosphorous minima in 1981 (22.5 cm) and between 1964 (55.5 cm) and 1968 (47.5 cm) were likely caused by below average flow.

Figure 21. Concentration-depth profile of phosphorous measured in Lake Tenkiller sediment collected from Station 5 in October 1993



The phosphorous profile exhibited an increase in the late 1960s and again in the early 1980s. In the late 1960s, the number of chickens (Figure 3) being raised in the Illinois River basin increased until the early 1970s, when the number decreased a great deal. In the early 1980s, the broiler (Figure 3) and hog (Figure 4) industries expanded in the Illinois River Basin. Unlike the increase which occurred in the late 1960s, the phosphorous levels since the early 1980s have not experienced a minima or returned to the lower concentrations observed before the increase. This is likely due to the continued growth of the chicken, broiler, and hog industries.

The phosphorous profile was significantly correlated with the calcium, iron and molybdenum profiles. Phosphorous is sedimented by sorption by iron oxides (Mackereth 1966, Engstrom and Wright 1984, Jones et al. 1993), precipitation as iron phosphates, and coprecipitation with carbonates (Wetzel 1983, Engstrom and Wright 1984). Therefore, the correlation of phosphorous with calcium and iron is likely due to it coprecipitating with iron and $CaCO_3$. This coprecipitation with iron was the likely cause of the corresponding iron and phosphorous peaks in 1980(25 cm). Molybdenum is most abundant in water when phosphorous is released from the sediments (Cole 1975). Therefore, the correlation between phosphorous and molybdenum was likely caused from both being released from the sediments at the same time.

Obviously, the phosphorous profile was primarily affected by flow and increasing input from developing agriculture in the basin. Phosphorous coprecipitation with calcium and iron also affected the profile, especially the phosphorous peak in 1980 (25 cm) which corresponded with an iron maxima.

QA Results

Overall, QA results were good. No contamination was found in the blanks, and percent recoveries were generally acceptable (Table 4). High percent recoveries for zinc, copper, and molybdenum were caused by chemical interferences. High copper concentrations in the spikes interfered with molybdenum and zinc analysis, and likewise, high molybdenum concentrations in the spikes interfered with copper analysis causing high percent recoveries (EPA 1986). Percent recoveries indicated that the analyses were accurate. Standard deviations were generally low, indicating good precision.

Table 4. Percent recovery of spiked sediment samples from Lake Tenkiller

Metal	Range of Percent Recovery	Mean Percent Recovery
Calcium	95 - 106	100
Copper	124 - 169	146
Molybdenum	170 - 233	202
Sodium	109 - 135	122
Zinc	150 - 175	162
Manganese	99 - 147	116
Iron	98 - 140	113
Phosphorous	117 - 124	120

CHAPTER V

SUMMARY AND CONCLUSIONS

Summary and Conclusions

Nutrients in the Illinois River have increased with time and resulted in an increasing rate of eutrophication (Gade 1990). Previous studies indicated that the hypolimnion of Lake Tenkiller experienced dissolved oxygen depletions during thermal stratification since impoundment. The studies also showed that Lake Tenkiller has experienced eutrophic conditions in its headwaters since the mid-1970s. Chlorophyll a concentrations at least doubled between 1975 and 1985. Nonpoint source phosphorous loading caused the eutrophication of Lake Tenkiller (Harton 1989).

Cesium-137 dating indicated that the average annual sedimentation rate at Station 5 was approximately 1.5 cm/year from 1954 to 1963 and 1.9 cm/year from 1964 to 1993. The sodium profile did not provide an adequate indicator of erosion; because, the digestion method used did not break down the mineral matrix completely. Thus the true sodium profile was not measured.

In Lake Tenkiller, hypolimnetic iron and manganese concentrations were greater than epilimnetic concentrations during stratification indicating their release from sediments or particulate matter indicating that redox changes affected iron and manganese. Highest manganese concentrations were observed at the end of summer indicating that it accumulated throughout the summer and did not precipitate. Iron, however, decreased as summer progressed, which was likely due to FeS precipitation. Post-depositional migration was insignificant in the iron profile. In contrast, sedimentary manganese concentrations steadily increased from 5 cm to the sediment surface indicating that post-depositional migration of manganese had occurred.

The validity of the manganese and Fe:Mn profiles as paleoredox indicators is questionable. The manganese profile indicated that post-depositional migration had occurred which altered the original profile lain down in the sediment. This resulted in the decreasing Fe:Mn from 5 cm to the sediment surface. Recent studies add further uncertainty to the use of manganese. Because manganese experiences post-depositional migration, can be rapidly reduced even when the hypolimnion is oxic (Davison et al. 1982), and is released under both oxic and anoxic conditions, it should not be used as an indicator of paleoredox or paleo-productivity. Since manganese is not a valid paleoredox indicator, the Fe:Mn ratio is also invalid. Based on recent developments and investigations, manganese and the Fe:Mn should not be used as paleolimnological indicators. Because no significant changes occurred in the iron profile, it was not useful in determining the paleoredox conditions or the paleo-productivity of the lake.

No significant changes occurred in the copper, zinc, molybdenum, Cu/Zn, or (Cu+Mo)Zn profiles; therefore, they were not useful in determining the length of seasonal anoxia in the hypolimnion or the paleo-productivity of Lake Tenkiller.

A significant trend of increasing concentrations with time occurred in the calcium profile. However, the calcium trend likely did not result from increased productivity. Calcium precipitation occurs only in highly productive hard water lakes. Lake Tenkiller is not a hard water lake; therefore, significant amounts of calcium precipitation due to increased productivity is unlikely. The trend of increasing calcium was likely due to the increasing discharge in the Illinois River reported by Gade (1990) and the resulting increased sedimentation rate. However, none of the calcium peaks corresponded with years of above average discharge. Thus, the calcium profile was not useful in determining the paleo-productivity of Lake Tenkiller.

The phosphorous profile was primarily affected by flows and increasing input from developing agricultural enterprises in the basin (resulting in an increase in phosphorous concentrations). Coprecipitation of phosphorous with calcium and iron also affected the profile. An increase in phosphorous concentrations occurred in the late 1960s and again in the early 1980s. These increases correspond with increases in several agricultural industries in the basin. However, the phosphorous profile was not useful in determining the paleo-productivity of Lake Tenkiller.

None of the methods used provided conclusive evidence of the paleo-productivity of Lake Tenkiller. Several difficulties exist in stratigraphic analysis of sediments. Sediments are heterogenous and there are various sources (allochthonous, autochthonous, anthropogenic, and natural) for the particulate matter in the sediment. In addition, diagenetic changes which occur after deposition further complicate interpretation. Most of the methods used were developed on lakes of glacial origin which have histories of several thousand years. In profiles from these glacial lakes, seasonal and natural background variation becomes insignificant. However, in reservoirs such as Lake Tenkiller, where the age of the lake is less than 50 years, seasonal and natural background variation is significant. Therefore, these methods should not be used on reservoirs.

In addition, hypolimnetic oxygen depletion and redox conditions may not be good paleolimnological indicators of reservoir trophic status, especially in Lake Tenkiller. Some oligotrophic and mesotrophic reservoirs in Oklahoma (Lakes Pawhuska and Bixhoma), exhibit seasonal hypolimnetic oxygen depletion (OCC 1994). This may be due to their situation on flowing rivers which drain large watersheds compared to reservoir surface area. This characteristic may lead to greater allogenic loadings (especially of organic matter), which could lead to depletion of hypolimnetic oxygen and resulting redox changes.

Suggestions for Future Research

I recommend using a corer long and heavy enough to collect the entire sediment column. The sediment core analyzed during this study only reached the depth which correlated with the year of 1964. In addition, I would section the sediment core before freezing. This would prevent alteration of the core which occurred as the core froze and the interstitial water expanded.

Future studies to determine the effect of redox on chemical stratigraphy in sediment cores would provide much needed information. This might be accomplished by comparing the paleoredox conditions of Lake Keystone (anoxic for a long period when first impounded) to Lake Tenkiller (experienced only seasonal anoxia) to examine differences between the extreme anoxia produced in Keystone and the associated sediment record and the short periods of anoxia experienced in Lake Tenkiller.

Numerous methods provide additional insight into the paleo-productivity and historic water quality of lakes. Stratigraphic analysis of the remains of aquatic biota may be useful for determining historical lake water quality (Charles and Smol 1994). Paleolimnological interpretation of sediment geochemical stratigraphy is more reliable when correlated with diatom stratigraphy (Vuorinen et al. 1986). Chlorophyll derivatives may provide a useful indicator of eutrophication (Kjensmo 1988). Sanger and Gorham (1972) determined that the ratio of total chlorophyll a pigments (TaP) to total carbon (TC) in sediments, expressed as TaP:TC, indicated eutrophy.

Future studies could compare the CRS:AVS ratio [chromium reducible sulfide (CRS) to acid-volatile sulfide (AVS) ratio], which reflects lake trophic status, to other paleolimnological indicators (Peiffer 1994). The ratio of organic matter:TKN has also been used as an indicator for lake productivity (Russell-Hunter 1970). The sedimentary C/N ratio provided a good indication of the trophic level in Florida Lakes. Low Al:Ca indicated high productivity in Florida Lakes while high Al concentrations indicated low TSI (Flannery et al. 1982).

Several authors state that the fine metal particles accumulate in protected areas where wind and wave action can not resuspend them. However, no quantitative data exists to verify this. Therefore, a study to determine if higher metal concentrations are found in protected areas with finer sediments would be useful (Horowitz 1991).

LITERATURE CITED

Adams, D.D., N.J. Fendinger, and D.E. Glotfelty. 1990. Chapter 7: Biogenic gas production and mobilization of in-place sediment contaminants by gas ebullition. In R. Baudo, J.P. Giesy, and H. Muntau, eds. Sediments: Chemistry and Toxicity of In-Place Pollutants. Lewis Publishers, Inc. Boca Raton, FL.

Adlard, E.R. 1979. The identification of oil spills by gas chromatography. In K.H. Altgelt and T.H. Gouw, eds. Chromatography in Petroleum Analysis. M. Dekker Publishers. New York, NY.

Anderson, N.J. and B. Rippey. 1988. Diagenesis of magnetic minerals in the recent sediments of a eutrophic lake. Limnology and Oceanography 33:1476-1492.

Blumer, M. and W.D. Snyder. 1965. Isoprenoid hydrocarbons in recent sediments: Presence of pristane and probable absence of phytane. Science 150:1588-1589.

Brooks, J.D., K. Gould, and J.W. Smith. 1969. Isoprenoid hydrocarbons in coal and petroleum. Nature 222:257-259.

Burns, N.M. 1976. Temperature, oxygen, and nutrient distribution patterns in Lake Erie, 1970. J. Fish. Res. Bd. Can. 33:485-511.

Carlson, R.E. 1977. A trophic state index for lakes. Limnology and Oceanography 22:361-369.

Carlton, R.G. and M.J. Klug. 1990. Chapter 4: Spatial and temporal variations in microbial processes in aquatic sediments: Implications for the nutrient status of lakes. In R. Baudo, J.P. Giesy, and H. Muntau, eds. Sediments: Chemistry and Toxicity of In-Place Pollutants. Lewis Publishers, Inc. Boca Raton, FL.

Chapra, S.C. and H.F.H. Dobson. 1981. Quantification of the lake trophic typologies of Naumann (surface quality) and Thienemann (oxygen) with special reference to the Great Lakes. J. Great Lakes Res. 7:182-193.

Charles, D.F. and J.P. Smol. 1994. Chapter 1: Long-term chemical changes in lakes: Quantitative inferences from biotic remains in the sediment record. In L.A. Baker, ed. Environmental Chemistry of Lakes and Reservoirs. American Chemical Society Publication. Washington, DC.

Coffey, S.W., W.S. Berryhill, M.D. Smolen, and D.W. Miller. 1989. Watershed Screening for Nonpoint Source Impacts and Controls. Cooperative Agreement 87-EXCA-3-8-30. North Carolina State University. Raleigh, NC.

Cole, G.A. 1975. Textbook of Limnology. C.V. Mosby Company. St. Louis, MO.

Davison, W. 1981. Supply of Fe and Mn to an anoxic lake basin. Nature 290:241-243.

Davison, W., C. Woof, and E. Rigg. 1982. The dynamics of iron and manganese in a seasonally anoxic lake; direct measurement of fluxes using sediment traps. Limnology and Oceanography 27:987-1003.

Didyk, B.M., B.R.T. Simoneit, S.C. Brassell, and G. Eglinton. 1978. Organic geochemical indicators of paleoenvironmental conditions of sedimentation. Nature 272:216-222.

Engstrom, D.R. and H.E. Wright. 1984. Chapter 1: Chemical stratigraphy of lake sediments as a record of environmental change. In E.Y. Hawthorne and J.W.G. Lund, eds. Lake Sediments and Environmental History. University of Minnesota Press. Minneapolis, Minnesota.

EPA (U.S. Environmental Protection Agency). 1974. An approach to a relative trophic index system for classifying lakes and reservoirs. Working Pap. No. 24. National Eutrophication Survey. Pacific Northwest Environmental Research Laboratory. Corvallis, OR.

EPA (U.S. Environmental Protection Agency). 1978. National Eutrophication Survey, Working Paper 593. Corvallis Environmental Research Laboratory and Las Vegas Environmental Monitoring Support Laboratory. Washington, DC.

EPA (U.S. Environmental Protection Agency). 1986. Test methods for evaluating solid waste. Vol. I, Section A, Part 1. EPA/SW-846. Washington, DC.

EPA (U.S. Environmental Protection Agency). 1987. Field Manual Physical/Chemical Methods. Volumes 1-8. EPA SW-846. PB88-239223/REB. EPA Office of Solid Wastes and Emergency Response, Washington, D.C.

Finnell, J.C. 1953. Dissolved oxygen and temperature profiles of Tenkiller Reservoir and tailwaters with consideration of these waters as a possible habitat for rainbow trout. Proceedings of the Oklahoma Academy of Sciences 65-72.

Flannery, M.S., R.D. Snodgrass, and T.J. Whitmore. 1982. Deepwater sediments and trophic conditions in Florida lakes. Hydrobiologia 92:597-602.

Frevert, T. and C. Sollmann. 1987. Heavy metals in Lake Kinneret (Isreal): III. Concentrations of iron, manganese, nickel, cobalt, molybdenum, zinc, lead, and copper in interstitial water and sediment dry weights. Archiv fuer Hydrobiologie 109:181-205.

Gachter, R. and J.S. Meyer. 1990. Chapter 5: Mechanisms controlling fluxes of nutrients across the sediment/water interface in a eutrophic lake. In R. Baudo, J.P. Giesy, and H. Muntau, eds. Sediments: Chemistry and Toxicity of In-Place Pollutants. Lewis Publishers, Inc. Boca Raton, FL.

Gade, D.R. 1990. Trend analysis of temporal nutrient concentrations in the Illinois River Basin in Oklahoma and Arkansas. Master's thesis, Oklahoma State University. Stillwater, OK.

Goldman, C.R. and A.J. Horne. 1983. Limnology. McGraw-Hill Book Company. New York, NY.

Hakanson, L. 1984. On the relationship between lake trophic level and lake sediments. Water Research 18:303-314.

Hallberg, R.O. 1972. Sedimentary sulfide mineral formation - An energy circuit system approach. Mineral. Deposita 7:189-201.

Harton, N. 1989. An analysis of uncertainty of point and non-point source loading on eutrophication on a downstream reservoir. Master's thesis, Oklahoma State University. Stillwater, OK.

Hickman, M. and D.M. Klarer. 1981. Paleolimnology of Lake Isle, Alberta, Canada (Including sediment chemistry, pigments, and diatom stratigraphy). Archiv fuer Hydrolobiologie 91:490-508.

Horowitz, A.J. 1991. A Primer On Sediment-Trace Element Chemistry: 2nd Edition. USGS Publication. Alexandria, VA.

Hounslow, A.W. 1993. Environmental Geochemistry. School of Geology, Oklahoma State University. Stillwater, OK.

Hsiung, Tung-Ming and T. Tisue. 1994. Chapter 16: Manganese dynamics in Lake Richard B. Russell. In L.A. Baker, ed. Environmental Chemistry of Lakes and Reservoirs. American Chemical Society Publication. Washington, DC.

Hutchinson, G.E. 1938. On the relation between the oxygen deficit and the productivity and typology of lakes. Int. Rev. Hydrobiol. 36:336-355.

Hutchinson, G.E. 1957. Treatise on Limnology, Volume 1. John Wiley & Sons. New York, NY.

Jenkins, R.M. 1953. Continued fisheries investigation of Tenkiller Reservoir, Oklahoma, during its first year of impoundment. Oklahoma Fisheries Laboratory Report 33:54. Oklahoma Department of Wildlife Conservation. Oklahoma, OK.

Jenne, E.A. and J.M. Zachara. 1987. Chapter 8: Factors influencing the sorption of metals. In K.L. Dickson, A.W. Maki, and W.A. Brungs, eds. Fate and Effects of Sediment Bound Chemicals in Aquatic Systems. SETAC Publication. Peroamon Press. New York, NY.

Kjensmo, J. 1988. Post-glacial sediments and stagnation history of the iron meromictic Lake Skjennungen, Eastern Norway. Archiv fuer Hydrobiologie 113:481-499.

Kuhn, A., C.A. Johnson, and L. Sigg. 1994. Chapter 15: Cycles of trace elements in a lake with a seasonally anoxic hypolimnion. In L.A. Baker, ed. Environmental Chemistry of Lakes and Reservoirs. American Chemical Society Publication. Washington, DC.

Leach, J.H. and R.C. Herron. 1992. Chapter 3: A review of lake habitat classification. In W.-Dieter N. Busch and P.G. Sly, eds. The Development of an Aquatic Habitat Classification System for Lakes. CRC Press. Boca Raton, FL.

Lind, O.W. 1985. Handbook of Common Methods in Limnology: Second Edition. Kendall/Hunt Publishing Company. Dubuque, IA.

Lueschow, L.A., J.M. Helm, D.R. Winter, and G.W. Karl. 1970. Trophic nature of selected Wisconsin lakes. Wisc. Acad. Sci. Arts Lett. 58:237-264.

Mackereth, F.J.H. 1966. Some chemical observations on post-glacial lake sediments. Philosophical Transactions of the Royal Society (Series B) 250:165-213.

McHenry, J.R., J.C. Ritchie, and C.M. Cooper. 1980. Rates of recent sedimentation in Lake Pepin. Water Resources Bulletin 6:1049-1056.

Moore, J.N. 1994. Chapter 14: Contamimant mobilization resulting from redox pumping in a metal-contaminated river-reservoir system. In L.A. Baker ed. Environmental Chemistry of Lakes and Reservoirs. American Chemical Society Publication. Washington, DC.

Morris, W.K. 1979. Tenkiller Ferry Reservoir and Lower Illinois River 1979 Temperature and Dissolved Oxygen Investigation. Oklahoma Water Resources Board, Water Quality Division. Publication 93. Oklahoma City, OK.

Nriagu, J.O. 1980. Zinc in the Environment Part I: Ecological Cycling. John Wiley and Sons. New York, NY.

Nolen, S., J.H. Carroll, D.L. Combs, J.C. Staves, and J.N. Veenstra. 1988. Limnology of Tenkiller Ferry Lake, Oklahoma, 1985-1986. U.S. Army Corps of Engineers. Tulsa, OK.

OCC (Oklahoma Conservation Commission). 1994. Macroinvertebrate and Fish Bioassessment Methods for Small to Medium Sized Reservoirs. 104(b)(3). OCC Water Quality Division. Oklahoma City, OK.

OSDH (Oklahoma State Department of Health). 1977. Water Quality Survey of the Illinois River and Tenkiller Reservoir: June 1976 to October 1977. Oklahoma City, OK.

OWRB (Oklahoma Water Resources Board). 1984. Oklahoma's Water Atlas. Oklahoma City, OK

Peiffer, S. 1994. Chapter 11: Reaction of hydrogen sulfide with ferric oxides: Some conceptual ideas on its significance for sediment-water interactions. In L.A. Baker ed. Environmental Chemistry of Lakes and Reservoirs. American Chemical Society Publication. Washington, DC.

Powell, T.G. and D.M. McKirdy. 1973. Relationship between ratio of pristane to phytane, crude oil composition and geological environment in Australia. Nature Physical Science 243:37-39.

Reckow, K.H. 1988. Empirical models for trophic state in southeastern U.S. lakes. Water Resources Bulletin 24:723-734.

Russell-Hunter, W.D. 1970. Aquatic Productivity - An Introduction to Some Basic Aspects of Biological Oceanography and Limnology. Macmillan Publishers. New York, NY.

Sakata, M. 1985. Diagenetic remobilization of Mn, Fe, Cu, and Pb in anoxic sediment of a freshwater pond. Water Research 19:1033-1038.

Sanger, J.E. and E. Gorham. 1972. Stratigraphy of fossil pigments as a guide to the postglacial history of Kirchner Marsh, Minnesota. Limnology and Oceanography 17:840-854.

Sekar, B., G. Rajagopalan, B.D. Nautiyal, and R.K. Dube. 1992. Chemical analysis of a sediment core from Paradip Lake, Orissa and its application to environmental reconstruction for 450 years. Current Science 63:571-573.

Smol, J.P. 1992. Paleolimnology: an important tool for effective ecosystem management. Journal of Aquatic Ecosystem Health 1:49-58.

Steel, R.G.D. and J.H. Torrie. 1960. Principles and Procedures of Statistics, A Biometric Approach. McGraw-Hill Publishers. New York, NY.

Summers, P.B. 1961. Observations on the limnological dynamics of Tenkiller Ferry Reservoir. Project Number F-7-R-1. Job Number 2. Oklahoma Department of Wildlife Conservation. Oklahoma City, OK.

ten Haven, H.L., J.W. de Leeuw, J. Rullkotter, and J.S. Sinninghe Damste. 1987. Restricted utility of the pristane/phytane ratio as a paleoenvironmental indicator. Nature 330:641-643.

Trusell, F.C. 1979. Gas chromatography of middle and heavy distillates. In K.H. Altgelt and T.H. Gouw eds. Chromatography in Petroleum Analysis. M. Dekker Publishers. New York, NY.

USGS (U.S. Geological Survey). 1965-1993. Water Resources Data for Oklahoma. USGS Water Resources Division. Oklahoma City, OK.

Uttormark, P.D. and J.P. Wall. 1975. Lake classification - a trophic characterization of Wisconsin lakes. EPA-660/3-75-033. U.S. Environmental Protection Agency. Washington, D.C.

Vollenweider, R.A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorous as factors in eutrophication. OECD Rep. DAS/SCI/68.27. U.N. Organization for Economic and Cultural Development. Paris, France.

Vollenweider, R.A. and L.L. Janus. 1982. Statistical methods for predicting hypolimnetic oxygen depletion rates. Mem. Ist. Ital. Idrobiol. pg. 1-24.

Vuorinen, A., P. Alhonen, and J. Suksi. 1986. Paleolimnological and limnogeological features in the sedimentary record of the polluted Lake Lippajarvi in Southern Finland. Environmental Pollution (Series A) 41:323-362.

Wakeham, S.G. 1993. Reconstructing past oceanic temperatures from marine organic biogeochemistry, chemical fossils and molecular stratigraphy. Environmental Science and Technology 27:29-33.

Walker, W.W. Jr. 1979. Use of hypolimnetic oxygen depletion rate as a trophic state index for lakes. Water Resources Research 15:1463-1470.

Wetzel, Robert G. 1983. Limnology. Saunders College Publishing. Philadelphia, PA.

APPENDIXES

APPENDIX A

Sodium concentrations (mg/g) measured in eight replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	3	4	5	6	7	8	Mean	Std Dev
1	0.119	0.145	0.140						0.135	0.014
2	0.058	0.102	0.068						0.076	0.023
3	0.060	0.121	0.076	0.064					0.080	0.028
4	0.069	0.079	0.071						0.073	0.005
5	0.081	0.078	0.108	0.083					0.088	0.014
6	0.069	0.090	0.068						0.075	0.012
7	0.073	0.093	0.072						0.079	0.012
8	0.071	0.066	0.066						0.068	0.003
9	0.072	0.090	0.054						0.072	0.018
10	0.096	0.076	0.083						0.085	0.010
12.5	0.064	0.104	0.092	0.085	0.111				0.091	0.018
15	0.087	0.111	0.075	0.086	0.086				0.089	0.013
17.5	0.088	0.104	0.102						0.098	0.009
20	0.083	0.114	0.078	0.113					0.097	0.019
22.5	0.100	0.132	0.122						0.118	0.016
25	0.099	0.099	0.099						0.099	0.000
27.5	0.094	0.075	0.089	0.075					0.083	0.010
30	0.079	0.110	0.081						0.090	0.018
32.5	0.086	0.126	0.124	0.097					0.108	0.020
35	0.077	0.090	0.079						0.082	0.007
37.5	0.100	0.081	0.061						0.081	0.020
40	0.087	0.085	0.103	0.065	0.079				0.084	0.014
42.5	0.084	0.095	0.073	0.105					0.089	0.014
45	0.088	0.092	0.087	0.104	0.105				0.095	0.009
47.5	0.083	0.104	0.096	0.075	0.116				0.095	0.016
50	0.092	0.078	0.099	0.100					0.092	0.010
52.5	0.078	0.068	0.108	0.070	0.086	0.097			0.085	0.016
55.5	0.070	0.093	0.079	0.071	0.080	0.080	0.083	0.108	0.083	0.012

APPENDIX B

Iron concentrations (mg/g) measured in seven replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	3	4	5	6	7	Mean	Std Dev
1	29.29	35.95	35.66					33.63	3.76
2	34.57	27.84	27.22					29.88	4.08
3	32.75	31.67	34.97	27.40				31.70	3.18
4	27.36	35.61	35.09					32.69	4.62
5	27.72	29.35	28.59					28.55	0.82
6	27.66	36.20	31.48					31.78	4.28
7	35.13	27.68	27.84					30.22	4.26
8	34.71	34.44	28.98					32.71	3.23
9	33.47	26.34						29.91	5.04
10	29.10	26.79	28.33					28.07	1.18
12.5	28.05	30.33	28.82	29.10	27.86			28.83	0.98
15	29.04	27.80	30.16	24.35				27.84	2.52
17.5	27.18	29.34	25.08					27.20	2.13
20	23.40	28.90	28.53					26.94	3.07
22.5	28.23	23.77	24.94					25.65	2.31
25	32.11	30.72	26.31					29.71	3.03
27.5	26.16	25.24	29.30					26.90	2.13
30	28.89	24.69	29.10					27.56	2.49
32.5	24.75	28.88	26.67					26.77	2.07
35	26.10	28.13	23.91					26.05	2.11
37.5	23.33	25.53	27.07					25.31	1.88
40	26.59	24.31	26.91	24.66	24.73			25.44	1.21
42.5	26.18	25.87	29.83					27.29	2.20
45	28.91	28.97	28.38	25.95	29.27			28.30	1.35
47.5	26.06	29.34	30.25	25.47				27.78	2.37
50	29.64	29.65	26.05					28.45	2.08
52.5	26.82	25.04	29.64	24.56	25.33			26.28	2.06
55.5	31.17	26.71	26.94	28.81	30.46	29.73	31.23	29.29	1.88

APPENDIX C

Manganese concentrations (mg/g) measured in seven replicates in a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	3	4	5	6	7	Mean	Std Dev
1	1.53	1.67	1.62					1.61	0.07
2	1.60	1.61	1.53					1.58	0.04
3	1.46	1.58	1.55	1.31				1.48	0.12
4	1.23	1.42	1.36					1.34	0.10
5	1.14	1.08	1.14					1.12	0.03
6	1.18	1.22	1.25					1.22	0.04
7	1.00	0.99	0.89					0.96	0.06
8	1.07	1.20	1.03					1.10	0.09
9	0.96	0.98						0.97	0.01
10	1.14	1.05	1.09					1.09	0.05
12.5	1.11	1.16	1.16	1.14	1.15			1.14	0.02
15	1.15	1.03	1.16	1.06				1.10	0.06
17.5	0.91	1.13	0.95					1.00	0.12
20	0.81	0.87	0.82					0.83	0.03
22.5	1.03	0.94	0.79					0.92	0.12
25	1.04	0.93	1.00					0.99	0.06
27.5	0.91	0.90	0.99					0.93	0.05
30	1.02	0.96	0.99					0.99	0.03
32.5	0.96	1.12	1.01					1.03	0.08
35	1.09	1.19	1.11					1.13	0.05
37.5	1.07	1.22	1.31					1.20	0.12
40	1.20	1.18	1.13	1.17	1.18			1.17	0.03
42.5	1.18	1.25	1.39					1.27	0.11
45	1.33	1.27	1.31	1.22	1.38			1.30	0.06
47.5	1.43	1.51	1.56	1.36				1.47	0.09
50	1.09	1.22	1.14					1.15	0.07
52.5	0.97	0.93	1.08	1.00	0.99			0.99	0.06
55.5	1.33	1.25	1.25	1.31	1.34	1.27	1.34	1.30	0.04

APPENDIX D

Copper concentrations (mg/g) measured in eight replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	3	4	5	6	7	8	Mean	Std Dev
1	0.024	0.012	0.013						0.016	0.006
2	0.021	0.017	0.013						0.017	0.004
3	0.019	0.013	0.014	0.013					0.015	0.003
4	0.018	0.012	0.011						0.014	0.004
5	0.016	0.017	0.018	0.016					0.017	0.001
6	0.017	0.012	0.014						0.014	0.003
7	0.014	0.016	0.014						0.015	0.001
8	0.017	0.013	0.014						0.015	0.002
9	0.021	0.019	0.013						0.018	0.004
10	0.019	0.019	0.014						0.017	0.003
12.5	0.019	0.017	0.014	0.016	0.013				0.016	0.003
15	0.016	0.014	0.017	0.013	0.013				0.015	0.002
17.5	0.017	0.014	0.014						0.015	0.002
20	0.020	0.016	0.018	0.012					0.016	0.003
22.5	0.015	0.014	0.012						0.014	0.002
25	0.018	0.016	0.012						0.015	0.003
27.5	0.016	0.015	0.015	0.011					0.014	0.002
30	0.014	0.014	0.012						0.014	0.001
32.5	0.015	0.014	0.013	0.012					0.013	0.001
35	0.016	0.013	0.013						0.014	0.002
37.5	0.014	0.013	0.011						0.013	0.001
40	0.013	0.013	0.013	0.014	0.012				0.013	0.001
42.5	0.014	0.015	0.014	0.011					0.014	0.002
45	0.017	0.014	0.011	0.012	0.012				0.013	0.002
47.5	0.015	0.014	0.011	0.010	0.010				0.012	0.002
50	0.015	0.014	0.010	0.012					0.013	0.002
52.5	0.016	0.013	0.014	0.014	0.014	0.013			0.014	0.001
55.5	0.017	0.017	0.016	0.015	0.015	0.013	0.013	0.013	0.015	0.002

APPENDIX E

Zinc concentrations (mg/g) measured in eight replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	3	4	5	6	7	8	Mean	Std Dev
1	0.124	0.091	0.089						0.101	0.020
2	0.104	0.103	0.106						0.104	0.002
3	0.099	0.191	0.089	0.082					0.115	0.051
4	0.104	0.087	0.084						0.092	0.010
5	0.115	0.099	0.106	0.093					0.103	0.010
6	0.102	0.107	0.090						0.100	0.008
7	0.105	0.104	0.089						0.100	0.009
8	0.108	0.082	0.090						0.093	0.014
9	0.097	0.107	0.079						0.095	0.014
10	0.110	0.096	0.084						0.097	0.013
12.5	0.098	0.109	0.108	0.102	0.106				0.105	0.005
15	0.091	0.102	0.098	0.088	0.112				0.098	0.010
17.5	0.096	0.102	0.098						0.098	0.003
20	0.093	0.100	0.090	0.099					0.095	0.005
22.5	0.090	0.109	0.095						0.098	0.010
25	0.094	0.099	0.094						0.096	0.003
27.5	0.096	0.122	0.100	0.095					0.103	0.013
30	0.097	0.094	0.085						0.092	0.006
32.5	0.095	0.095	0.097	0.099					0.096	0.002
35	0.090	0.095	0.085						0.090	0.005
37.5	0.092	0.095	0.088						0.092	0.004
40	0.098	0.095	0.094	0.089	0.088				0.093	0.004
42.5	0.092	0.094	0.089	0.091					0.091	0.002
45	0.093	0.092	0.086	0.113	0.088				0.094	0.011
47.5	0.088	0.090	0.097	0.094	0.102				0.094	0.005
50	0.093	0.095	0.094	0.092					0.093	0.001
52.5	0.089	0.086	0.103	0.094	0.093	0.094			0.093	0.006
55.5	0.091	0.102	0.096	0.091	0.103	0.092	0.087	0.094	0.094	0.005

APPENDIX F

Molybdenum concentrations (mg/g) measured in eight replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth cm	1	2	3	4	5	6	7	8	Mean	Std Dev
1	0.0010	0.0013	0.0011						0.0011	0.0001
2	0.0010	0.0007	0.0012						0.0010	0.0003
3	0.0008	0.0009	0.0012	0.0011					0.0010	0.0002
4	0.0009	0.0014	0.0012						0.0012	0.0003
5	0.0010	0.0010	0.0011	0.0006					0.0009	0.0002
6	0.0009	0.0009	0.0018						0.0012	0.0005
7	0.0010	0.0007	0.0021						0.0013	0.0007
8	0.0013	0.0021	0.0018						0.0017	0.0004
9	0.0010	0.0018	0.0021						0.0016	0.0006
10	0.0011	0.0009	0.0005						0.0009	0.0003
12.5	0.0011	0.0013	0.0013	0.0007	0.0009				0.0011	0.0003
15	0.0012	0.0013	0.0008	0.0006	0.0009				0.0010	0.0003
17.5	0.0011	0.0007	0.0008						0.0009	0.0002
20	0.0011	0.0008	0.0010	0.0007					0.0009	0.0002
22.5	0.0007	0.0006	0.0008						0.0007	0.0001
25	0.0011	0.0007	0.0006						0.0008	0.0003
27.5	0.0010	0.0006	0.0006	0.0007					0.0007	0.0002
30	0.0010	0.0008	0.0006						0.0008	0.0002
32.5	0.0012	0.0007	0.0009	0.0007					0.0009	0.0002
35	0.0012	0.0006	0.0006						0.0008	0.0003
37.5	0.0011	0.0006	0.0008						0.0008	0.0003
40	0.0008	0.0009	0.0013	0.0006	0.0006				0.0008	0.0003
42.5	0.0008	0.0008	0.0006	0.0007					0.0007	0.0001
45	0.0008	0.0006	0.0007	0.0007	0.0007				0.0007	0.0001
47.5	0.0007	0.0006	0.0007	0.0008	0.0006				0.0007	0.0001
50	0.0009	0.0009	0.0007	0.0012					0.0009	0.0002
52.5	0.0008	0.0005	0.0006	0.0006	0.0007	0.0007			0.0006	0.0001
55.5	0.0010	0.0009	0.0008	0.0008	0.0009	0.0007	0.0012	0.0013	0.0010	0.0002

APPENDIX G

Calcium concentrations (mg/g) measured in eight replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	3	4	5	6	7	8	Mean	Std Dev
1	4.18	4.44	4.58						4.40	0.20
2	4.66	4.15	4.98						4.60	0.42
3	3.75	2.95	3.24	3.81					3.44	0.41
4	2.90	2.79	3.26						2.99	0.25
5	2.39	3.73	2.33	3.02					2.87	0.65
6	2.95	2.55	2.76						2.75	0.20
7	2.06	2.96	2.70						2.57	0.46
8	3.08	3.48	4.38						3.65	0.67
9	3.64	2.42	5.43						3.83	1.51
10	2.79	3.04	3.39						3.07	0.30
12.5	1.86	1.35	1.30	2.40	1.85				1.75	0.45
15	2.18	0.91	1.99	2.28	1.85				1.84	0.55
17.5	2.27	1.93	2.52						2.24	0.29
20	4.66	3.95	3.99	4.37					4.24	0.34
22.5	2.29	3.01	2.31						2.54	0.41
25	3.03	2.32	2.45						2.60	0.38
27.5	1.96	2.33	1.17	1.43					1.72	0.52
30	1.16	1.80	1.76						1.57	0.36
32.5	1.32	1.63	0.93	0.68					1.14	0.42
35	1.46	0.82	0.93						1.07	0.34
37.5	1.78	1.50	1.38						1.55	0.21
40	0.81	1.18	1.61	1.13	0.93				1.13	0.31
42.5	1.22	0.94	1.40	2.10					1.42	0.49
45	1.79	2.47	1.95	1.78	1.65				1.93	0.32
47.5	1.21	1.21	1.02	1.03	1.23				1.14	0.10
50	1.05	0.97	0.47	0.68					0.79	0.27
52.5	0.73	0.57	0.55	0.85	0.52	0.52			0.62	0.14
55.5	0.94	0.81	0.65	1.25	0.86	0.61	1.20	0.83	0.89	0.23

APPENDIX H

Phosphorous concentrations (mg/g) measured in two replicates from a sediment core from Station #5 at Lake Tenkiller, 1993

Depth (cm)	1	2	Mean	Std. Dev.
1	1.43	1.58	1.50	0.10
2	1.26	1.10	1.18	0.11
3	1.62	1.29	1.46	0.23
4	1.44	1.64	1.54	0.14
5	1.16	1.16	1.16	0.00
6	1.25	1.13	1.19	0.08
7	0.85	1.47	1.16	0.44
8	1.15	1.16	1.15	0.01
9	1.40	1.54	1.47	0.10
10	1.21	1.25	1.23	0.03
12.5	1.13	1.28	1.21	0.11
15	1.22	1.12	1.17	0.07
17.5	0.74	1.30	1.02	0.40
20	1.09	0.62	0.85	0.33
22.5	0.90	0.84	0.87	0.05
25	1.28	1.12	1.20	0.12
27.5	0.97	0.97	0.97	0.00
30	1.06	0.99	1.02	0.05
32.5	0.90	0.95	0.93	0.03
35	1.21	1.17	1.19	0.03
37.5	1.14	1.19	1.16	0.03
40	0.97	1.10	1.04	0.09
42.5	0.90	1.07	0.99	0.12
45	0.82	0.96	0.89	0.10
47.5	0.78	0.75	0.77	0.02
50	0.79	0.71	0.75	0.06
52.5	0.81	0.70	0.75	0.08
55.5	0.63	0.70	0.67	0.05

APPENDIX I

Correlation coefficients (r) among parameters

Parameter	Ca	Cu	Fe	Mn	Mo	Na	Zn	Fe:Mn	Cu/Zn	(Cu+Mo)/Zn	P
Ca	1.00	0.72	0.61	0.19	0.55	0.01	0.43	0.19	0.59	0.58	0.62
Cu	0.72	1.00	0.38	0.04	0.46	0.06	0.39	0.30	NA	NA	0.47
Fe	0.61	0.38	1.00	0.48	0.70	0.13	0.34	NA	0.25	0.34	0.60
Mn	0.19	0.04	0.48	1.00	0.04	0.05	0.26	NA	0.18	0.23	0.28
Mo	0.55	0.46	0.70	0.04	1.00	0.40	0.09	0.34	0.47	NA	0.55
Na	0.01	0.06	0.13	0.05	0.40	1.00	0.08	0.09	0.18	0.26	0.16
Zn	0.43	0.39	0.34	0.26	0.09	0.08	1.00	0.08	NA	NA	0.34
Fe:Mn	0.19	0.30	NA	NA	0.34	0.09	0.08	1.00	0.38	0.50	0.03
Cu/Zn	0.59	NA	0.25	0.18	0.47	0.18	NA	0.38	1.00	NA	0.37
(Cu+Mo)/Zn	0.58	NA	0.36	0.23	NA	0.26	NA	0.50	NA	1.00	0.41
P	0.62	0.47	0.60	0.28	0.55	0.16	0.34	0.03	0.37	0.41	1.00

NA = CORRELATION DOES NOT APPLY (AUTO-CORRELATION)

VITA

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Master of Science

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