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Stable Isotopic Composition and Phosphorus Concentration in Sediment From Two Southern California Lakes

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Stable Isotopic Composition and Phosphorus Concentration in Sediment From Two Southern California Lakes

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by

Simone Claire Boudreau

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ABSTRACT OF THE THESIS

Stable Isotopic Composition and Phosphorus Concentration in Sediment From Two Southern California Lakes

by

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Master of Science, Graduate Program in Environmental Sciences
University of California, Riverside, December 2015
Dr. Michael A. Anderson, Chairperson

Excessive nutrient loading to lakes reduces water clarity, degrades biological habitat, limits light penetration, and often results in anoxia. Increased watershed urbanization is a major contributing factor of externally loaded nutrients. But even in lakes that have successfully reduced external nutrient loading rates, high nutrient concentrations may persist due to internal nutrient recycling within lake sediments. Internal phosphorus (P) cycling dynamics are a balance between sedimentation, which depends on the mineralization rate of settling organic matter; diagenetic processes within the sediment after deposition; and remobilization of P after deposition, which depends on mobile P content and elemental composition of the sediment. The interplay between these processes determines whether phosphorus is recycled or sequestered in the sediment, as well as how long it remains bioavailable. Measurement of the stable isotopes of carbon and nitrogen in sediment have enabled assessment of the sources and degree of cycling of organic matter, which is important in controlling P burial and release. In this study, stable isotopic composition, elemental composition, and phosphorus forms in the sediment from two southern California lakes that are impaired due to nutrients are assessed to determine how dynamic hydrologic conditions and management actions have influenced water and sediment quality in order to gain insight into how sediment properties and biogeochemical processes respond to varying conditions in each lake. The results of the study provide a comprehensive understanding of the sedimentological processes occurring in the lakes, which is imperative to accurately predict eutrophication trajectories and the impact that future events will have on water quality in order to develop the most effective nutrient mitigation strategies.

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Chapter 1 – Introduction

Freshwater lakes provide many ecological and societal benefits, including wildlife habitat, drinking water supply, recreational use, and aesthetic pleasure. Unfortunately, beneficial uses are increasingly being compromised due to agricultural, urban, and other forms of development that can yield enhanced nutrient loading to lakes from the watershed. Inorganic nutrients are essential to the growth and metabolism of primary producers in freshwater lakes. However, excessive nutrient input to lakes, particularly nitrogen and phosphorus, results in degradation of water quality through human-induced eutrophication. Nutrients derive from a variety of anthropogenic sources including animal waste from agriculture, fertilizers, sewage, household detergents, and fossil fuels (Wetzel, 2001). Eutrophication is characterized by increased primary production which depletes water clarity and leads to a cascade of negative effects on water quality. Decomposition of large amounts of decaying algal biomass depletes dissolved oxygen, which limits species diversity and causes fish kills, and induces even more nutrients to be released from the sediment, initiating a positive feedback loop (Horne & Goldman, 1994). Not only is this detrimental to the lake's ecosystem and wildlife, it can also produce algal toxins, odors, and poor recreational conditions.

In order to mitigate the damages to lakes, under the Clean Water Act of 1972, Section 303(d), lakes with low water quality are placed on a list of impaired water bodies. State governments are then required to establish water quality based effluent limits that support the beneficial uses determined for that specific lake and set total maximum daily loads (TMDLs) in order to achieve those standards. TMDLs signify the maximum amount of nutrients that can be loaded to a lake from point sources and nonpoint sources (including sediment) without exceeding the set standards (USEPA). However, even in lakes that have effectively reduced external nutrient input, sediments sometimes remain a significant source of nutrients to the water column as a result of nutrients accumulated during prolonged periods of high external loading. Determining the length of time that nutrients remain bioavailable as well as the processes that govern their recycling enables appropriate establishment of TMDLs and implementation of in-lake management strategies. Phosphate (PO_4^{3-}) is most often the limiting nutrient in freshwater lakes and is easier to control, thus many management strategies are specifically designed to reduce P internal loading. P loading from sediment can occur under a variety of different conditions, and in order to use the most effective management techniques, it is essential to identify the P forms present in the sediment to determine what loading mechanisms are taking place in a specific lake.

Phosphorus exists in different forms within lake sediments; each varying in bioavailability and reactivity. These forms can be broadly categorized into labile and refractory. The sediment pool of labile, or mobile-P, consists of pore-water and loosely-adsorbed P on clay particles and redox-sensitive P adsorbed on iron and manganese-oxides (Rydin, 2000; Søndergaard et al., 2003). Pore-water P is transported to the water column through diffusion due to a concentration gradient between P in bottom water and P in the sediment (Søndergaard et al., 2003). Under anoxic conditions, redox-sensitive P will be released, for example, when iron (III) is reduced to iron (II). Increased pH also induces P release from this fraction (the P-binding capacity of iron decreases with increasing pH as hydroxyl ions compete with P ions). Refractory forms of P include P adsorbed to aluminum oxides, which are not redox-sensitive, and P adsorbed to calcite. These fractions are generally considered unreactive and represent permanent burial in the sediment. Organic P includes labile and refractory forms and usually makes up the majority of total P in lakes (Wetzel, 2001; Søndergaard et al., 2003). Mineralization of labile organic matter by hydrolysis of phosphate-ester bonds results in P loading to the water column or pore-water and is intensified under high temperatures. Resuspension due to wind turbulence or bioturbation and ebullition of gases produced by microbial processes have also been established as mechanisms of internal P loading (by accelerating P diffusion/disrupting gradients) (Wetzel, 2001; Søndergaard et al., 2003).

In-lake management strategies that aim to reduce P loading include aeration and destratification, alum treatment, water level stabilization, and dredging. Aeration systems specifically reduce P release from redox-sensitive fractions by either directly injecting oxygen through pipelines at the lake bottom or by inducing destratification which increases circulation through the mixing of oxygen-rich surface waters to the hypolimnion (Task Force, 2010). Aluminum sulfate addition effectively renders P unavailable by the formation of aluminum hydroxide which binds to P and forms a flocculent, settling out on the bottom of the lake and keeping P unavailable while suppressing further P release from sediment (Wetzel, 2001; Pilgrim et al., 2007). Shallow water levels increase resuspension of sediment as well as concentrate nutrients in the water column. Thus, maintaining constant lake level reduces reintroduction of P to the water column (Wetzel, 2001). Dredging removes nutrient-rich sediment and also increases lake depth (Task Force, 2010). While not as widely utilized as other techniques, water level stabilization and sediment removal can be effective in lakes in southern California, where large fluctuations in lake level occur due to a dry climate and high water demands.

Implementation of the most effective lake management operations requires determination of the amount of potentially bioavailable P in the sediment and the sediment depth that represents active P recycling, which varies from lake to lake. Researchers have utilized sequential fractionation procedures to separate and identify different forms of sediment phosphorus and to distinguish mobile and refractory P species (Psenner et al., 1988; Pilgrim et al., 2007). The distinction between P burial and P release in the sediments is dependent on mineralization rates of OM, availability of minerals in the sediment that are capable of binding P, and the transport of dissolved P in sediment (which depends on oxygen content as well as sedimentation rate) (Moosmann et al., 2006). In lakes with large Fe:P ratios, P retention and burial depends on the oxic conditions of bottom water, whereas in lakes with low Fe:P ratios (<10), it is predominantly influenced by the composition of the sediment and organic matter mineralization (Hiriart-Baer et al., 2011). For example, shifts from algal-dominated to terrestrial-dominated organic matter decrease decomposition rates and increase P burial (Wetzel, 2001). Therefore, in addition to variations in the elemental composition of sediment, changes in mineralization due to shifting OM sources or changes in its cycling are important in controlling P burial and release, and can be interpreted from the stable carbon and nitrogen composition of sediment.

Analysis of the stable isotopic composition of OM in the sediment has proved a useful tool in inferring sources of organic matter and processes occurring during its cycling. Watershed disturbances as well as changes in nutrient loading, and subsequent shifts in dominant sources of organic matter and cycling of that matter can be inferred from sedimentary stable isotope composition analysis. Stable isotopes are forms of an element, with a different number of neutrons in the nucleus, which do not undergo radioactive decay. In lighter isotopes, fewer neutrons in the nucleus means bonds are easier to break so these elements have faster reaction rates than their heavier counterparts. Fractionation, or the difference in reaction rates (or the separation of heavy and light isotopes during biological and chemical reactions), results in changes in the ratio of heavy to light isotope (i.e. $^{13}C/^{12}C$) in residual (unreacted) material. Therefore, the ratio of heavy to light isotope in a sample, relative to a known standard, can elucidate how much cycling has taken place. Stable isotopic composition is expressed in delta notation in terms of the heavier isotope, and is defined as the ratio of heavy to light isotope, relative to a standard, with units expressed as per mil (per thousand) (Fry, 2006). For example, $\delta^{13}C$ is calculated as:

$$\delta^{13}C = \left[\left(\frac{{}^{13}C/{}^{12}C_{sample}}{{}^{13}C/{}^{12}C_{standard}}\right) - 1\right] * 1000 \tag{1-1}$$

A negative delta value indicates that the material contains more of the light isotope relative to heavy isotope. In lake analyses, the N and C isotope composition of suspended particulate OM or bulk sediment OM has been useful in determining the origin of the organic matter (Dean, 2006; Machiwa, 2010; Hiriart-Baer et al., 2011). Fractionation effects on isotopic signatures during photosynthesis and decomposition, as well as reactions during the nitrogen cycle are essential in understanding OM cycling (Hodell & Schelske, 1998; Teranes & Bernasconi, 2000; Lehmann et al., 2002; Fry, 2006).

During photosynthesis, plants fractionate CO_2 and selectively utilize ^{12}C over ^{13}C, resulting in distinct isotopic compositions depending on the photosynthetic pathway. C3 terrestrial plants (i.e. trees) exhibit an average $\delta^{13}C$ of -28‰ while C4 plants have $\delta^{13}C$ values between -14 and -10‰ (Fry, 2006; Machiwa, 2010). Autochthonous organic matter typically has a more positive $\delta^{13}C$ (-19 to -24‰) due to CO_2 limitation in lake water (Fry, 2006). Unlike atmospheric CO_2 which is essentially limitless, CO_2 can become depleted in epilimnetic water during algal blooms. Depletion of epilimnetic CO_2 results in progressive enrichment in $\delta^{13}C$ of the residual CO_2 pool as algae remove ^{12}C faster than ^{13}C, which in turn leads to progressive enrichment in $\delta^{13}C$ of algae. As their CO_2 source becomes more enriched in ^{13}C relative to ^{12}C, algae utilize increasing amounts of ^{13}C, leading to an enrichment in their isotope signatures. So in highly productive lakes, algae are commonly enriched in ^{13}C (more positive δ^{13}C values). Due to this phenomenon, past lacustrine productivity can be inferred from sedimentary analysis. In a study on three Florida lakes of different trophic levels, the hypereutrophic lake (Apopka) exhibited the highest δ^{13}C in surface sediment (-18.5‰) and the oligo-mesotrophic lake (Annie) had the lowest average sediment value (-29.5‰) (Torres et al., 2012). In Lake Ontario, δ^{13}C of OM in sediment was significantly correlated with the amount of total phosphorus in the epilimnion at the beginning of the corresponding growing season (Hodell & Schelske, 1998). Similarly, when nitrate becomes limited during large phytoplankton blooms, uptake of ^{15}N increases, resulting in an increase in δ^{15}N of algal biomass. However, δ^{15}N enrichment of algae with increasing productivity only occurs in systems in which N is a limiting nutrient. Sediment in Lake Baldeggersee, Switzerland exhibited positive shifts in δ^{15}N in years in which large phytoplankton blooms led to depletion of epilimnetic concentrations of NO_3 (Teranes & Bernasconi, 2000).

During decomposition, δ^{13}C typically declines by 1.6 to 1.8‰ due to selective decomposition of more easily degradable carbohydrates and proteins, which happen to be more enriched than constituents that are resistant to decay, as well as the contribution of ^{13}C-depleted bacterial biomass (Lehmann et al., 2002). In anoxic sediments, methanogenesis and sulfate reduction lead to a depletion in the δ^{13}C of organic matter due to the contribution of chemotrophic bacteria, which are depleted in

^{13}C. Sediment δ^{13}C values less than -30‰ in Yellowstone National Park lakes were attributed to sulfate reduction occurring in the hypolimnion (Dean, 2006). In highly productive, eutrophic lakes, the shear abundance of enriched C produced in the epilimnion tends to overprint any depleted contribution from microbial biomass (Dean, 2006).

The δ^{15}N signature of autochthonous organic matter is highly variable and depends on the nitrogen sources utilized, biogeochemical processes, and degree of nitrate utilization (Lehmann et al., 2002). If the majority of nitrate is produced through nitrogen fixation, organic matter will exhibit lower δ^{15}N because there is little fractionation during N-fixation and atmospheric N_2 has a δ^{15}N of zero (Fry, 2006). N-fixing organisms such as cyanobacteria possess a δ^{15}N of -2 to +2‰ (Teranes & Bernasconi, 2000). Preferential metabolism and excretion of ^{14}N ammonia leaves residual N in organisms more enriched. This process results in a 2.2 to 3.4‰ increase in δ^{15}N with each trophic level increase (on the food web). Thus, human and animal waste (wastewater) has a δ^{15}N 10-20‰ (Teranes & Bernasconi, 2000). Increasing wastewater input to lakes and the resulting integration of enriched nitrate and ammonium has been ascribed to increases of δ^{15}N in the sediment of 6‰ in Lake Baldeggersee, Switzerland (Teranes & Bernasconi, 2000). Denitrification also results in enrichment of residual N (due to the preferential reduction of ^{14}N-rich nitrate), resulting in signatures of 10-20‰, which overlap those of wastewater (Teranes & Bernasconi, 2000). Examination of additional water quality parameters such as wastewater additions and dissolved oxygen in the hypolimnion are often necessary to differentiate between the two processes. In Lake Baldeggersee, denitrification is limited due to artificial aeration in the hypolimnion, therefore it was ruled out as being a potential cause for the $\delta^{15}N$ increase that was observed (Teranes & Bernasconi, 2000). Gradually increasing $\delta^{15}N$ values (1.2‰ increase) in Lake Erie's central basin sediments were attributed to denitrification, as they matched the history of anoxia observed in the hypolimnion (Lu et al., 2010).

During the decomposition of organic matter, changes to the $\delta^{15}N$ sedimentary signature are the result of two opposing processes, ammonium production during OM decomposition which leads to enriched $\delta^{15}N$ in residual OM due to the preferential mineralization of ^{14}N ammonium and the contribution of bacterial biomass which is ^{15}N-depleted (Torres et al., 2012). During periods of anoxic conditions and stratification, sedimentary $\delta^{15}N$ typically decreases by 2.5-4‰ due to the increasing contribution of depleted bacterial biomass and utilization of ammonium by phytoplankton (ammonium release is high under anoxic conditions) (Hodell & Schelske, 1998; Teranes & Bernasconi, 2000).

Sedimentary stable isotopic composition analysis has enabled the elucidation of changing proportional contributions of autochthonous vs. allochthonous organic matter as well as the extent of decomposition of that organic matter. Together with elemental composition, the C and N isotopic composition can help to determine if stratigraphic changes in P concentrations and bioavailability are due to changes in diagenetic processes, sediment chemistry, OM type, or productivity. Comparing multiple sedimentary parameters enables a more complete understanding of the processes that influence nutrient cycling as well as overall lake productivity.

The research presented in the following chapters examines the phosphorus speciation, and elemental and stable isotopic composition of sediment from two southern California lakes that are both impaired due to nutrients. The objective of this research was to determine how the dynamic hydrologic conditions and management histories of Lake Elsinore and Big Bear Lake have influenced sediment properties, including organic matter mineralization, nutrient recycling, and biogeochemical processes. Results of this study provide a better understanding of how sediment processes in each lake respond to changing hydrologic and climatic conditions and can be applied as a type of sediment "fingerprint" to predict eutrophication trajectories and prevent significant reductions in water quality under future lake conditions through implementation of effective management strategies.

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Chapter 2 – Stable Isotopic Composition, Bulk Elemental and Phosphorus Concentrations in Lake Elsinore Sediment

Introduction

Lake Elsinore is a shallow, polymictic, recreational lake located in southwestern Riverside County in the San Jacinto River watershed. The natural lake formed tectonically thousands of years ago in a down-faulted graben and is functionally a terminal basin for the San Jacinto River (Byrne, 2004). As a result, lake dimensions vary; Lake Elsinore presently has a surface area of about 3,000 acres, an average depth of about 4 meters, and a maximum depth of 6.7 meters (Anderson, 2010; EVMWD). At capacity, (lake level elevation 385 meters) mean and maximum depth are approximately 10 meters and 15 meters, respectively (Anderson, 2010; EVMWD). The lake is bordered on the west by the Santa Ana Mountains (Cleveland National Forest) and on the east by the high density residential city of Lake Elsinore which has experienced consistently increasing urbanization and decreasing agricultural land-use since 1980 (City of Lake Elsinore, 2006). The semi-arid regional climate induces very little annual precipitation (10.6 inches), the majority occurring during winter, as well as high evaporation rates (15,000 acre-ft. per year, equivalent to a 1.4 meter reduction in lake level) (Lake Elsinore/Canyon Lake TMDL Task Force, 2007; Horne, 2009; Comprehensive Nutrient Reduction Plan for Lake Elsinore and Canyon Lake (CNRP), 2013). The lake is the terminus of the ephemeral San Jacinto River, thus inflow is limited to winter months during very wet years as well as run-off events from precipitation in the local watershed. Average inflow to Lake Elsinore (over the past 30 years) is about 13,900 acre-ft. per year, which includes local precipitation as well as inflow from the San Jacinto River when the upstream Canyon Lake dam overflows (USGS, #11070500). However, inflow in the past three years has been substantially less, averaging 1,700 acre-ft. per year (USGS, #11070500). Consequently, lake levels are prone to extreme variability. Together with urbanization and high levels of nutrient loading to the lake, fluctuating lake levels have created extremely eutrophic conditions in the lake.

Lake Elsinore experiences poor water quality due to high internal and external loading of nutrients that is exacerbated by high evaporation rates and limited flow-through, resulting in the concentration of nutrients and total dissolved solids (TDS) in the water column. TDS has been increasing since 2005 and in 2014 reached 2,577 mg/L, the highest recorded concentration since regular water quality monitoring began in Lake Elsinore in 2000 (Noblet, unpublished data). Nutrient concentrations in the lake are elevated and also variable, with total phosphorus (TP) and total nitrogen (TN) concentrations in the water column averaging 0.3 and 4 mg/L, respectively (Noblet, unpublished data). High nutrient concentrations have induced massive phytoplankton blooms in recent years. Chlorophyll concentrations can exceed 300 µg/L during dry years and 100 µg/L during wet years, such as in 2005 (Horne, 2009). In 2014, chlorophyll concentrations peaked during the winter months at 375 µg/L (Noblet, unpublished data). Phytoplankton blooms also reduce water clarity, often generating average Secchi depths of 0.5 meters or less (CNRP, 2013). Despite the shallow water level in Lake Elsinore, transient stratification and the associated development of anoxic conditions frequently occur in the hypolimnion due to massive amounts of decaying algal biomass.

Lake Elsinore was added to the Clean Water Act, Section 303(d) list in 1994 by the Santa Ana Regional Water Quality Control Board due to impairment caused by excessive nutrients (nitrogen and phosphorus) and low dissolved oxygen; the listing was approved by the USEPA in 2005 (CNRP, 2013). Total maximum daily loads (TMDLs) were set for total phosphorus and total nitrogen at 28,584 mg/kg TP and 239,025 mg/kg TN in order to comply with numeric targets of 0.1 mg/L annual average TP and 0.75 mg/L annual average TN (Basin Plan, 1995). Despite some reduction in external nutrient loading, internal loading from the sediments remains a predominant source of nutrients to the water column. Average sediment flux rates of ammonium-N and phosphate-P are 86 mg m^{-2} d^{-1} and 10.2 mg m^{-2} d^{-1}, respectively (CNRP, 2013).

In-lake management projects that have been implemented to improve water quality include a project to reduce lake surface area, installation of a destratification/diffused aeration system, and lake-level stabilization through the addition of recycled wastewater. Because Lake Elsinore is typically P-limited, mitigation strategies are focused on reducing P loading (external and internal). The Lake Elsinore Management Project, which included the construction of a levee, decreased the surface area from 6,000 to 3,000 acres and increased lake mean depth in order to reduce evaporation rates, increase water quality, and provide flood control. The project began in 1988 and was completed in 1995 (City of Lake Elsinore, 2006). The first part of the in-lake aeration system was implemented in 2004 when axial flow pumps were installed to promote destratification by transporting oxygen-rich surface water to bottom waters (Task Force, 2007). A bubble-diffuser was installed a few years later and began operating in 2008. Twelve diffused air pipelines on the lake bottom lift oxygen-poor water to the surface to be resaturated by the atmosphere (CNRP, 2013). The aeration system functions during summer months, when bottom waters are often depleted in dissolved oxygen (DO) (Task Force, 2007). Due to widely fluctuating lake levels having a significant impact on water quality, about 5,000 acre-ft. per year of highly treated wastewater is supplied to the lake by the Elsinore Valley Municipal Water District (EVMWD) (Task Force, 2007). The addition of reclaimed wastewater began in 2002. Inputs were briefly suspended following the El Niño winter of 2004/2005 and resumed again in 2007 (Task Force, 2007). Because wastewater contains substantial levels of nutrients, EVMWD is required to reduce phosphorus and nitrogen concentrations before discharging to Lake Elsinore. The waste load allocations under the TMDL for reclaimed wastewater are 7.4 and 3.7 tons per year of TN and TP (Horne, 2009). The final nutrient concentration requirement for the wastewater was developed with the intention of being offset by the reduction in external loading from point sources, as well as the predicted 30-35% reduction in nutrient (P) loading from the sediments due to aeration and subsequent formation of iron oxides which bind P to the sediments (Horne, 2009). However, waste load allocations have been exceeded, especially in terms of TN, and despite the introduction of an aeration system, sediment remains anoxic and bottom water often exhibits depleted DO conditions as well (Lake Elsinore & Canyon Lake TMDL Task Force, 2010).

In order to restore water quality in Lake Elsinore for ecological and recreational beneficial uses, it is essential to understand nutrient (especially P) and organic matter biogeochemical processes that contribute to recycling vs. permanent burial in the sediment. Identifying mobile and refractory P forms in the sediment is essential to understanding its mobility. Diagenetic processes can influence P and N concentrations and can mobilize organic and inorganic P and N forms.

Diagenesis can also alter the stable isotopic composition of sediment. The $\delta^{13}C$ and $\delta^{15}N$ signatures of sediment can enable interpretation of the diagenetic processes of organic matter due to fractionation during biological and chemical reactions, and stable isotopes have also been a useful tool in inferring sources of organic matter and processes occurring during its cycling (Hodell & Schelske, 1998; Teranes & Bernasconi, 2000; Lehmann et al., 2002; Fry, 2006; Dean, 2006; Machiwa, 2010; Hiriart-Baer et al., 2011).

Analysis of the variations in stable isotopic composition, elemental composition, and phosphorus concentration in sediment can be used as a fingerprint to infer how lake processes have affected the cycling of organic matter and nutrients in lakes in response to varying conditions. Lake Elsinore sediments were analyzed for the aforementioned properties with the objective of determining how sediment depositional and biogeochemical processes respond to dynamic hydrologic conditions and management actions.

Methods

Sample Collection

Two replicate intact cores were collected from profundal sediment ("Site 6", 33.66879° N, 117.35127° W) in Lake Elsinore on July 17, 2014 with a 1 meter polycarbonate tube with a 6.5 cm diameter. Water was carefully siphoned off the top of each core and the sediment was sectioned into 1 cm (for the top 10 cm) or 2 cm (for sediment deeper than 10 cm) intervals. Each section was homogenized and stored at 4°C under N_2 conditions in 50 mL polypropylene centrifuge tubes. A subsample from each interval was used for water content determination. To calculate water content, the wet sediment was pre-weighed into tin cups and oven-dried at 105°C until reaching a constant weight (1-2 days).

Water was collected from 0.5 meters below the water surface at Site 6 on September 17, 2014 and June 18, 2015 and analyzed for isotopic composition of suspended organic matter (mainly phytoplankton). The water was stored in 20 L Nalgene jugs at 4°C until later filtration. The water collected in 2014 was stored for six months, over which it experienced an unknown period of time at about 25°C, due to technical issues. Therefore suspended organic matter (SOM) experienced some decay over this period of time. Due to the shallow nature of Lake Elsinore, sediment often exhibits the same temperature as the water column, which averages 26-28°C in surface and bottom water during the summer (Lawson & Anderson, 2007). Consequently, this decay is thought to reflect, to at least some degree, natural decomposition processes operating within the lake.

Elemental Composition (XRF)

Bulk elemental composition was determined on sediment samples using a Spectro XEPOS HE Benchtop X-ray Fluorescence Spectrometer flushed with 85 L hr^{-1} of helium gas (modified EPA Method 6200). Approximately 5 g of wet sediment from each sediment core interval was dried at 50°C and ground with a mortar and pestle prior to X-ray fluorescence analysis. One source energy and four excitation targets were utilized per sample at count times of 200 seconds: excitation energy of 40 kiloelectron volts (kV) and 1 mA current; 60 kV and 0.66 mA; 25 kV and 1.6 mA; 20 kV and 2 mA.

Phosphorus Species

Forms of P in bottom sediment were extracted using the fractionation scheme described in Pilgrim et al. (2007). 0.2-0.25 grams of wet sediment was added to 50 mL polycarbonate centrifuge tubes, followed by a sequential phosphate extraction which utilized different reagents to measure the amount of phosphate in three different fractions within the sediment. The reagent solutions were 1M ammonium chloride (NH_4Cl) which extracts pore-water and loosely-adsorbed P, followed by bicarbonate buffered dithionite solution (0.11M $NaHCO_3$/0.11M NaS_2O_4) that extracts redox-sensitive P bound to iron and manganese hydroxides (Fe-P), and lastly 0.1M sodium hydroxide, NaOH, that extracts non-reducible, aluminum-bound P (Al-P). The sum of the phosphate extracted in the first two steps represents mobile phosphorus, or phosphorus that can be released to the water column under certain conditions. Aluminum-bound phosphate is generally considered to be a recalcitrant form that will not be released. 10 mL of each extract was added to the centrifuge tube. After each sequential reagent addition, the samples were placed on a shaker table for varying amounts of time: two hours for loosely-adsorbed P, one hour for Fe-P, and 16 hours for Al-P (Pilgrim et al., 2007). Subsequent to each reagent addition and mixing, samples were centrifuged at 3,000 rpm for 20 minutes. The supernatant was decanted, filtered through 0.45 µm membrane filters, and stored in 20 mL HDPE scintillation vials in the freezer until analysis. The residual sediment continued on in the procedure after the supernatant from each step was decanted. One out of every 10 samples was replicated and 2 method blanks per core were used (no sediment, just reagent and centrifugation). Soluble reactive phosphorus was determined colorimetrically for each supernatant on a Seal AQ2 discrete analyzer following the automated ascorbic acid reduction method 4500-P F (APHA, 1998). Absorbance was measured at 880 nm. Calibration control blanks and calibration control verifications were used to verify accuracy.

Stable Isotopic Composition

Sediment subsamples were dried at 50°C and ground to a homogenous mixture with a mortar and pestle. The dried sediment was fumigated with concentrated HCl (12N) in a desiccator for 24 hours in order to remove inorganic C. Replicate samples were analyzed without fumigation to ensure all $CaCO_3$ had been removed. Suspended organic matter from epilimnetic water was filtered through 47 mm Whatman glass microfiber filters and then oven-dried at 50°C. Stable C and N isotopic compositions as well as %OC (weight percent) and %N were analyzed on a Costech elemental analyzer coupled to a Delta V Advantage Isotope Ratio Mass Spectrometer at the Facility for Isotope Ratio Mass Spectrometry (FIRMS) at University of California, Riverside. One in every ten samples was replicated.

Results

Using the sedimentation rate of 1.27 cm/year previously determined by Byrne et al. (2004), the dates corresponding to given sediment depths were calculated using the formula shown below and plotted on each depth profile as a secondary y-axis to allow comparison of sediment properties over time and with lake management activities.

$$t_z = t_0 - (z/1.27\ \text{cm yr}^{-1}) \qquad (2\text{-}1)$$

where t = date (decimal year) at sediment depth z

t_0 = date at time of sediment collection (2014.5)

z = sediment depth (cm)

Historical lake management activities are summarized in Figure 2-1 for reference. Prior to the completion of the Lake Elsinore Management Project (LEMP) in 1995, Lake Elsinore was larger and shallower with presumably greater mixing and circulation. The completion of the project in 1995 marks the transition to a deeper mean lake depth with a reduced surface area. Addition of supplemental recycled wastewater began in 2002 and continued through 2004 and from 2008-present.

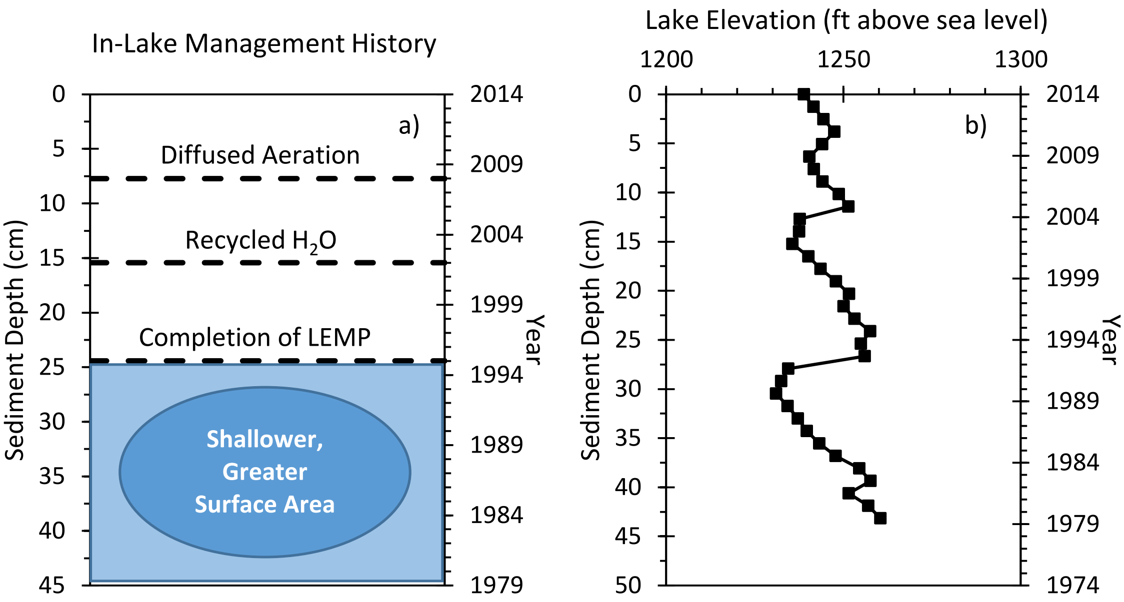

Figure 2-1. a) Historical lake management in Lake Elsinore: Completion of LEMP, 1995; Supplemental recycled wastewater begins, 2002; Aeration system begins operating, 2008. b) Lake Elsinore water surface elevation in feet above sea level.

Water Content

Water content of sediment increased with decreasing depth (and time), from about 70% to 90%, with the exception of a decrease in water content (which is reflected in both replicates) from a depth of 22 cm to 10 cm in core 6-A and 22 cm to 16 cm in core 6-B. Water content is significantly correlated with organic carbon, total nitrogen, and calcium (Table 2-1).

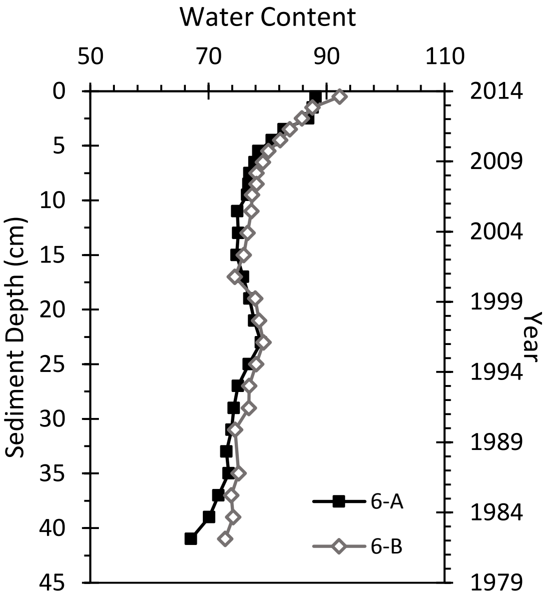

Figure 2-2. Water content (%) depth profiles at Site 6.

Elemental Composition

Organic carbon increased by 5% from the bottom to the top of the cores (Figure 2-3a). Organic carbon and total nitrogen concentrations reflect an increase from 30 cm to 25 cm as well as an increase up-core in the top 10 cm. Nitrogen increased from 0.25

to 0.75% throughout the length of the cores (Figure 2-3b). Organic carbon and nitrogen are significantly correlated in both cores at p=0.001 (r=0.97) (Table 2-1). The gradual increase in OC in the top 10 cm reflects an exponential increasing trend with decreasing depth, as the data better fit an exponential function (average r=0.88) than a linear function (average r=0.84). Similarly, the up-core increase in N in the top 10 cm better fit an exponential function (r=0.84) than a linear function (r=0.79). OC:N remained relatively constant with depth in both cores, at a value of 10, with minor fluctuations (Figure 2-3c). The OC:N of suspended organic matter collected in June 2015 was 6.9±0.2. Total phosphorus increased from 0.1% at the bottom of the core to 0.15% at the top of the core (Figure 2-3d). TP exhibits an up-core exponential increase in the top 10 cm (r=0.86 vs. r=0.84 for linear fit). The depth profiles for silicon and aluminum reveal an increase between 25 and 30 cm after which the concentrations returned to background levels and remained relatively constant to the top of the cores (Figure 2-4a, b). Silicon and aluminum are significantly correlated (r=0.99), and their stoichiometric ratios suggest the presence of alumino-silicate minerals such as montmorillonite (Wetzel, 2001) which has a 2:1 molar ratio of Si to Al. Calculation of the ratio of moles of Si per gram (0.006) to moles Al per gram (0.003) in Lake Elsinore sediments resulted in a value of 2. Sulfur (S) increased from 6,000 µg/g in 1989 to 2,000 µg/g in 1994 after which it remained constant with sediment depth (Figure 2-4c). Calcium (Ca) increased from 4% at the bottom of the core to 10% at the top (Figure 2-4d). The increase was not a gradual, constant increase. Instead calcium increased from the bottom of the core to 25 cm (1994). It remained constant from 1994 to 10 cm (2007), after which it increased exponentially to the top of the core (r=0.93 for exponential fit, vs. r=0.91 for linear fit). Calcium also exhibits a significant correlation with OC and N (Table 2-1). Iron showed a similar but opposite trend as calcium, decreasing until 1994, remaining relatively constant until 2006, then decreasing to the top of the core (Figure 2-5). Iron and calcium are significantly negatively correlated (Table 2-1).

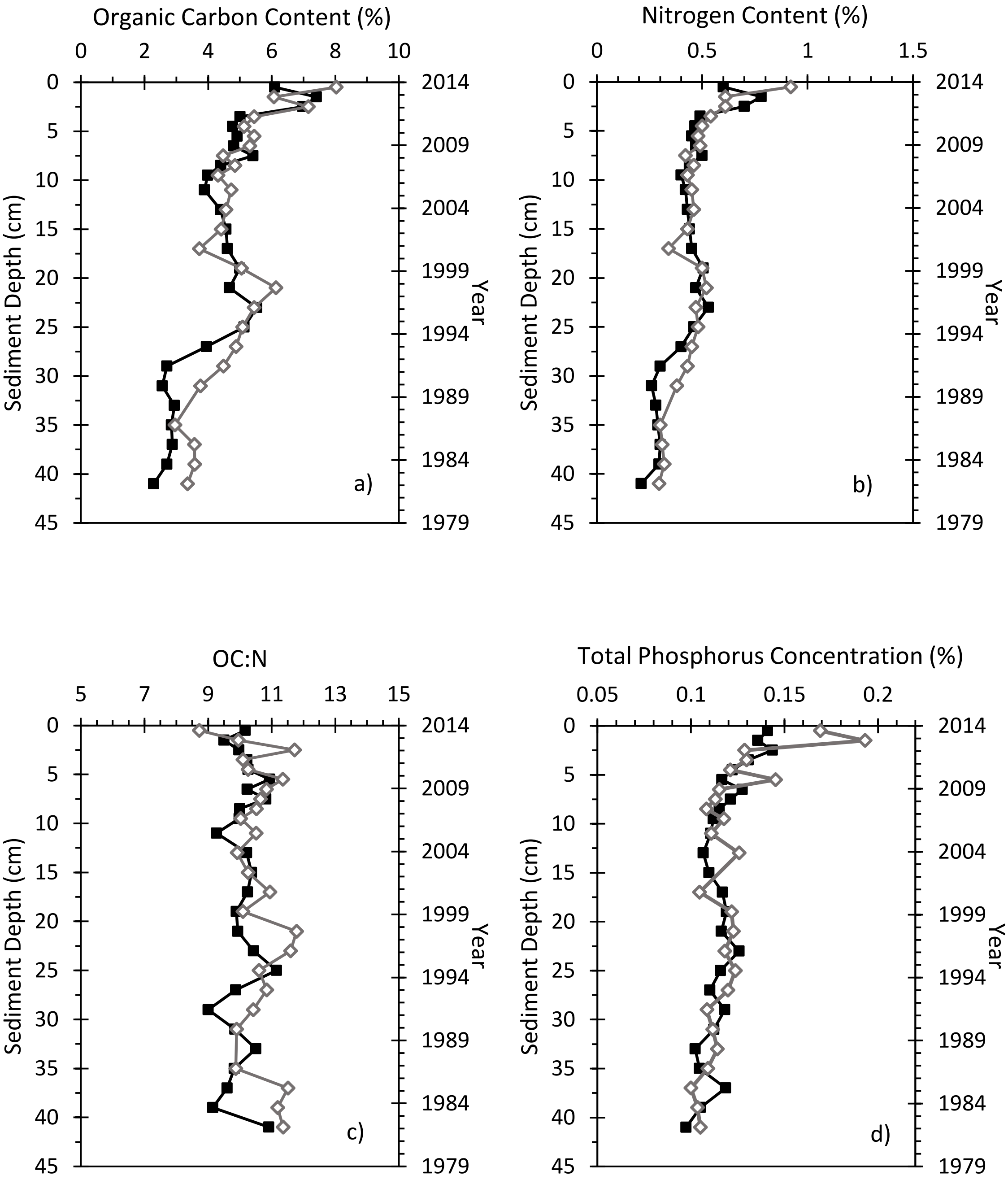

Figure 2-3. Sediment depth profiles of a) organic carbon content, b) total nitrogen content, c) OC:N ratio, and d) total phosphorus concentration in Lake Elsinore. Solid, black squares represent data points in core 6-A. Open, grey diamonds represent data points in core 6-B.

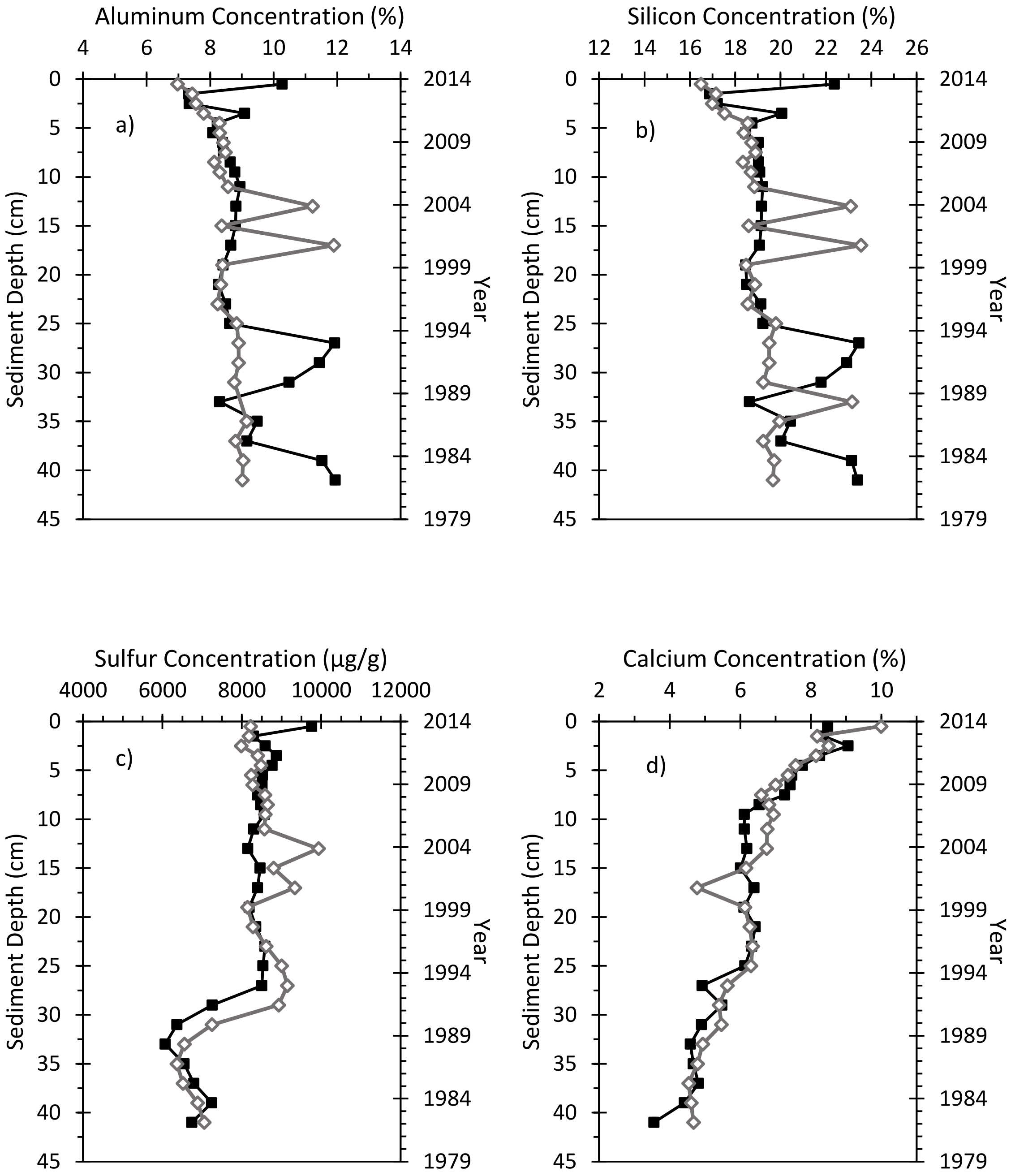

Figure 2-4. Sediment depth profiles of a) aluminum, b) silicon, c) sulfur, and d) calcium concentrations in Lake Elsinore. Solid, black squares represent data points in core 6-A. Open, grey diamonds represent data points in core 6-B.

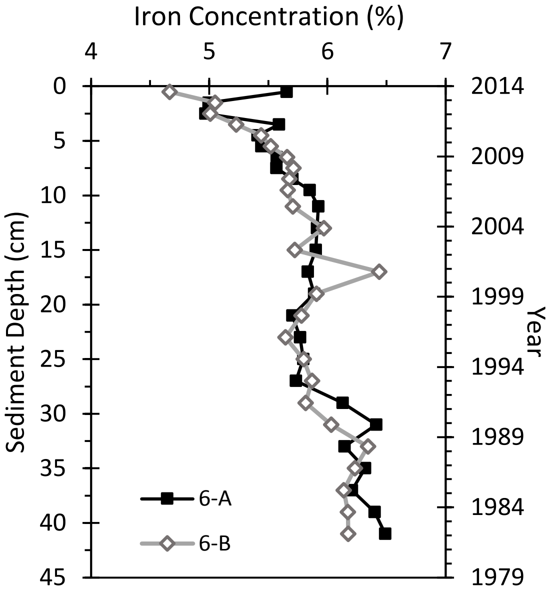

Figure 2-5. Iron concentration depth profiles in Lake Elsinore sediment.

Table 2-1. Correlation table showing r values for bulk elemental properties in Lake Elsinore sediment. With n=26, an r value of 0.51 is statistically significant at p=0.001.

	Depth	Water	%OC	%N	Al	Si	P	S	K	Ca	Ti	Fe
Depth	1.00											
Water	-0.79	1.00										
%OC	-0.75	0.89	1.00									
%N	-0.75	0.91	0.97	1.00								
Al	0.48	-0.56	-0.62	-0.59	1.00							
Si	0.48	-0.53	-0.60	-0.57	0.99	1.00						
P	-0.57	0.72	0.63	0.68	-0.39	-0.35	1.00					
S	-0.67	0.49	0.58	0.57	-0.04	-0.02	0.43	1.00				
K	0.91	-0.79	-0.86	-0.85	0.58	0.58	-0.58	-0.73	1.00			
Ca	-0.90	0.94	0.88	0.90	-0.60	-0.58	0.70	0.56	-0.88	1.00		
Ti	0.88	-0.87	-0.87	-0.87	0.50	0.50	-0.65	-0.66	0.95	-0.93	1.00	
Fe	0.81	-0.89	-0.89	-0.90	0.70	0.69	-0.66	-0.49	0.91	-0.93	0.94	1.00

Phosphorus Species

Redox-sensitive phosphate was the least abundant fraction, averaging about 75 µg/g dry weight (dw) throughout the length of the cores and remaining constant with depth (Figure 2-6). Loosely-adsorbed and pore-water phosphate represented the majority of the mobile-P (~60%). With the exception of two noticeable increases at 20 and 35 cm, loosely-adsorbed/pore-water P remained at about 150 µg/g dw below 10 cm depth. In the upper 10 cm, the fluctuations stabilized, and smaller variations centered around 125 µg/g dw. This signifies a shift to lower pore-water P concentrations in more recently deposited sediment. Aluminum-bound P was the most abundant of the fractions measured using the sequential extraction procedure, with concentrations ~135 µg/g dw at the bottom of the cores. The concentration exhibited a large increase to ~200 µg/g dw at about 25 cm, followed by a shift to greater concentrations in depths <25 cm, averaging 150-160 µg/g dw. The increase and subsequent shift to greater mean concentrations occurred in 1994, around the same time the Lake Elsinore Management Project was completed (Figure 2-1; Figure 2-6).

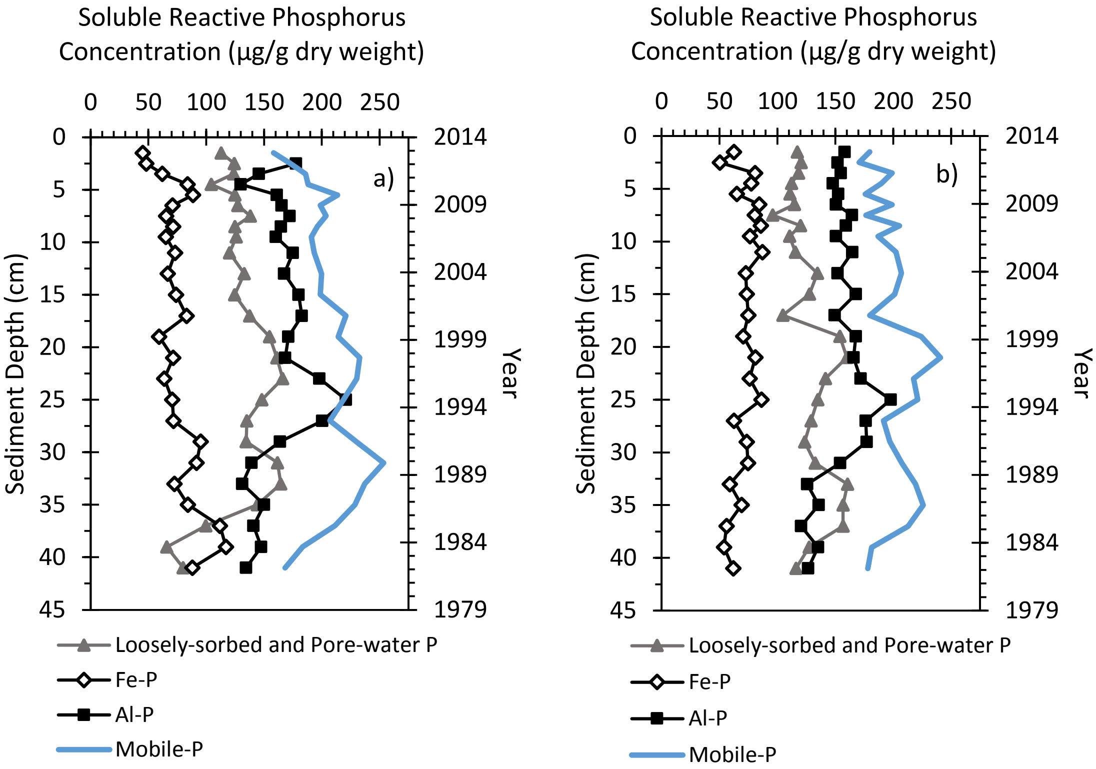

Figure 2-6. Phosphorus species concentration depth profiles in a) core 6-A and b) core 6-B.

Stable Isotopic Composition

Stable isotopic composition results are presented in delta notation relative to the Vienna Pee Dee Belemnite Standard (for C) and Air N_2 standard (for N) and calculated using the equation, exemplified below for ^{13}C:

$$\delta^{13}C = \left[\left(\frac{{}^{13}C/{}^{12}C_{sample}}{{}^{13}C/{}^{12}C_{standard}}\right) - 1\right] * 1000 \qquad (2\text{-}2)$$

The filters exhibited suspended organic matter (SOM) with $\delta^{13}C$ values of -20.2±0.6‰ and -23.7±0.4‰ in the fresh and decomposed samples, respectively (Table 2-2). The measured $\delta^{15}N$ of the SOM was 5.8±0.2‰ and 10.2±1.6‰ in the fresh and decomposed samples, respectively. The decomposed SOM exhibited about a 3‰ higher $\delta^{15}N$ than the top sediment and about a 4‰ more negative $\delta^{13}C$ than the top sediment. Fresh SOM reflect the same $\delta^{13}C$ values as the top sediment and slightly lower (0.7‰ difference) $\delta^{15}N$.

Values of $\delta^{13}C$ gradually increased in both cores from approximately -24‰ at 29 cm to -20‰ at the top of the cores (Figure 2-7a). In both replicate cores, $\delta^{13}C$ increased from about -25‰ at the bottom of the core to -20‰ at the top of the core. This gradual 5‰ increase towards the top of the core represents a significant change with depth in core 6-A sediment (r=0.85).

The $\delta^{15}N$ depth profiles reflect three distinct periods which have significantly different mean $\delta^{15}N$ values. From 41 to 35 cm (the bottom section of the core), mean $\delta^{15}N$ values were 6.2±0.4‰ and 6.5±0.4‰ for cores 6-A and 6-B, respectively

(Figure 2-7b). This section represents the time frame from approximately 1982 to 1988, when the lake was shallow, prior to completion of the Lake Elsinore Management Project. After 1988, during the transition from a shallower, larger surface area lake to a deeper lake with a smaller surface area, $\delta^{15}N$ shifted to lower, more variable values with means 5.3±0.5‰ and 5.8±0.4‰. This period lasted from 31 cm to 17 cm (1990-2001), after which point the signatures increased to 7.1±0.4‰ and 6.9±0.6‰ in cores 6-A and 6-B, respectively. In the top layer of sediment, $\delta^{15}N$ values vary little and the high values extend to the top of the cores.

Table 2-2. Stable isotopic composition of suspended organic matter (SOM)

Sample	$\delta^{13}C$ (‰ vs. VPDB)	$\delta^{15}N$ (‰ vs. Air N_2)
SOM, Decayed	-23.7±0.4	10.2±1.6
SOM, Fresh	-20.2±0.6	5.8±0.2

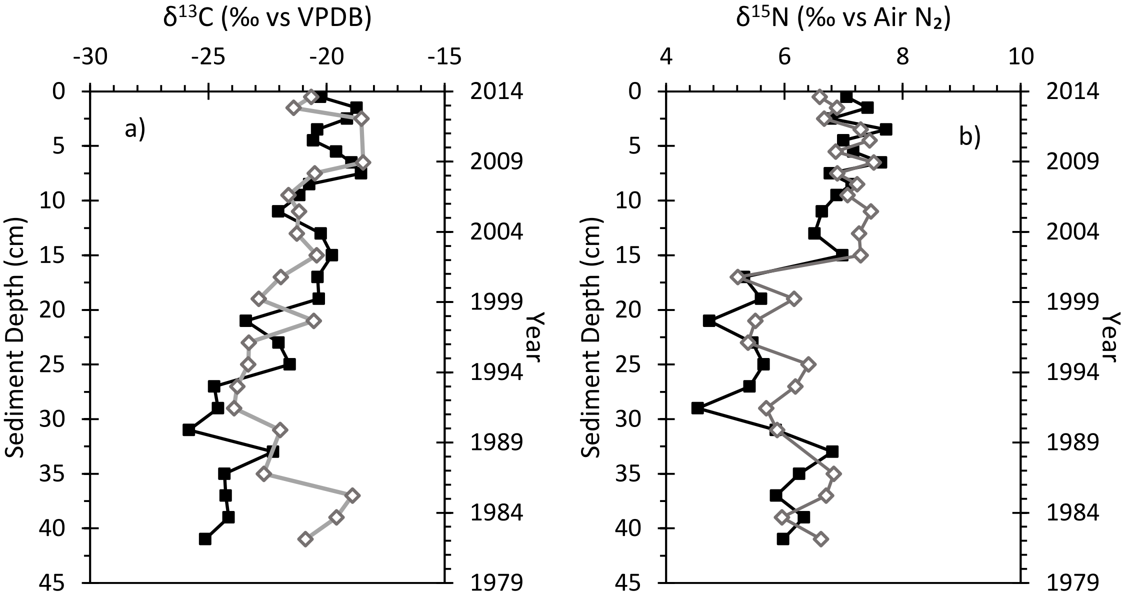

Figure 2-7. Stable carbon (a) and nitrogen (b) isotopic composition of Lake Elsinore sediment relative to standards. Solid, black squares represent data points in core 6-A. Open, grey diamonds represent data points in core 6-B.

Discussion

Elemental Composition

The organic carbon and total nitrogen concentrations increased around the same time that the Lake Elsinore Management Project was completed and mean lake depth/surface elevation increased (Figure 2-1b; Figure 2-3). A greater water depth would have resulted in enhanced organic matter preservation due to increased stratification and less mixing, and thus depleted oxygen levels. Another possible explanation for the increase is the amount of organic matter delivered to a given surface area of sediment would have increased when the lake surface area decreased and depth increased, assuming comparable levels of productivity. An exponential decrease with depth in the top sediments of organic carbon and nitrogen profiles is generally representative of decomposition (Wetzel, 2001). Sediment at the top of the core has experienced less diagenetic degradation than sediment at 10 cm depth and therefore will contain more organic matter. The fact that OC and N are significantly correlated is further confirmation that the decrease in concentrations with depth is due to decomposition because N is utilized by bacteria during respiration and conversion of organic carbon into CO_2, and N typically decomposes at a similar rate as OC (DiToro, 2001). In addition, supplemental water column nitrogen data does not reflect an exponential increase up-core; concentrations vary with no significant trend (Figure 2-8). Anderson (2010) indicated that total nitrogen content in sediment grab samples (top 10 cm) from fine-textured profundal sediment collected in 2000 and 2010 did not significantly change. This observation further supports the argument that the exponential increase in N toward the top of the sediment is due to degradation processes.

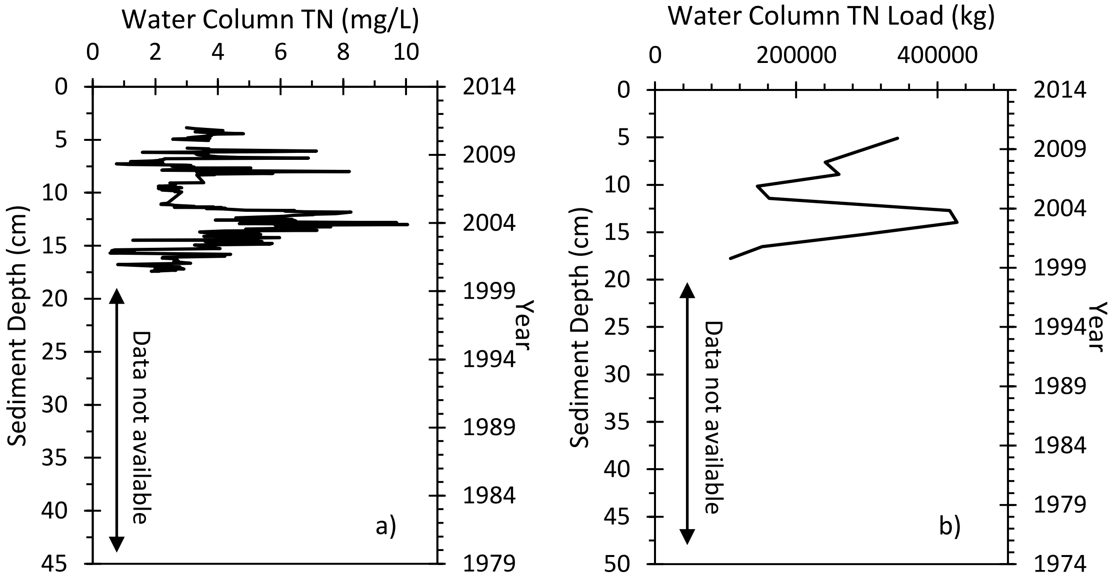

Figure 2-8. Average total nitrogen concentrations (a) and total nitrogen load (b) in Lake Elsinore's water column plotted against time and corresponding sediment depth (supplemental data from James Noblet).

It is common for the C:N ratio of organic matter to increase with depth in the sediment as N is preferentially utilized (Lehman et al., 2002). The fact that OC:N in Lake Elsinore sediment remains approximately constant with depth suggests that OM is already highly mineralized in the water column before it reaches the sediment (Figure 2-3c). The OC:N of suspended organic matter was 6.9, which is 3.1 lower than the sediment, indicating N is selectively recycled as organic matter is settling and/or resuspended. These results are similar to those detected in 2003 in which C and N content of sediment traps was compared to that of the sediment. The C and N contents both decreased from the sediment trap to the sediment and C:N increased from 7.7 to 8.6, indicating greater recycling of N relative to C, although both elements showed evidence of recycling in the water column. From the results of the study, it was concluded that there is substantial recycling occurring on settling particles in the water column (Anderson, 2011). In a study on Lake Simcoe, Canada, in 2011, the deepest bay, Kempenfelt Bay, exhibited constant C:N with sediment depth and this was attributed to the OM being highly recycled in the water column prior to sedimentation (Hiriart-Baer et al., 2011).

Average TP concentration in Lake Elsinore sediment (0.125% or 1,250 µg/g) is consistent with concentrations quantified on other eutrophic lake sediments, which typically range from 1,000 to 1,900 µg/g in surficial sediments (Rydin, 2000; Kapanen, 2012; Dittrich et al., 2013). The depth profile for total phosphorus also reflects an exponential decrease in concentration with sediment depth in the top 10 cm (Figure 2-3d). This exponential decrease in total phosphorus is typical for eutrophic lakes and generally represents mineralization of organic phosphorus (Carey & Rydin, 2011). Fitting an exponential equation to TP concentration in the top 10 cm results in r=0.85 and 0.79 for cores 6-A and 6-B respectively, verifying the exponential trend. We assume that this trend is in fact due to the decomposition of organic matter and not due to increased total phosphorus loading to the lake because organic carbon and TP are significantly correlated in the top 10 cm and the decrease in OC with sediment depth is assumed to be the result of decomposition (see above). Correlation of TP to OC could in some cases reflect increasing chlorophyll biomass (OC) due to an increase in TP loading. However, water quality chlorophyll concentrations in Lake Elsinore do not reflect similar trends (Figure 2-9c). Also, external P loading has not been increasing in the past 10 years as revealed in the water column TP concentrations from 2000 to 2014 (Figure 2-9a, b). Total phosphorus concentration and load in the water column peaked in 2005 and has been variable since then, rather than exponentially increasing (Anderson, 2010). Anderson (2010) measured a decrease in mean TP concentrations in sediment grab samples from 916 mg/kg in 2000 to 785 mg/kg in 2010, although the difference was not statistically significant. These results further demonstrate that diagenetic processes are occurring in the surficial sediment. If the increase in TP toward the top of the sediment reflected increased TP loading to the lake, TP in the grab samples would be expected to increase from 2000 to 2010, not decrease or remain the same. He also concluded that pore-water P concentrations were significantly correlated with organic carbon (r^2=0.87). A study on a core collected from Lake Elsinore in 2001, however, found that TP was unchanged with depth but that organic P showed an exponential decrease. This difference is interesting, in that it suggests a greater contribution of other P forms to total P in 2001 compared to 2014 (CNRP, 2013).

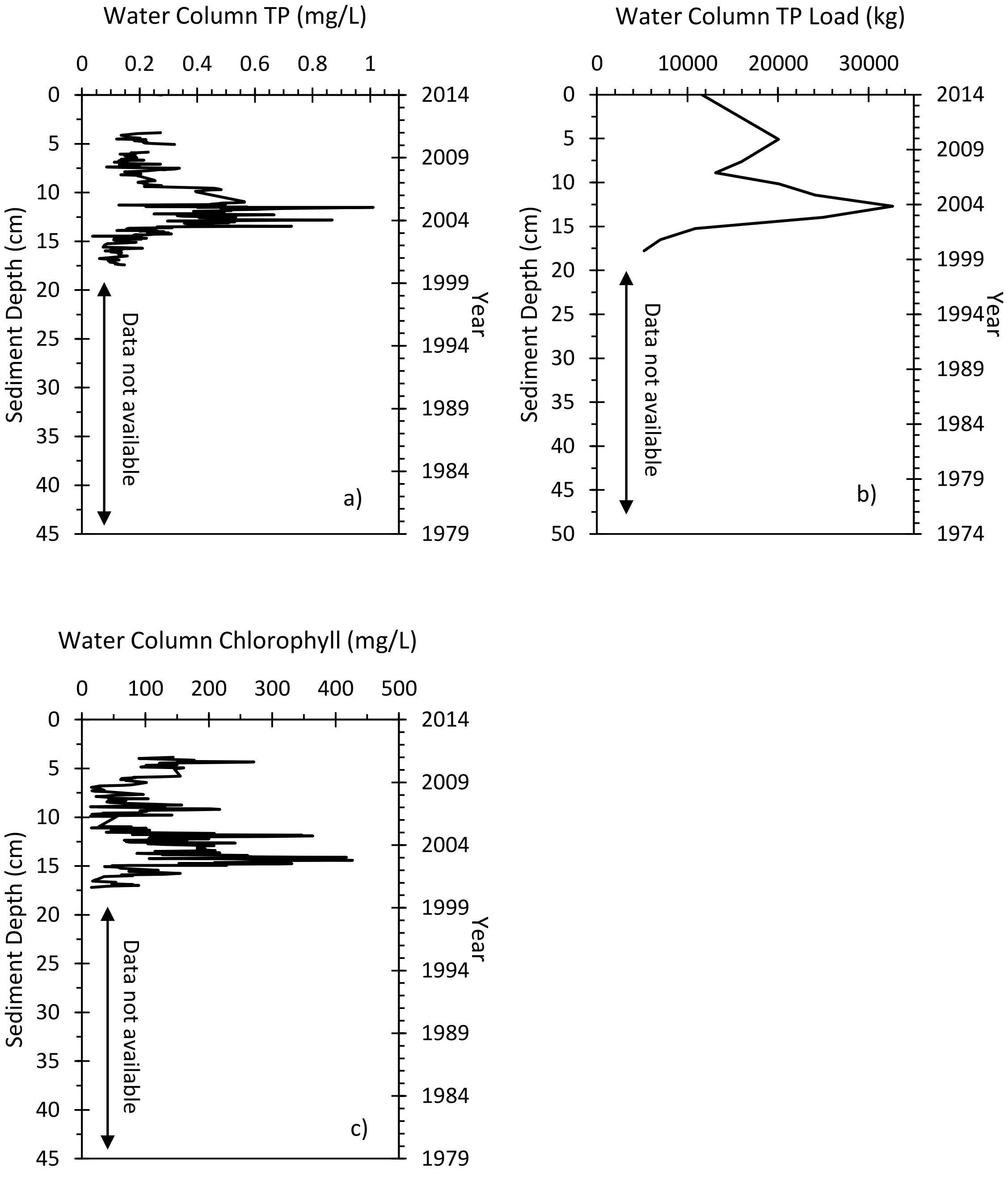

Figure 2-9. Average total phosphorus concentration (a), total phosphorus load (b), and chlorophyll concentration (c) in Lake Elsinore's water column plotted against time and corresponding sediment depth (supplemental data from James Noblet).

Calcium and organic carbon are significantly correlated in both cores (Table 2-1). This correlation suggests calcium carbonate ($CaCO_3$) co-precipitation with organic matter. This process occurs in the epilimnion, when primary production raises the pH, enabling calcite precipitation, and organic matter serves as a nuclei for the precipitation (Wetzel, 2001). Anderson (2010) attributed the increase in $CaCO_3$ of sediment grab samples collected from Lake Elsinore from 2000 to 2010 to increased precipitation of calcite in the water column due to erosion of Ca from the watershed in El Niño year 2005 as well as increased productivity and TDS in 2003 and 2004 (Anderson, 2010). The exponential decrease of Ca concentration with depth in the top 10 cm (Figure 2-4d), as well as the correlation with organic carbon, suggest this decrease is due to $CaCO_3$ dissolution coupled to organic matter decomposition. Respiration leads to increasing carbon dioxide in pore-water which lowers the pH and causes dissolution of $CaCO_3$. Considerable CO_2 concentrations were measured in Lake Elsinore sediments in July 2010 (concentrations reaching 3.8±0.6%) which is about 100x atmospheric concentrations, confirming the presence of elevated amounts of CO_2 in pore-water that can contribute to $CaCO_3$ dissolution, the proposed mechanism for exponential decline with depth (Anderson, 2010). Similar to OC and N, calcium concentrations increased around the year 1994 due to greater preservation of OC, which is precipitated with Ca, resulting in increased preservation of Ca as well.

In order to confirm that diagenesis is the driving force for the decreasing trends in the top 10 cm of OC, N, TP, and Ca profiles, the data was fit to an exponential function, because organic matter decomposition is an (exponential) first order decay process (Wetzel, 2001).

$$C_t = C_0e^{-kt} \tag{2-3}$$

Fitting the data to an exponential function also enables the calculation of the rate constants, depicting the rate of mineralization, or loss of the element. In equation 2-3, k is the slope of the function and represents rate change per depth in the sediment with units of cm^{-1}. To calculate the rate per time, k_r, the k is multiplied by sedimentation rate (ω):

$$k_r = k\omega \tag{2-4}$$

Once k_r is calculated, half-life can be calculated following the equation 2-5. Rate constants for the exponential decline in OC, N, and TP concentrations in the top 10 cm with depth were calculated to confirm diagenesis is the driving force for these trends. Rate constants for each element were averaged between the two replicate cores and that average was used to calculate half-life, using the equation:

$$t_{1/2} = 0.693/k_r \tag{2-5}$$

The exponential fit to OC was statistically significant at $p=0.001$ with $r=0.84$ and 0.87. The exponential fit to N was statistically significant at $p=0.01$ but the goodness of fit wasn't as strong, with $r=0.82$ and 0.85 (for 6-B, $p=0.001$). TP fit the exponential function at $p=0.001$ with $r=0.89$ and 0.80. This discrepancy may have skewed the TP average half-life. For 6-A the calculated half-life was 21.5 years and for 6-B the half-life was 12.16 years, yielding an average of 15.4 years (Table 2-3), although it may be a little longer than that, due to 6-A (half-life 21.5 years) demonstrating a better fit to the exponential function. The exponential fit to calcium in Lake Elsinore sediment was significant at 0.001 with r=0.95 and 0.90. The goodness of fit for calcium was greater than the other three elements. The significance of the goodness of fit of each element to an exponential function indicates that the decrease in depth can be attributed to sedimentary diagenesis, or decomposition.

The rate constants for OC and N were slightly greater than those for TP and Ca, suggesting that OC and N mineralize at about 1.5x the rate than TP and Ca, indicating that OC and N do not remain bioavailable for as long as TP and Ca (Table 2-3). OC and N had very similar rate constants and therefore very similar half-lives, of about 10 years. This value differs from the half-life for OC and N determined on cores collected in 2001, which was concluded to be in between 24 and 30 years (Anderson, 2011). The 95% upper and lower confidence intervals represent the error in fitting the data to an exponential curve. The half-lives calculated for the upper and lower rate constants confidence intervals were about 18 and 6.5 years. Even taking this error into consideration, the half-lives of OC and N in Lake Elsinore sediment in 2014 are significantly lower than those measured in 2001. These results suggest that OC and N are being mineralized at faster rates and are not remaining bioavailable for as long as they were in 2001. Although the diffused aeration system implemented in 2008 has not been sufficient to reverse anoxia above the sediments, it may reduce its intensity and duration, providing enough dissolved O_2 to increase rates of mineralization of organic matter in the water column.

The half-lives for calcium and total phosphorus were similar, at around 15 years. This similarity further corroborates the concept of $CaCO_3$ dissolution with increasing sediment depth due to decreasing pH and subsequent SRP and Ca^{2+} release to pore-water.

The average half-life for total phosphorus was 15.4 years, but the error was greater than that for OC and N (Table 2-3). However, the r value was not low enough to warrant the rejection of an exponential decrease in TP. Similar to the results for organic phosphorus from 2001, TP had a rate constant that was about half that of OC and N, indicating slower mineralization and thus P remains reactive for a longer period of time following burial. However, taking error into consideration, the half-life for TP calculated in this study (15.4 years with upper confidence interval 37.2 years) is about half of that calculated for organic P in 2001 (60.4 years) (Anderson, 2011). The decrease in half-life of P suggests that P is more reactive and is being mineralized faster than it was in 2001. The reason for this may be that aeration is increasing mineralization of org-P in the water column.

Table 2-3. Rate constants and half-lives (with 95% confidence intervals) for organic carbon, total nitrogen, total phosphorus, and calcium.

	k_r (yr^{-1})	$t_{1/2}$ (yr^{-1})	Lower 95% C.I.	Upper 95% C.I.
Organic Carbon	0.066±0.003	10.5	6.9	18.8
Total Nitrogen	0.073±0.0	9.5	6.3	17.8
Total Phosphorus	0.045±0.018	15.4	7.8	37.2
Calcium	0.046±0.003	15.1	11.5	24.9

Iron content of sediments decreased from 6.2% prior to 1990 to 5.8% by about 1994 and then is constant until about 2006, before declining more recently (Figure 2-5). Similarly, sulfur (S) increased in 1994 and is constant to the top of the core (Figure 2-4c). Following completion of LEMP in 1994/1995, mean lake depth increased, and presumably there was less circulation and less DO reaching the sediment surface and hypolimnion. This would lead to reduction of iron and sulfate and cause precipitation of FeS. Prior to this time, the redox conditions may have resulted in iron reduction and release to the water column but the redox conditions were not low enough to enable sulfate reduction until the lake deepened. Iron increases with depth in the top 10 cm due to increasing precipitation of FeS with depth, as more and more sulfate is reduced during organic matter decomposition. According to Wakefield (2001), sulfate concentrations in Lake Elsinore pore-water decreased with depth and sulfide concentrations increased which she attributed to increased FeS precipitation with depth as sulfate reduction takes place (greater with depth because DO in sediment pore-water decreases with depth). This iron then becomes locked up and is no longer able to bind to P.

The increase in silicon and aluminum concentrations between 25 and 30 cm corresponds to the time period when the Lake Elsinore Management Project was in progress (Figure 2-4a, b). Levee construction and construction of a new inlet and outlet channel would have resulted in increased erosion and dredging, causing a large influx of inorganics to the sediment. The transition from a large and shallow mean depth lake to a deeper mean depth lake, however, did not result in lasting changes to these elements' concentrations in the sediment, as after 1995, concentrations returned to background levels.

Table 2-4. Correlation table showing r values for hydrologic properties and inflows to Lake Elsinore for period 1981-2014 (entire core length). With n=26, an r value of 0.38 is statistically significant at $p<0.05$, and 0.51 is statistically significant at $p<0.001$. USGS data from gage #11070500.

	Avg. Area	SJ Inflow	Local Runoff	Recycled H_2O[a]	Avg. Elev.
$\delta^{13}C$	-0.14	-0.19	-0.30	0.50	-0.07
$\delta^{15}N$	-0.24	-0.23	-0.55	-0.63	-0.16
%OC	-0.22	-0.16	-0.42	0.89	0.01
%N	-0.27	-0.16	-0.44	0.82	-0.06
Al-P	0.04	0.22	0.16	-0.08	0.08
Mobile-P	-0.10	-0.05	0.14	-0.12	-0.25
Al	0.20	0.36	0.43	-0.16	-0.48
Si	0.22	0.36	0.43	-0.15	-0.48
P	-0.30	-0.22	-0.39	0.27	-0.76
S	-0.21	0.12	-0.18	-0.07	-0.26
K	0.38	0.12	0.49	-0.41	0.61
Ca	-0.41	-0.29	-0.62	0.55	0.78
Ti	0.33	0.11	0.50	-0.55	-0.81
Fe	0.30	0.17	0.49	-0.46	-0.71

[a] Note: Recycled water r values correspond to years 2008-2014; n=7, an r value of 0.669 is statistically significant at $p=0.05$.

Table 2-5. Correlation table showing r values for hydrologic properties and inflows to Lake Elsinore for period 1995-2014 (after LEMP completion). With n=17, an r value of 0.41 is statistically significant at $p=0.05$, and 0.61 is statistically significant at $p=0.005$. USGS data from gage #11070500.

	Avg. Area	SJ Inflow	Local Runoff	Recycled H_2O[a]	Avg. Elev.
$\delta^{13}C$	-0.43	-0.20	-0.31	0.50	-0.46
$\delta^{15}N$	-0.47	0.01	-0.51	-0.63	-0.43
%OC	0.01	-0.34	-0.28	0.89	-0.01
%N	-0.06	-0.33	-0.32	0.82	-0.07
Al-P	0.12	-0.01	0.15	-0.08	-0.18
Mobile-P	0.23	0.12	0.35	-0.12	0.19
Al	-0.15	0.22	0.16	-0.16	-0.18
Si	-0.14	0.20	0.15	-0.15	-0.18
P	-0.19	-0.33	-0.27	0.27	-0.23
S	-0.17	0.07	-0.02	-0.07	-0.22
K	0.20	0.24	0.54	-0.41	0.18
Ca	-0.18	-0.29	-0.54	0.55	-0.15
Ti	0.18	0.26	0.55	0.55	0.17
Fe	0.08	0.31	0.45	-0.46	0.06

[a] Note: Recycled water r values correspond to years 2008-2014; n=7, an r value of 0.669 is statistically significant at $p=0.05$.

Correlation analysis comparing sediment properties with sources of inflow and physical hydrologic characteristics of the lake revealed a few notable significant relationships at $p<0.05$ (Table 2-4; Table 2-5). The correlation between local runoff and aluminum, silicon, potassium, titanium, and iron reflects erosional inputs to the lake from the surrounding watershed during precipitation events (Table 2-4). The significant negative correlation of organic carbon, nitrogen, and calcium with local runoff suggests dilution of organic constituents corresponding to an influx of large amounts of inorganic elements in local runoff (Table 2-4). In comparison, inflow from the San Jacinto River exhibits weaker, non-significant relationships with elements, which can be attributed to sediment trapping in upstream Canyon Lake (Table 2-4). Recycled water inputs are significantly correlated with OC and N, suggesting contribution to organic matter production in the lake through increased nutrient inputs in wastewater. With shallower mean lake depth prior to LEMP completion, fluctuating water levels had a greater influence on depositional processes. After the completion of LEMP, inflow from local runoff does not exhibit as strong of a correlation with sediment composition (Table 2-5). With the transition to a smaller surface area and deeper mean lake depth, the distance from source (eroded soils) and sink (bottom sediments) would have increased, thus the settling rates and deposition of inorganic elements decreased.

Phosphorus Species

The average concentration of loosely-adsorbed/pore-water P in Lake Elsinore (125 µg/g) is greater than many other studied eutrophic lakes, including Lake Peipsi, Estonia (11 µg/g) and Lake Erken, Sweden (53 µg/g) (Rydin, 2000; Kapanen, 2012). Generally in eutrophic lakes, mobile P (specifically loosely-adsorbed/pore-water P) will increase toward the sediment surface which indicates diffusion to the water column (Rydin, 2000). However, in such a shallow lake as Lake Elsinore, diffusion may be very rapid, such that an exponential increase toward the sediment surface is not depicted in the profiles. In addition, the ebullition of CH_4 , CO_2, and N_2 gas bubbles generated by microbes can stimulate the diffusion of P toward the water column (Wetzel, 2001, Kapanen, 2012). In 2010, elevated levels of gas in the sediment were measured at multiple sites in Lake Elsinore, including the site where these cores were collected. The majority of the gas was CH_4, with lower concentrations of CO_2 and N_2 (Anderson & Martinez, 2013).

The trend of increased mobile P with depth in Lake Elsinore sediment may also be due to desorption of P from Ca or $CaCO_3$. This relationship between pore-water P and Ca is corroborated in Wakefield (2001) in which a relationship between Ca^{2+} in pore-water, and SRP in pore-water was found (r^2=0.89). Wakefield demonstrated that calcite was dissolving in the sediments and SRP was being released in the process (both were increasing with depth from surface). This may explain why loosely-adsorbed/pore-water P slightly increases with depth (Figure 2-6). $CaCO_3$ would dissolve with decreasing pH due to CO_2 accumulation in the sediment.

The relatively low concentrations of iron-bound P in Lake Elsinore sediment (Figure 2-6) are unusual compared to other eutrophic lakes which exhibit very little contribution of loosely-adsorbed phosphate to mobile P (Pilgrim et al., 2007). In the Lake Elsinore sediment cores, Fe-P represents 40% of mobile P and averages about 50 µg/g, which is greater than other eutrophic lakes but the proportion of Fe-P to mobile-P is low compared to other studies. In Big Bear Lake, a mesotrophic lake located in the Santa Ana River Watershed, mobile P of surface sediments consists of 99% Fe-P. Canyon Lake, the reservoir located upstream from Lake Elsinore, contains 87% Fe-P (unpublished data). The disparity between Fe-P in Lake Elsinore compared with other lakes in the region and with many other eutrophic lakes may be explained by a low influx of iron to the lake due to sedimentation of iron behind the Canyon Lake dam.

The large influx of Al-P to lake sediment around a depth of 25 cm (Figure 2-6) is reflected in aluminum and silicon profiles and corresponds to the year 1994 which is around the time of completion of the LEMP. The construction involved in the project likely increased deposition of inorganics to the sediment and increased precipitation of aluminum-bound phosphate (see Elemental Composition discussion above).

Stable Isotopic Composition

The gradual increase in $\delta^{13}C$ toward the top of the sediment cores (Figure 2-7a) may result from either diagenetic processes or from increasing eutrophic conditions in the lake. Diagenetic processing of organic matter in the sediment typically accounts for a decrease of 1.6-1.8‰ due to selective decomposition of enriched carbohydrates and proteins, which are easier to degrade, as well as the addition of depleted microbial biomass (Lehmann et al., 2002). A study on Lake Lugano found that sediment was depleted by 1.5‰ compared to sediment traps corresponding to the same time period (Lehmann et al., 2002). However, suspended organic matter resulted in $\delta^{13}C$ of -20‰, which is the same as the sediment. If OC is being degraded in the water column, as evidenced in Anderson (2010), then this indicates that at least during early diagenesis, there is very little fractionation effect or change on $\delta^{13}C$ values. The decomposed suspended organic matter resulted in a $\delta^{13}C$ of -23.7‰, which indicates a -3.7‰ shift during diagenesis. However, because this SOM spent an unknown amount of time incubating at room temperature, it may have undergone more decomposition than SOM typically would in Lake Elsinore before sedimentation and permanent burial (less prone to decay with increased burial).

Increasing eutrophication has also been determined to lead to increases in $\delta^{13}C$ of sediment. A study of three Florida lakes of different trophic levels reported that $\delta^{13}C$ was lowest in the oligotrophic lake and highest in the eutrophic lake and that in the hypereutrophic lake, Lake Apopka, $\delta^{13}C$ increased up-core from -23 to -18‰, which is approximately the same magnitude increase as in the Lake Elsinore cores (Torres et al., 2012). A study on Lake Ontario found a progressive increase in $\delta^{13}C$ of organic matter with increasing phosphorus loading and water column P concentrations, which also supports the hypothesis that $\delta^{13}C$ reflects lacustrine productivity. In that study, $\delta^{13}C$ increased from -27 to -25‰. A significant correlation between organic carbon and calcium carbonate was observed in Lake Ontario as well, which suggests photosynthesis generated calcite co-precipitation increases the sedimentation of organic matter and enhances its preservation in the sediment (Hodell & Schelske, 1998). If this is the case in Lake Elsinore, diagenesis may only be affecting $\delta^{13}C$ for a short period of time before permanent burial preserves the $\delta^{13}C$ signature of organic matter. Correlation analysis between stable isotopic composition of Lake Elsinore sediment and hydrologic characteristics of the lake resulted in significant negative correlations of $\delta^{13}C$ with average lake surface area and lake surface elevation (Table 2-5). Smaller lake depth and volume result in more eutrophic conditions as nutrients become concentrated in the water column and CO_2 is depleted quickly (due to limited amount), resulting in an increase in $\delta^{13}C$ of algae. Similarly, increases in lake volume and depth result in more negative $\delta^{13}C$ values, as CO_2 is essentially unlimited and algal fractionation selectively utilizes ^{12}C, resulting in more negative $\delta^{13}C$ values of algal biomass. However, without water quality data dating back to the early 1980s, it is difficult to determine whether the increasing trend in $\delta^{13}C$ toward the top of the core is due to increasing primary production or simply reflects sedimentary diagenesis.

The $\delta^{15}N$ results (Figure 2-7b) reflect three distinct periods in Lake Elsinore's recent history. The section at bottom of the core from 41 to 35 cm corresponds to the period of time when the lake was shallow, with presumably greater circulation and mixing. The transition to a deeper lake with the completion of the Lake Elsinore Management Project resulted in a decrease in sedimentary $\delta^{15}N$. The reason for this decline lies predominantly in the fact that increased mean lake depth led to a decrease in circulation and increase in stratification and anoxia. With the completion of the Lake Elsinore Management Project and resulting increase in mean lake depth, nitrate-nitrogen would have been less available than ammonium, and increasing incorporation of ammonium by phytoplankton could have resulted in the decrease in $\delta^{15}N$. During assimilation, phytoplankton fractionate ammonium by about -10‰ and nitrate by -1 to -3.4‰, so increased ammonium uptake relative to nitrate-nitrogen would result in a decline in $\delta^{15}N$ of algal biomass (Teranes & Bernasconi, 2000; Lu et al., 2010). Also, the majority of NH_4 is generated from organic matter mineralization in which ^{14}N is preferentially mineralized over ^{15}N during organic matter hydrolysis so ammonium is more depleted in ^{15}N than nitrate even before uptake by phytoplankton (Lehmann et al., 2002; Torres et al., 2012).

In addition to increased utilization of ammonium over nitrate, during oxic decomposition of algal biomass, there is typically very little change in $\delta^{15}N$, but during anoxic decay (in the sediments or anoxic bottom water), $\delta^{15}N$ typically decreases by 2.5 to 4‰ due to the input of depleted microbial biomass (Lehmann et al., 2002). Bacterial growth and consumption of the depleted ammonium from decomposition in addition to fractionation during bacterial excretion of ammonia which preferentially excretes ^{15}N leads to the depletion of $\delta^{15}N$ of bacterial biomass (Lehmann et al., 2002). When there is a large amount of bacterial growth and activity in the sediment, as is usually the case in stratified lakes with anoxic bottom water, it can cause a reduction in the $\delta^{15}N$ of sediment (Lehman et al., 2002).

Increasing autochthonous productivity can lead to increases in sedimentary $\delta^{15}N$ signatures when phytoplankton become more enriched in ^{15}N. However, this only occurs if surface waters become depleted in N, which typically only happens if a lake is nitrogen-limited (Teranes et al., 2000; Torres et al., 2012). Analysis of sedimentary $\delta^{15}N$ in Lake Simcoe, a eutrophic lake in Canada, revealed an up-core increase from 4.5‰ to 7.3‰ due to increasing productivity (Hiriart-Baer et al., 2011). The N:P in the water column in Lake Elsinore (17.4) verifies that Lake Elsinore is not N-limited and water column concentrations of TN do not wane in recent years (Figure 2-8), therefore the increase to higher $\delta^{15}N$ values around 2002 cannot be attributed to changes in N loading and availability in the water column (Figure 2-8) (CNRP, 2013).

The shift to higher $\delta^{15}N$ values around the year 2002 is more likely due to the input of supplemental wastewater. Sewage, composed of human and animal waste, has nitrate with $\delta^{15}N$ between 10 and 20‰. Nitrate input from soils and terrestrial organic matter in the watershed has values between 2-5‰ while fertilizers exhibit lower $\delta^{15}N$, approximately 3‰ (Teranes & Bernasconi, 2000; Machiwa, 2010; Torres et al., 2012).

Assuming a $\delta^{15}N$ value of 3‰ for nitrate input from local runoff and San Jacinto River inflow and a value of 15‰ for nitrate input from recycled wastewater, one can calculate predicted $\delta^{15}N$ values of Lake Elsinore sediment. Using assumed N isotope signatures for each source of water to the lake as well as average annual inflow (2008-present) of 10,000 acre-ft. from local runoff/San Jacinto River and 5,600 acre-ft. from recycled wastewater, the predicted $\delta^{15}N$ value is calculated as 7.4‰. The actual $\delta^{15}N$ at site 6 in Lake Elsinore was on average 7.1‰ from 2001 to present which is very similar to the predicted value, with a 3.5% error.

Denitrification in the water column also results in $\delta^{15}N$ enrichment of the sediment because denitrification preferentially reduces ^{14}N over ^{15}N, leaving residual nitrate enriched in ^{15}N (Teranes & Bernasconi, 2000; Lu et al., 2010). In Lake Ontario, Canada, an increase in $\delta^{15}N$ of 0.3‰ over a period of ten years, and subsequent stabilization of $\delta^{15}N$ were attributed to denitrification (Hodell & Schelske, 1998). Prior to wastewater additions, denitrification rates in the water column were fairly low due to low concentrations of nitrate (Horne, 2009). Therefore, wastewater input may be enabling denitrification by providing NO_3 for the reaction. Denitrification is likely occurring in the water column near the sediment-water interface because sedimentary denitrification does not result in a fractionation effect and $\delta^{15}N$ of suspended organic matter (5.8‰) was lower than the sediment top values, indicating that denitrification is occurring in the benthic boundary layer or bottom of the water column prior to permanent sedimentation (Terranes & Bernasconi, 2000). Another reason that suspended organic matter is more depleted in $\delta^{15}N$ than sediment is that as it is settling, OM degradation results in enrichment of residual OM as ^{14}N ammonium is preferentially released (Lehmann et al., 2002; Torres et al., 2012). The suspended organic matter sample that experienced decomposition resulted in a $\delta^{15}N$ of 10‰, which is greater than the top sediment isotopic signature. This discrepancy signifies that the algal biomass experienced greater decay than it would have in the lake, where it would be progressively buried in the sediment (N recycling decreases with increasing sediment depth; see Elemental Composition section above).

Comparison of $\delta^{15}N$ with hydrologic properties of the lake (Table 2-5), indicates a significant negative correlation between local runoff and $\delta^{15}N$ which can be attributed to the fact that the nitrogen in local runoff, compared to other sources of inflow, is presumably mainly fertilizer-N which has a low $\delta^{15}N$ content of about 3‰ (Machiwa, 2010).

Conclusion

The isotopic and elemental analysis of Lake Elsinore sediment resulted in a comprehensive interpretation of depositional history and biogeochemical cycling of organic matter and nutrients in this eutrophic lake. Organic matter is highly mineralized in the water column prior to permanent sedimentation. The transition from shallow to deeper lake with the completion of LEMP resulted in increased organic matter preservation in the sediment, evidenced by an increase in OC, N, Ca, and S during this time. The lack of correlation between iron and phosphorus, yet significant correlation between phosphorus and organic carbon/calcium in the top 10 cm suggests P cycling is controlled by calcium and organic matter rather than redox conditions. Fitting OC, TN, TP, and calcium data to exponential functions revealed that their decline with sediment depth is due to diagenetic processes rather than changes in external loading and water column concentrations. Furthermore, the mean half-lives for these elements lie in between 10 and 15 years, a shorter length of time than those calculated in 2001, which may be due in part to installation and operation of the axial flow pumps and diffused aeration system in the lake that has increased the delivery of O_2 to the sediment-water interface. The $\delta^{15}N$ value of sediment demonstrates a shift to higher values due to wastewater input and denitrification.

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Chapter 3 – Elemental Composition, Phosphorus Speciation, and Stable Isotopic Composition of Big Bear Lake Sediments

Introduction

Big Bear Lake is a shallow, moderately eutrophic lake located in the San Bernardino Mountains in Southern California at an elevation of 2,055 meters (Rothenberg et al., 2010). The lake formed when Bear Valley Dam was constructed in 1884 to provide water for agricultural irrigation in the valley at the base of the mountains (Brown & Caldwell, 2010). Presently, the lake is used for recreational purposes, irrigation, and municipal and domestic supply. Water released through the dam enters Bear Creek, which is a tributary of the Santa Ana River, about eight miles downstream (URS, 2006). Big Bear Lake is 7 miles long, oriented east-west and has westerly prevailing winds (URS, 2006). At capacity, the lake has a surface area of approximately 3,000 acres, volume of 75,332 acre-ft., average depth of 7.3 meters, and a maximum depth of 22 meters (Brown & Caldwell, 2010). Inflow sources are precipitation and snowmelt, delivered to the lake through surface runoff from the surrounding watershed and streams (Brown & Caldwell, 2010). The watershed that drains to the lake is mostly United States Forest Service land (61% of total watershed), but also includes resort (3%), residential (16.7%), and high density urban (5.5%) (Big Bear Municipal Water District (BBMWD), 2005). On the western end of the lake, near the dam, deeper waters enable the formation of thermal stratification during summer months (beginning in June) in which the surface waters warm up, creating a density gradient (limiting mixing) with the deeper, colder waters. Because the deeper waters are unable to mix with surface waters, they become depleted in oxygen. The water column typically mixes again around September, producing uniform temperatures and DO throughout the water column (BBMWD, 2011). Big Bear Lake is typically phosphorus-limited, but has been shown to be N-limited under certain conditions (Godwin-Saad, 2005; Brown & Caldwell, 2011). The east end of the lake exhibits more eutrophic conditions, with higher chlorophyll concentrations, lower Secchi depth, and higher pH than the west end of the lake (Dyal, 2003; BBMWD, 2005).

As previously mentioned, Big Bear Lake formed in 1884 with the creation of the Bear Valley Dam. Prior to 1977, Bear Valley Mutual Water Company was required to provide water for irrigation in the valley through releases to Bear Creek regardless of annual precipitation or snowmelt, thus the water level of Big Bear Lake fluctuated greatly. The reservoir completely dried up in 1898, 1899, 1900, and 1904. During this period of time, Big Bear Lake had a much lower capacity and an average depth of only 4.3 meters, which enabled the proliferation of macrophytes (Leidy, 2006). Due to increasing water demands for irrigation, a larger dam was constructed 300 ft. to the west of the original dam in 1912 which led to a doubling of average lake depth (Leidy, 2006). In 1964, Big Bear Municipal Water District (BBMWD) was created with the goal of lake level stabilization for recreational purposes. BBMWD acquired the dam in 1977 and initiated stabilization through the in-lieu water program (Brown & Caldwell, 2010).

Through this program, to meet the irrigation needs in the valley, BBMWD can supply that water from the lake itself, or purchase water from another source such as the State Water Project or the Santa Ana Groundwater Basin. Since this program was put in place, lake drawdowns during periods of drought are nowhere near as great as they were prior to this agreement (Brown & Caldwell, 2010).

Big Bear Lake is moderately eutrophic; it suffers from nuisance aquatic macrophytes and elevated nutrient levels (Rothenberg et al., 2010). The lake was added to the list of impaired waters under Section 303(d) of the Clean Water Act due to nutrients in 1998 (Brown & Caldwell, 2011). In 2006, a total maximum daily load (TMDL) for phosphorus was established in order to achieve protection of beneficial uses and a numeric target of 35 µg/L (annual average) for dry hydrologic conditions was set to be achieved by 2015 (Brown & Caldwell, 2011). An implementation and monitoring program was created as well to achieve the TMDLs which included establishment of 4 TMDL monitoring stations (Brown & Caldwell, 2011). The main internal sources of nutrients are sediment and decomposition of aquatic plants. Years of heavy nutrient loading from the watershed resulted in accumulation within the sediment, which, under certain conditions, can be re-released (through decomposition of OM and periods of low dissolved oxygen). High rates of nutrient fluxes from the sediment induce excessive algae blooms which reduce the water clarity. Nutrients and other factors have also enabled the proliferation of nuisance aquatic plants, including Eurasian Water Milfoil (*Myriophyllum spicatum*), Coontail (*Ceratophyllum demersum*), American Elodea, and

Curlyleaf pondweed. Coontail and milfoil have been present in abundance since the early 1900s (BBMWD, 2006). Besides interfering with recreational uses, macrophytes also serve as storage reservoirs for nutrients during the growing season, and contribute to nutrient loading through senescence of plant tissue during dormancy (BBMWD, 2006).

In order to control the spread of these nuisance plants, BBMWD implemented an Aquatic Plant Harvesting Program in the early 1980s in which plant biomass was mechanically removed from the lake during the growing season (May to September). The program was active from the early 1980s to 2001 and then again from 2009 to present (BBMWD, 2006). In 2002 and 2003, aquatic herbicide was applied to the east end of Big Bear Lake (Boulder Bay, Mallard Lagoon, and Metcalf Bay), Papoose Bay, Main/Marina Bay, and the Rock Wall area (BBMWD, 2005). The 2-year treatment was successful; it reduced 85% of nuisance plant biomass, however, it also resulted in the loss of a major “storage reservoir” for nutrients during the summer months. Reduction in macrophyte biomass also increased sediment resuspension and increased dissolved nutrient concentrations in the water column due to release from the decomposing plant biomass (Godwin-Saad, 2005).

Unfortunately, this resulted in a major decline in water clarity due to increased nutrients in the water column and the resulting algal blooms. Because of the immediate degradation in water quality following herbicide treatment, in 2004, an alum application was implemented which treated 1,330 acres of the lake (Godwin-Saad, 2005).

Aluminum sulfate (alum) functions as a coagulant that binds to phosphorus, producing a flocculent that settles out on the sediment surface. The flocculent also forms a layer on the sediment-water interface that prevents further P release from the sediments. SRP flux from the sediments was reduced by over 90% at TMDL Site 1, over 80% at TMDL Sites 2 and 6, and 45% at TMDL Site 9 (Godwin-Saad, 2005). Water clarity was the best ever recorded in June 2005 (Secchi depth 13 ft. in the west and 11 ft. in the east (BBMWD, 2011).

Additional in-lake management strategies BBMWD has implemented include sediment dredging (near the mouths of bays) and aeration. The primary purpose for dredging is boating navigation improvement but as a secondary benefit, nutrient-rich sediment is removed. In 2005 a large-scale dredging of the east end of the lake next to Stanfield cutoff resulted in decreased phosphorus release from sediment (Brown & Caldwell, 2010). An aeration system began operating in the lake in 2004 in order to prevent fish kills and suppress phosphorus release from sediment due to low dissolved oxygen. The system is comprised of an Aquatic Eco-Systems Airlift Diffuser which transports bottom water to the air-water interface to be reoxygenated by the atmosphere and an aerator which functions to destratify the water column by pumping water 12 ft. below the surface into the atmosphere where it is cooled and reoxygenated before returning to the lake (BBMWD, 2011).

Despite the effectiveness of individual in-lake management projects, as well as TMDL creation and monitoring, Big Bear Lake is still considered moderately eutrophic, with the eastern region of the lake often exhibiting eutrophic conditions. Even with the aeration system in place, TMDL Sites 1 and 2 often become anoxic in the early summer, suggesting that sediment oxygen demand exceeds the oxygen currently available through aeration. In order to maintain the health of the lake as well as continue to protect its beneficial uses, a comprehensive depiction is needed of the biogeochemical and depositional processes operating within the sediment and their relation to nutrient recycling and changes in productivity. In this study, phosphorus concentrations, bulk elemental composition, and C and N stable isotopic composition were analyzed in Big Bear Lake sediments to better understand how past management activities and hydrologic dynamics have altered the depositional processes in the lake and resulting sediment composition, which can be used to infer future changes in sediment and water quality as watershed and climatic changes continue to impact biogeochemical cycling and water quality of the lake.

Methods

Sample Collection

Four sediment cores were collected on June 17, 2014 from TMDL Sites 1 and 6 (2 replicates from each site) with a 1 meter polycarbonate tube with a diameter of 6.5 cm. TMDL 1 (34°14'14.9"N; 116°57'59.9") is located near the dam at a water depth of 13 meters at time of collection, in the deeper, western region of the lake, and TMDL 6 (34°15'7.2"; 116°55'18.3") is located in the middle of the lake, at water depth of 8 meters at time of collection, near the solar observatory. The profundal sediment at Site 1 captures depositional history and watershed events, while sediment at Site 6 reflects the successional state of the lake from terrestrial soil to wetland/littoral to lake. Water was carefully siphoned off the top of each core and the sediment was sliced/sectioned into 1 cm (for the top 10 cm) or 2 cm (for sediment deeper than 10 cm) intervals. Each section was homogenized and stored at 4°C under N_2 headspace in sealed 50 mL polypropylene centrifuge tubes. A subsample from each interval was used for water content determination. To calculate water content, the wet sediment was pre-weighed into tin cups and oven-dried at 105°C until reaching a constant weight (1-2 days).

Terrestrial vegetation samples were collected from Big Bear Valley on January 17, 2015. Aquatic vegetation samples were collected June 17, 2014. All samples were frozen until isotopic analysis.

Water was collected from the lake surface water on August 19, 2014 and May 19, 2015 and analyzed for isotopic composition of suspended organic matter (mainly phytoplankton). The water was stored in 20 L Nalgene jugs at 4°C until later filtration. The water collected in 2014 was stored for six months, over which time it experienced an unknown period of time at 25°C, due to electrical issues. Therefore suspended organic matter (SOM) experienced some decay over this period of time.

Elemental Composition (XRF)

Bulk elemental composition was determined on sediment samples using a Spectro XEPOS HE Benchtop X-ray Fluorescence Spectrometer flushed with 85 L hr^{-1} of helium gas (modified EPA Method 6200). Approximately 5 g of wet sediment from each sediment core interval was dried at 50°C and ground with a mortar and pestle prior to X-ray fluorescence analysis. One source energy and four excitation targets were utilized per sample at count times of 200 seconds: excitation energy of 40 kiloelectron volts (kV) and 1 mA current; 60 kV and 0.66 mA; 25 kV and 1.6 mA; 20 kV and 2 mA.

Phosphorus Species

Forms of P in bottom sediment from Site 1 were extracted using the fractionation scheme described in Pilgrim et al. (2007). Approximately 0.2-0.25 grams of wet sediment was added to 50 mL polycarbonate centrifuge tubes, followed by a sequential phosphate extraction which utilized different reagents to measure the amount of phosphate in three different fractions within the sediment. The reagent solutions were 1M ammonium chloride (NH_4Cl) which extracts pore-water and loosely-adsorbed P, followed by bicarbonate buffered dithionite solution (0.11M $NaHCO_3$/0.11M NaS_2O_4) that extracts redox-sensitive P bound to iron and manganese hydroxides (Fe-P), and lastly 0.1M sodium hydroxide, NaOH, that extracts non-reducible, aluminum-bound P (Al-P). The sum of the phosphate extracted in the first two steps represents mobile phosphorus, or phosphorus that can be re-released to the water column under certain conditions. Aluminum-bound phosphate is generally considered to be a recalcitrant form that will not be re-released. 10 mL of each extract was added to the centrifuge tube. After each sequential reagent addition, the samples were placed on a shaker table for varying amounts of time: two hours for loosely-adsorbed P, one hour for Fe-P, and 16 hours for Al-P (Pilgrim et al., 2007). Subsequent to each reagent addition and mixing, samples were centrifuged at 3,000 rpm for 20 minutes. The supernatant was decanted, filtered through 0.45 µm membrane filters, and stored in 20 mL HDPE scintillation vials in the freezer until analysis. The residual sediment continued on in the procedure after the supernatant from each step was decanted. One out of every 10 samples was replicated and 2 method blanks per core were used (no sediment, just reagent and centrifugation). Soluble reactive phosphorus was determined colorimetrically for each supernatant on a Seal AQ2 discrete analyzer following the automated ascorbic acid reduction method 4500-P F (APHA, 1998). Absorbance was measured at 880 nm. Calibration control blanks and calibration control verifications were used to verify accuracy. Only the cores collected from Site 1 were fractionated for sedimentary P species due to the higher sand content and fibrous organics at Site 6 which prevented separation of supernatant from sediment during centrifugation.

Stable Isotopic Composition

Sediment subsamples were dried at 50°C and ground to a homogenous mixture with a mortar and pestle. The dried sediment was fumigated with concentrated HCl (12N) in a desiccator for 24 hours in order to remove inorganic C. Replicate samples were analyzed without fumigation to ensure all $CaCO_3$ had been removed. Suspended organic matter from epilimnetic water was filtered through 47 mm Whatman glass microfiber filters and then oven-dried at 50°C. Stable C and N isotopic composition as well as %OC (weight percent) and %N were analyzed on a Costech elemental analyzer coupled to a Delta V Advantage Isotope Ratio Mass Spectrometer at the Facility for Isotope Ratio Mass Spectrometry (FIRMS) at University of California, Riverside. One in every ten samples was replicated.

Results

Using the sedimentation rate of 0.79 cm/year for TMDL 1 and 0.20 cm/year for TMDL 6 previously determined by Kirby (2005), the dates corresponding to given sediment depths were calculated using equations 3-1 and 3-2 and plotted on each depth profile as a secondary y-axis to allow comparison of sediment properties over time and with lake management activities.

$$t_z = t_0 - (z/0.79\ \text{cm yr}^{-1})\quad \text{(Site 1)} \tag{3-1}$$

$$t_z = t_0 - (z/0.20\ \text{cm yr}^{-1})\quad \text{(Site 6)} \tag{3-2}$$

where t_z = date (decimal year) at sediment depth z

t_0 = date at time of sediment collection (2014.5)

z = sediment depth (cm)

A timeline of in-lake management activities and watershed events is portrayed in Figure 3-1 for convenient comparison with sediment properties at corresponding dates/sediment depths. The present lake formed in 1884 with the completion of dam construction. The region experienced a drought in the 1950s and 1960s which resulted in low lake levels. Water levels experienced great fluctuations, which often resulted in a complete drying-up of the lake bed, until implementation of the in-lieu water program in 1977. 2004 marks the implementation of an aeration system as well as alum treatment in the western region of the lake.

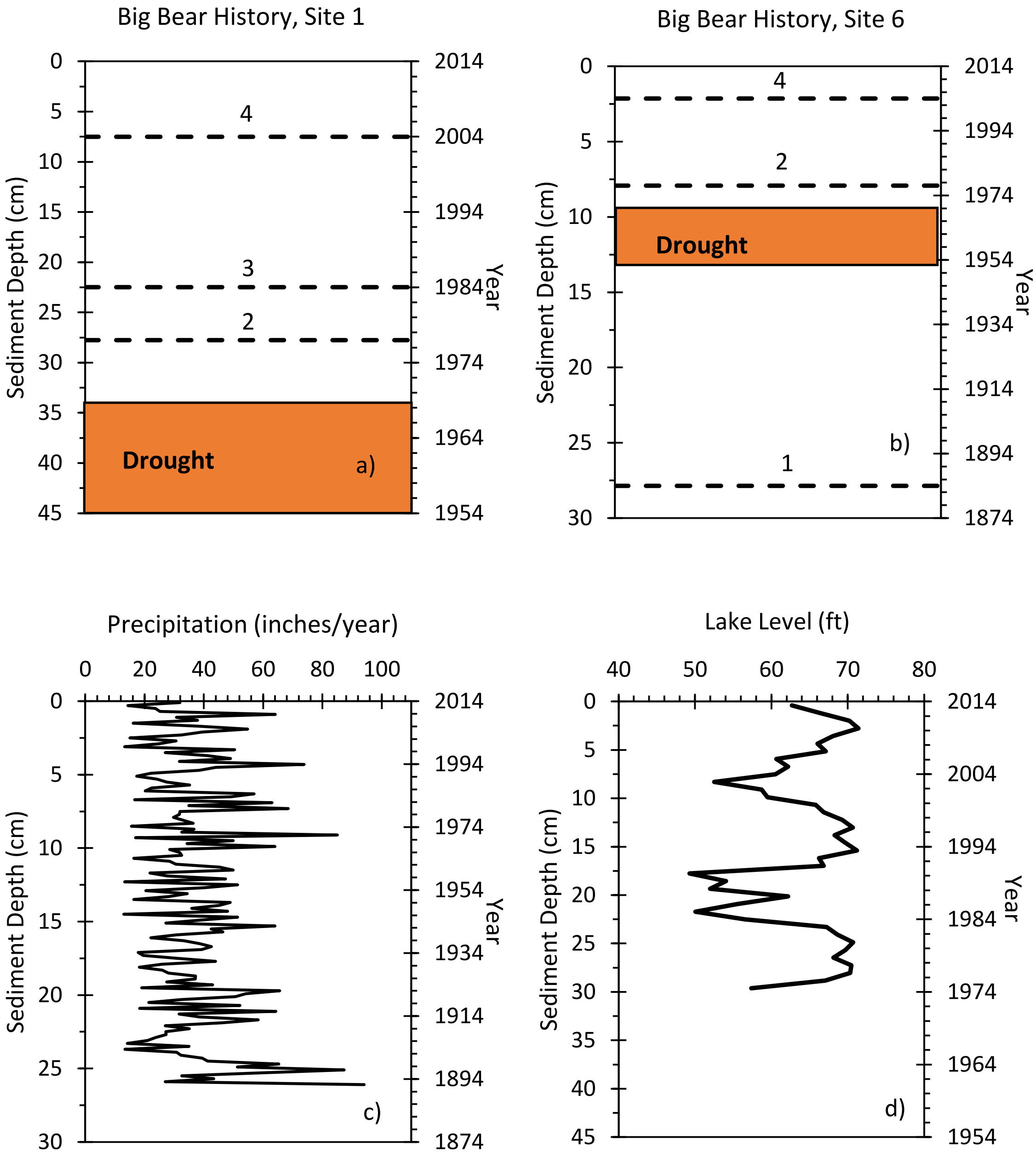

Figure 3-1. Historical management activities at Big Bear Lake in comparison to sediment depth at Site 1 (a) and Site 6 (b). 1=formation of the lake with completion of dam. 2=end of withdrawal requirement for irrigation and beginning of lake level stabilization. 3= large erosional event. 4=alum treatment and aeration implementation. Panel c) shows annual average precipitation to Big Bear Lake in relation to Site 6 sediment depths (Big Bear Municipal Water District, unpublished data). Panel d) shows lake level in relation to Site 1 sediment depths (Big Bear Municipal Water District, unpublished data).

Water Content

Water content is often quantified in sedimentary studies, as it is closely related to particle size, which contributes to the ability of the sediment to hold onto pollutants and nutrients as opposed to rapidly releasing them to the water column. For example, typically the greater the clay content of sediment, the greater its capacity to adsorb many pollutants, including phosphorus (Horne, 1994). Water content of sediment at Site 1 increased with decreasing depth (and time), from about 80 to 85% at 40 cm depth (1964) to about 90% near the surface in cores 1-A and 1-B (Figure 3-2a). Water content of sediment at Site 6 decreased up-core from about 80% at the bottom of the cores to 70% at 10 cm (Figure 3-2b). In upper sediment, the trend changed directions and water content increased up-core from about 70% to 80%. The trend reversal at 10 cm corresponds to the year 1974±5 years.

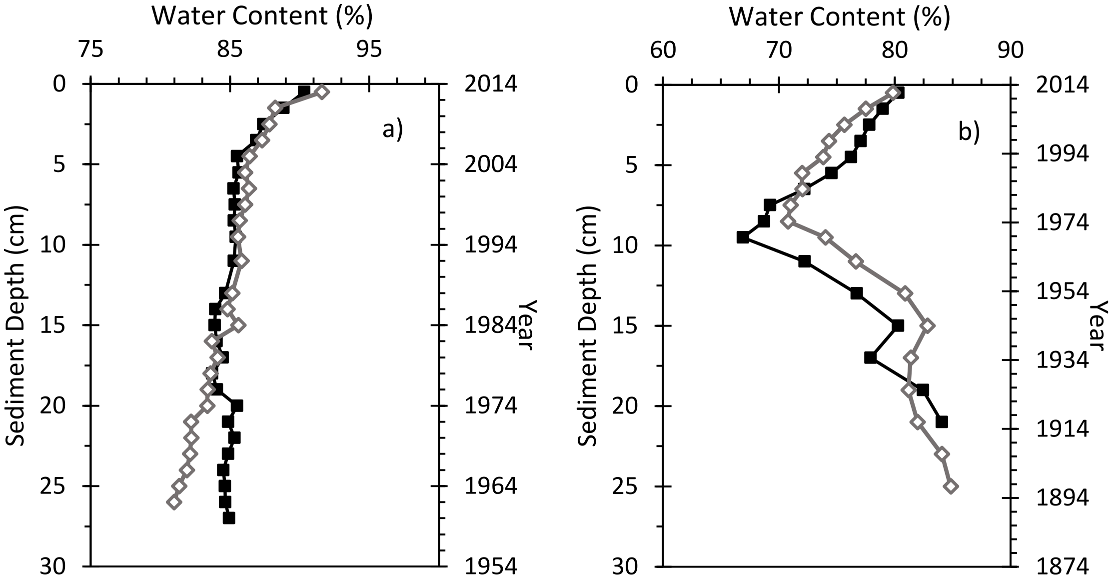

Figure 3-2. Water content depth profiles at a) Site 1 and b) Site 6. Solid, black squares represent cores 1-A and 6-A. Open, grey diamonds represent cores 1-B and 6-B.

Elemental Composition

Terrestrial and Aquatic Vegetation

Organic carbon and nitrogen content of terrestrial and aquatic plants in comparison with the content of the sediment enables analysis of changing relative contribution of autochthonous vs. allochthonous organic matter input to the lake over time. Organic carbon and nitrogen content of terrestrial and aquatic vegetation is shown in Table 3-1.

Table 3-1. Carbon and nitrogen content, and stable isotopic composition of vegetation samples.

Sample Description	Vegetation Type	Organic Carbon Content (%)	Nitrogen Content (%)	OC:N	$\delta^{13}C$	$\delta^{15}N$
Pine (*Pinus sp.*)	Coniferous Needles	50.0±0.8	0.8±0.1	60.7±9.6	-26.4±0.6	0.8±0.1
Juniper sp.	Coniferous Needles	48.2±0.9	0.8±0.04	59.0±2.7	-29.1±0.4	-1.0±0.5
Incense Cedar (*Calocedrus decurrens*)	Coniferous Needles	48.3±1.0	0.99±0.1	48.5±2.1	-23.9±1.1	-0.02±0.5
California Black Oak (*Quercus kelloggi*)	Deciduous Leaves	45.3±0.5	0.4±0.02	108.8±3.5	-28.4±0.5	-6.9±0.3
Grass	Grass	43.7±0.1	0.2±0.02	190.0±17.0	-28.8±0.2	-3.1±0.2
Salt Cedar (*Tamarix ramosissima*)	Shrub	46.2±1.0	0.7±0.2	64.2±17.3	-24.3±0.3	-1.8±0.4
Eurasian Water Milfoil (*Myriophyllum spicatum*)	Submerged Macrophyte	12.4±0.63	0.8±0.2	16.6±2.4	-11.1±3.7	3.3±0.6
Macroalgae (*Chara sp.*)	Detached algae	32.5±0.4	1.1±0.1	29.7±1.7	-23.7±0.5	5.5±0.2

Site 1 Sediment

Organic carbon at Site 1 remained constant with depth at about 6% from the bottom of the cores to a depth of 5 cm (Figure 3-3a). In the top 5 cm, OC increased from about 6% to 7%. Similarly, total nitrogen content was constant with depth at 0.7% from the bottom of the cores to a depth of 5 cm, where it then increased up-core from 0.7% to 0.85% (Figure 3-3b). OC:N was constant with depth throughout both cores, at a value of 8, with minor fluctuations (Figure 3-3c).

Although the two replicates were quite variable in aluminum concentrations below a depth of about 25 cm, both replicates reflect slightly decreasing concentrations up-core from about 8.5% at 25 cm to 8% at the surface (Figure 3-4a). Concentrations exhibited less fluctuation in the top 5 cm.

Aluminum, silicon, and potassium exhibited a brief period of increased deposition at about 25 cm, corresponding to the year 1984 (Figure 3-4). These elements are also significantly correlated in core 1-A (r=0.87 for Si and Al; r=0.86 for Al and K).

Sulfur concentration increased from 2,000 µg/g at 25 cm (1980) to 4,000 µg/g at about 10 cm. In the top 10 cm, this trend reversed and sulfur decreased up-core from 4,000 to 2,500 µg/g in both cores (Figure 3-3d).

Total phosphorus was relatively constant at 0.1% from the bottom of the core to about 5 cm in core 1-A (Figure 3-4d). In the top 5 cm, concentrations increased up-core to 0.125%. In core 1-B, concentrations began to increase up-core from 10 cm (0.1%) to 0.15% at the top of the core.

Calcium slightly increased from the bottom of the cores to about 30 cm, then it decreased from 30 cm to 25 cm (Figure 3-5). Calcium then increased from 1.5% at 25 cm to 2.5% at 10 cm, after which it became relatively constant in both cores at 2.5 cm.

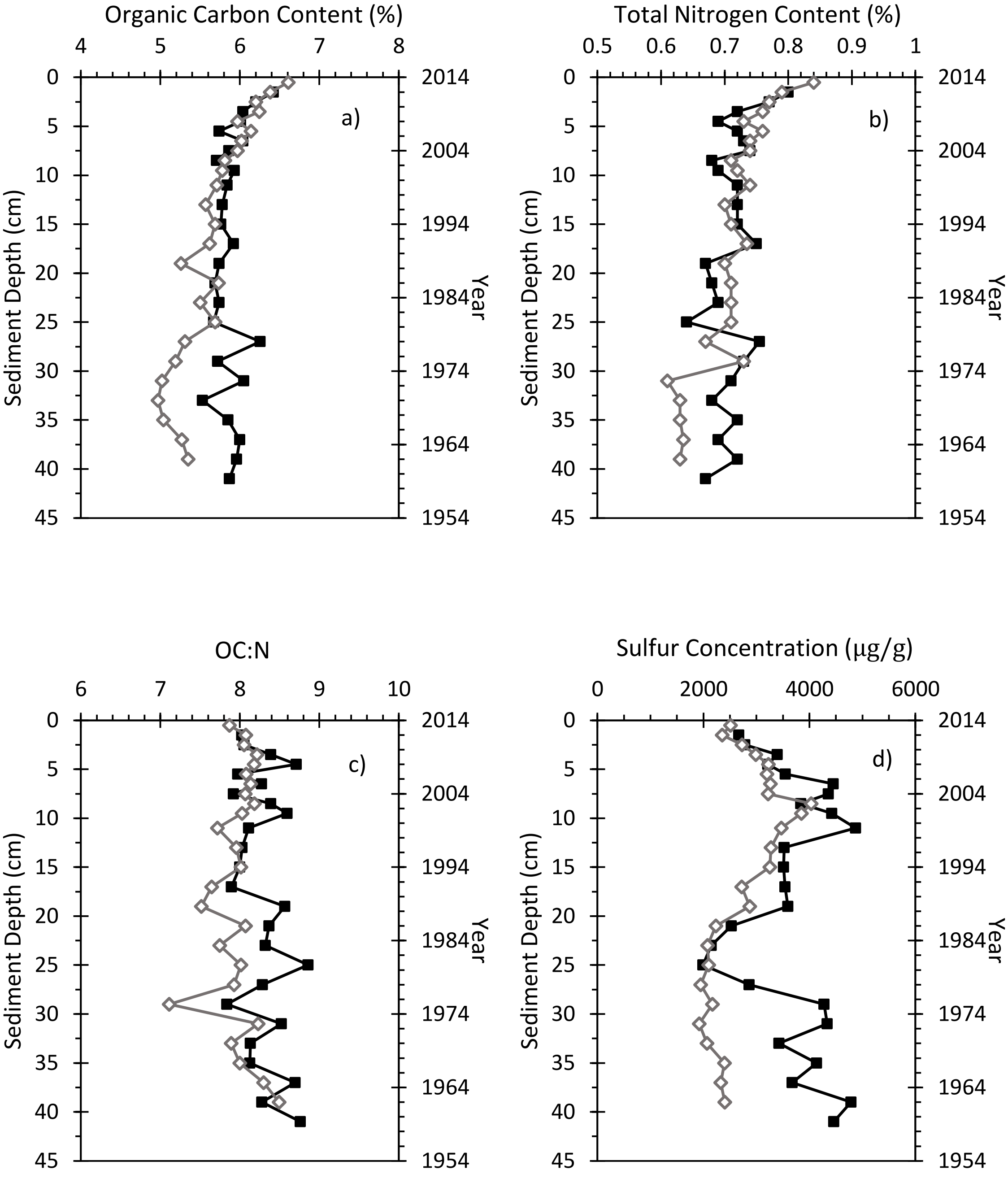

Figure 3-3. Sediment depth profiles of a) organic carbon, b) total nitrogen, c) OC:N, and d) sulfur concentrations at Site 1. Solid, black squares represent data points in core 1-A. Open, grey diamonds represent data points in core 1-B.

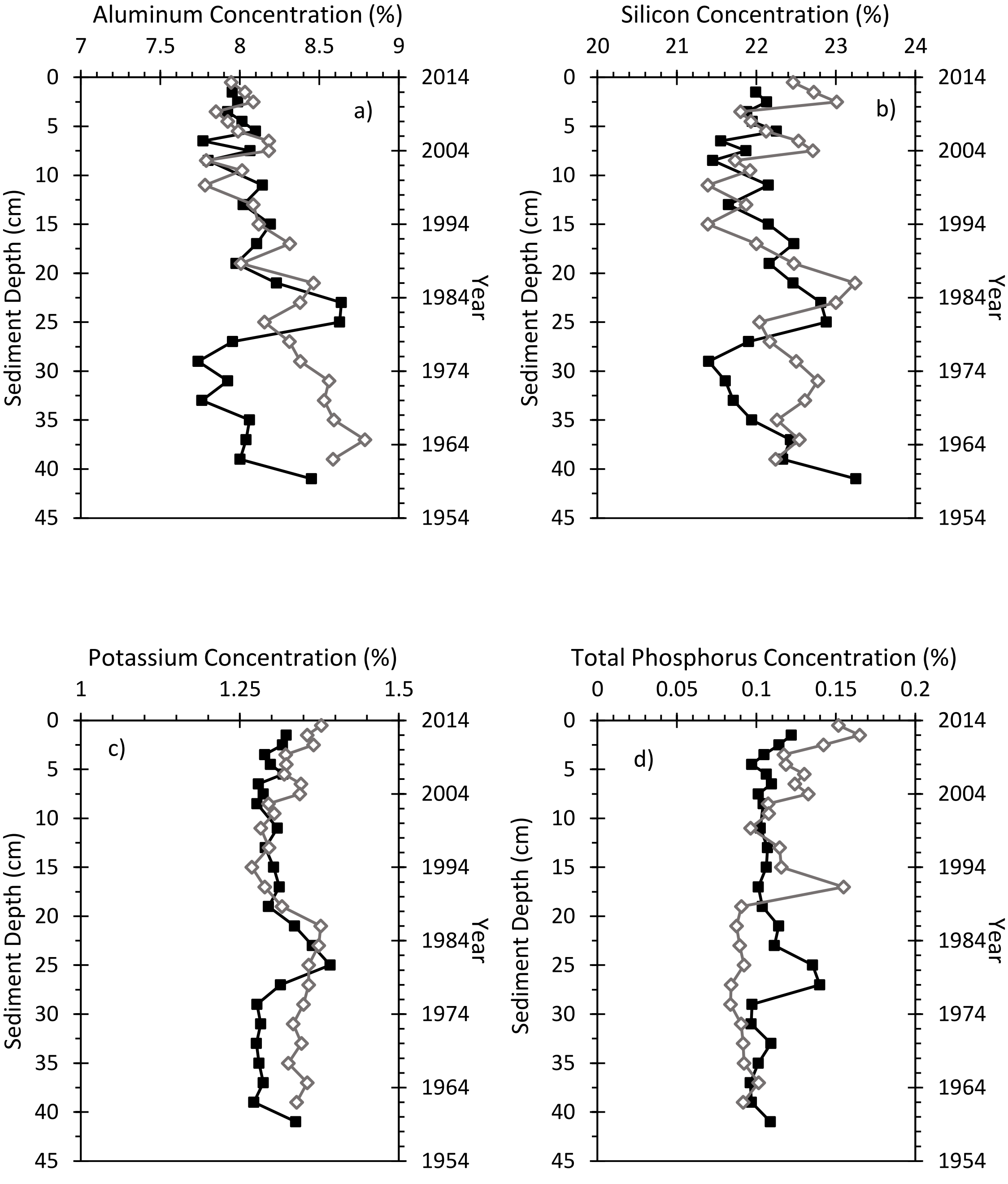

Figure 3-4. Sediment depth profiles of a) aluminum, b) silicon, c) potassium, and d) total phosphorus concentrations at Site 1. Solid, black squares represent data points in core 1-A. Open, grey diamonds represent data points in core 1-B.

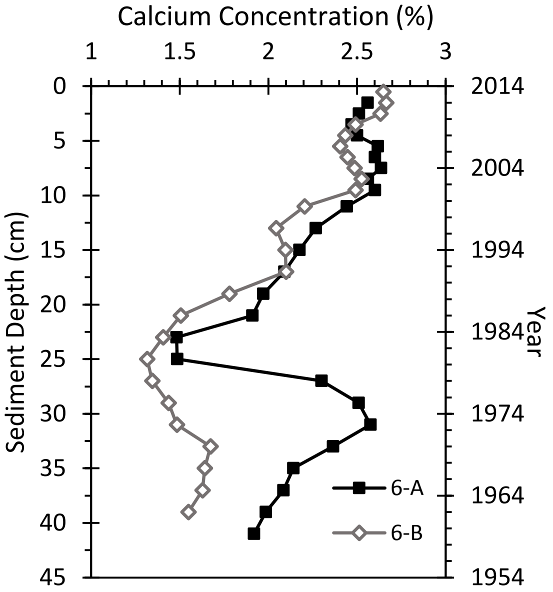

Figure 3-5. Calcium concentration depth profile of Site 1 sediment.

Table 3-2. Correlation table showing average r values at Site 1. With n=26, an r value 0.496 is statistically significant at p=0.005.

	Depth	$\delta^{13}C$	$\delta\ ^{15}N$	%OC	%N	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Ni	Cu
Depth	1.00																
$\delta^{13}C$	0.45	1.00															
$\delta^{15}N$	-0.09	0.05	1.00														
%OC	-0.58	-0.58	0.12	1.00													
%N	-0.65	-0.59	0.00	0.81	1.00												
Mg	-0.66	-0.69	0.01	0.67	0.61	1.00											
Al	0.53	0.58	-0.21	-0.47	-0.57	-0.36	1.00										
Si	0.25	0.26	0.01	-0.09	-0.21	-0.08	0.69	1.00									
P	-0.40	-0.17	0.16	0.50	0.39	0.48	-0.05	0.12	1.00								
S	-0.20	-0.42	0.24	0.19	0.22	0.13	-0.57	-0.45	-0.18	1.00							
K	0.07	0.21	-0.08	0.01	-0.09	0.12	0.63	0.79	0.30	-0.69	1.00						
Ca	-0.71	-0.73	0.12	0.59	0.64	0.70	-0.76	-0.50	0.26	0.57	-0.46	1.00					
Ti	0.49	0.67	-0.13	-0.54	-0.53	-0.41	0.83	0.61	-0.11	-0.71	0.72	-0.84	1.00				
Mn	-0.39	-0.37	0.14	0.47	0.52	0.55	-0.27	0.09	0.60	-0.13	0.27	0.45	-0.17	1.00			
Fe	0.02	-0.10	0.08	0.17	0.03	0.29	0.30	0.52	0.54	-0.08	0.50	-0.01	0.16	0.47	1.00		
Ni	-0.03	-0.04	-0.12	-0.04	-0.02	0.08	0.24	0.09	-0.01	-0.20	0.11	-0.08	0.20	0.05	0.17	1.00	
Cu	0.64	0.66	-0.18	-0.66	-0.75	-0.52	0.84	0.46	-0.15	-0.58	0.49	-0.84	0.82	-0.36	0.17	0.17	1.00

Site 6 Sediment

Site 6, which is located in much shallower water than Site 1 and is more sensitive to lake level changes, exhibited very different elemental composition than Site 1. While most elemental concentrations remained constant with depth at Site 1, concentrations in Site 6 sediment reflect large changes with depth from the bottom of the core to a depth of about 10 cm, corresponding to the year 1974. Organic carbon decreased from 40% at the bottom of the cores (~1900) to 10% at 10 cm depth, corresponding to the year 1974±5 years, where it then remained at 10% from 10 cm to the top of the cores (Figure 3-6a). OC is significantly correlated with depth (r=0.93). At about 15 cm (1954) there was a deflection in the up-core decreasing trend, and OC briefly increased. Organic carbon is significantly negatively correlated with inorganics, which showed the opposite trends (Table 3-3). Total nitrogen content exhibited similar trends as OC (Figure 3-6b). It increased from 3% at the bottom of the cores to 1% at 10 cm, then remained constant at 1% to the top of the core. N also reflects a brief increase beginning around 17 cm. It is significantly correlated with depth (r=0.92) and negatively with inorganic elements (Table 3-3). Organic carbon and nitrogen are significantly correlated at Site 6 (r=0.99). OC:N decreased from about 14 at the bottom of the cores to 10 at the top of the sediment (Figure 3-6c).

Aluminum, potassium, silicon, iron, and copper expressed the opposite trend as organic carbon and nitrogen, and increased drastically from the bottom of the cores to a depth of 10 cm, which corresponds to the time frame 1900-1974. After 1974, concentrations stabilized and remained fairly constant with slight increases from 10 cm to the top of the core (Figure 3-7a, b).

Calcium and sulfur decreased drastically up-core from the bottom of the core to 10 cm (1974). Concentrations become much more stable in the top 10 cm (Figure 3-7c, d).

Although total phosphorus is not significantly correlated with water content, the two properties exhibited similar trends, decreasing from the bottom of the cores to about 8 cm and then increasing to the top of the core (Figure 3-2b; Figure 3-6d). Average phosphorus concentration throughout the length of the core was 0.12% or 1,200 μg/g.

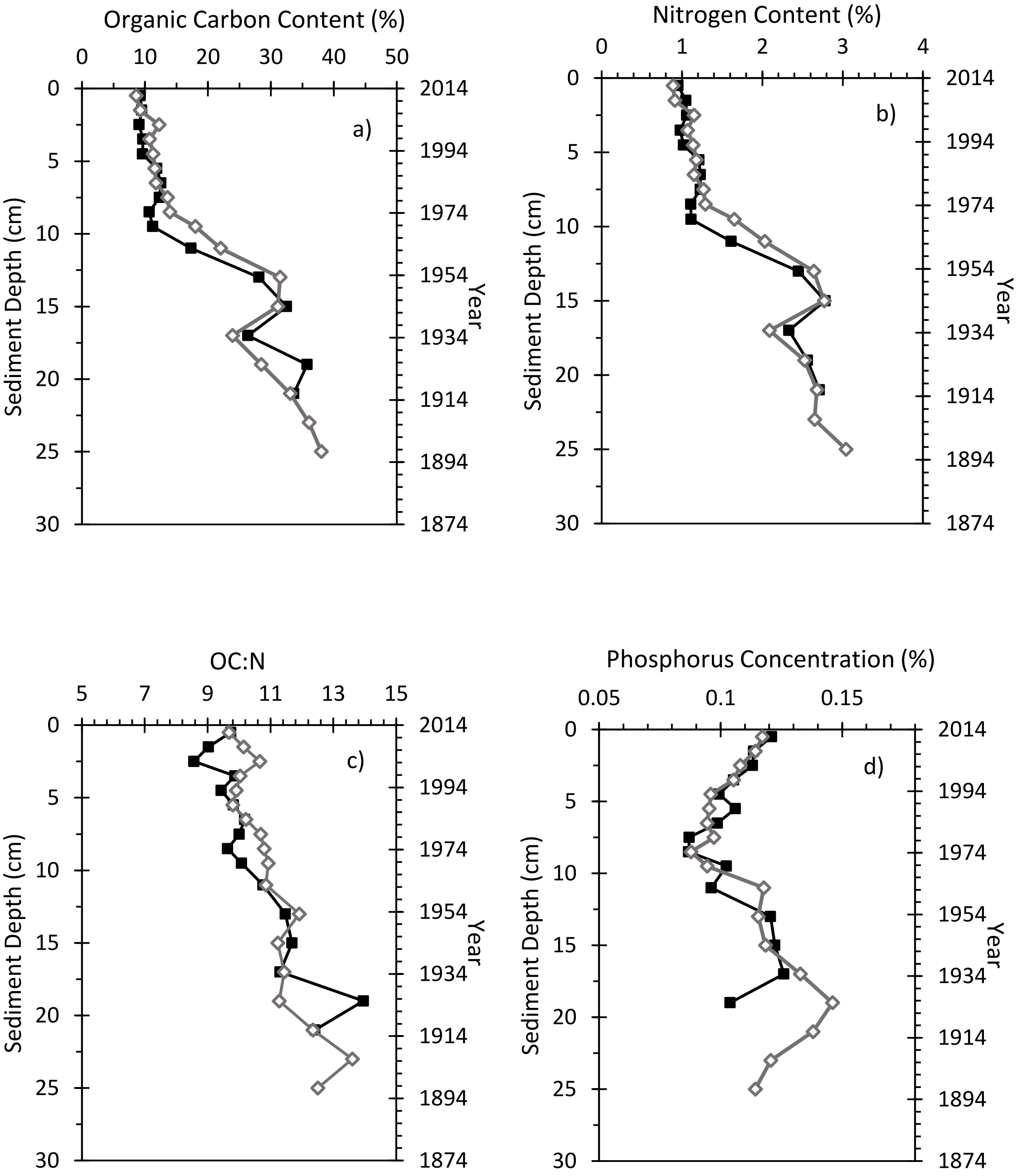

Figure 3-6. Sediment depth profiles of a) organic carbon, b) total nitrogen, c) OC:N, and d) total phosphorus concentrations at Site 6. Solid, black squares represent data points in core 6-A. Open, grey diamonds represent data points in core 6-B.

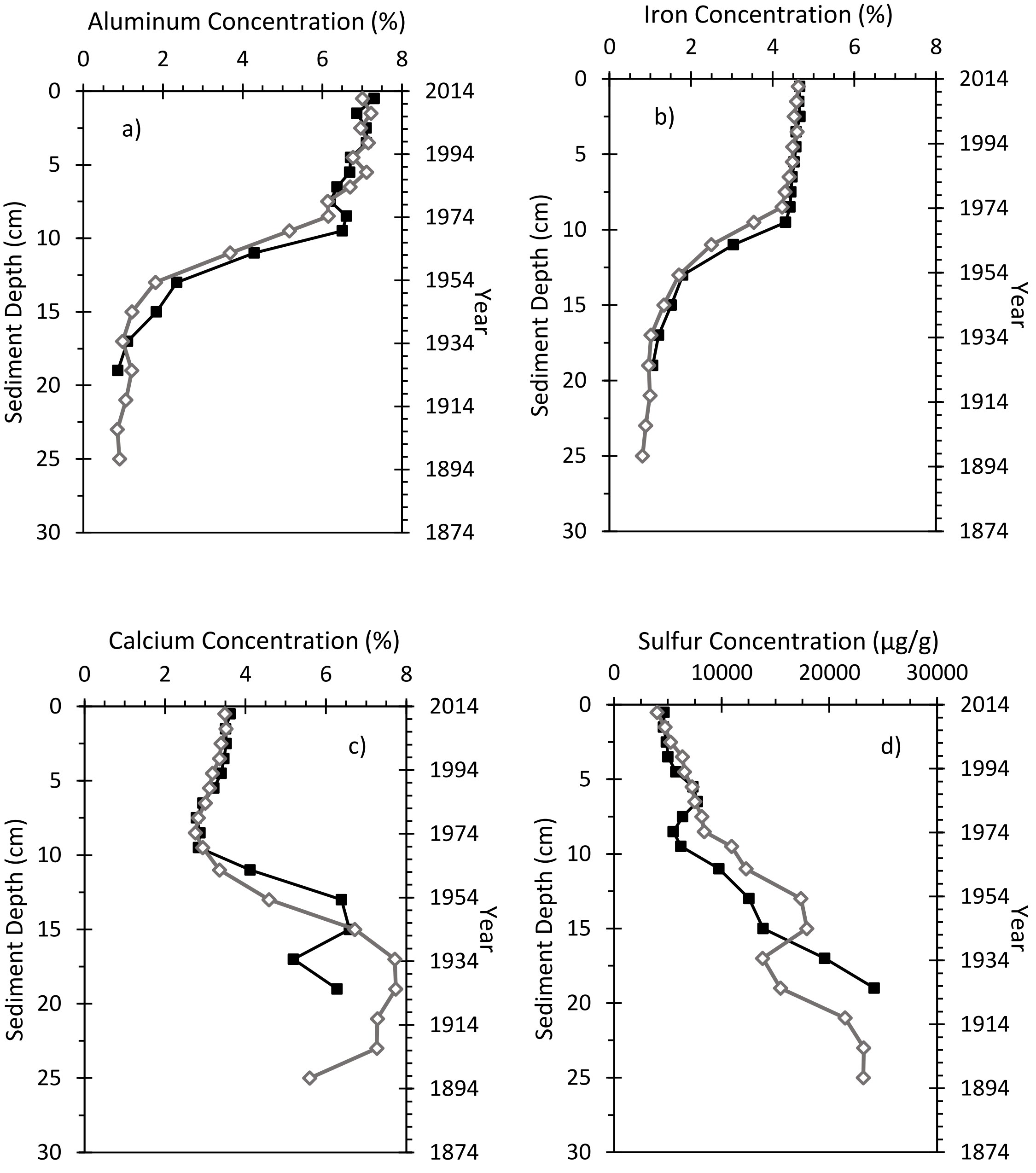

Figure 3-7. Sediment depth profiles of a) aluminum, b) iron, c) calcium, and d) sulfur concentrations at Site 6. Solid, black squares represent data points in core 6-A. Open, grey diamonds represent data points in core 6-B.

Table 3-3. Correlation table showing average r values from Site 6. With n=18, an r value 0.59 is statistically significant at p=0.005.

	Depth	$\delta^{13}C$	$\delta^{15}N$	%OC	%N	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Ni	Cu
Depth	1																
$\delta^{13}C$	-0.91	1															
$\delta^{15}N$	-0.84	0.84	1														
%OC	0.93	-0.92	-0.80	1													
%N	0.91	-0.93	-0.82	0.99	1												
Mg	0.01	0.05	0.01	0.02	0.01	1											
Al	-0.22	0.19	0.21	-0.23	-0.24	0.75	1										
Si	-0.94	0.89	0.86	-0.94	-0.92	-0.04	0.22	1									
P	0.48	-0.66	-0.41	0.60	0.63	0.23	0.08	-0.56	1								
S	-0.02	0.03	0.06	-0.02	-0.04	-0.91	-0.73	0.00	-0.29	1							
K	-0.95	0.92	0.84	-0.96	-0.96	0.02	0.27	0.96	-0.64	0.02	1						
Ca	-0.09	-0.04	0.11	0.05	0.05	-0.86	-0.60	0.04	-0.04	0.83	-0.01	1					
Ti	-0.94	0.95	0.85	-0.97	-0.97	0.01	0.24	0.97	-0.66	0.02	0.99	-0.03	1				
Mn	-0.92	0.82	0.81	-0.83	-0.84	-0.05	0.11	0.84	-0.37	0.18	0.86	0.19	0.85	1			
Fe	-0.91	0.94	0.84	-0.96	-0.97	0.03	0.26	0.95	-0.65	0.02	0.97	-0.06	0.99	0.84	1		
Ni	-0.90	0.93	0.84	-0.95	-0.95	0.94	0.98	0.94	-0.41	-0.94	0.98	-0.87	0.98	0.67	0.97	1	
Cu	-0.81	0.94	0.72	-0.94	-0.95	0.90	0.96	0.87	-0.60	-0.89	0.95	-0.96	0.96	0.53	0.97	0.94	1

Phosphorus Species

In addition to water content and total elemental composition, the forms of phosphorus within sediments from Site 1 were also quantified.

At site 1, redox-sensitive phosphate (Fe-P) was the most abundant form of mobile-P, averaging about 150 µg/g dry weight throughout the length of the cores and remaining relatively constant with depth (Figure 3-8). The sediment contained very little loosely-adsorbed/pore-water P which was essentially zero in both replicates. Aluminum-bound P made up the majority of total phosphorus. In core 1-A, Al-P decreased from 1000 µg/g at 25 cm to 500 µg/g at the sediment surface. In core 1-B, Al-P remained relatively constant with depth, at 500 µg/g. Both cores exhibited an increase in Al-P concentration that coincided with an increase in TP, at 25 cm in core 1-A and 20 cm in core 1-B.

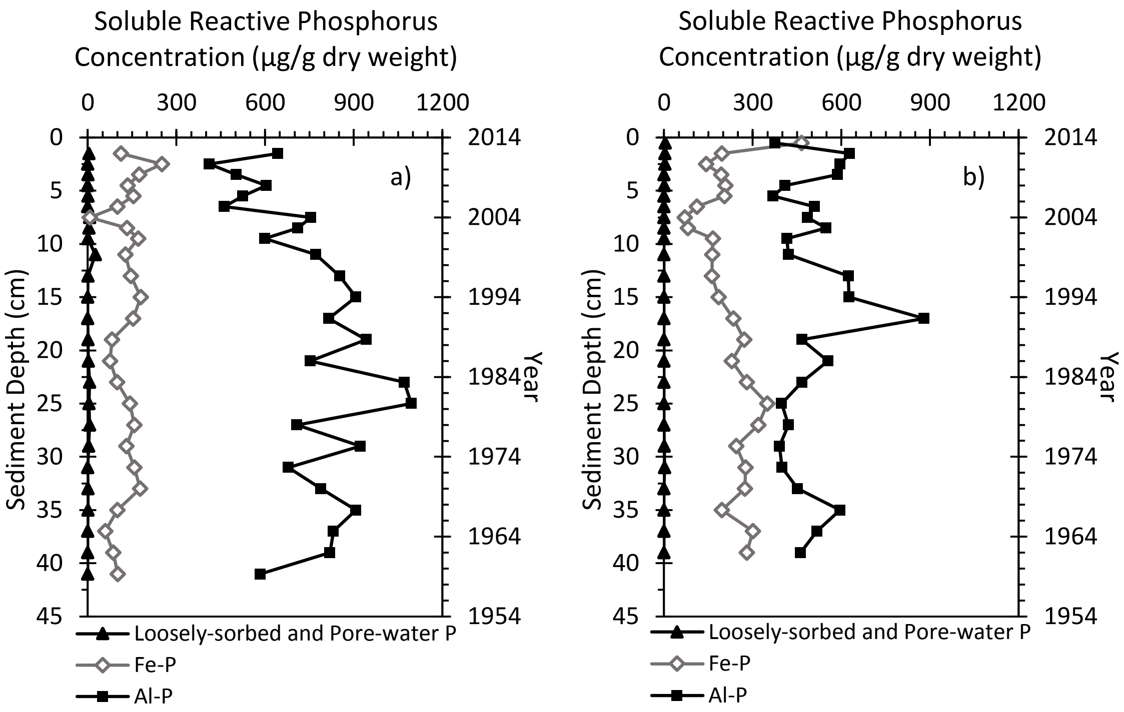

Figure 3-8. Sediment depth profiles of phosphorus species in a) core 1-A and b) core 1-B.

<u>Stable Isotopic Composition</u>

Terrestrial and Aquatic Vegetation

Stable isotopic composition results of collected terrestrial and aquatic plant samples, suspended organic matter, and sediment are presented in delta notation relative to the Vienna Pee Dee Belemnite standard (for C) and Air N_2 standard (for N).

Suspended organic matter in epilimnetic water, as measured from filters, exhibited suspended organic matter (SOM) with $\delta^{13}C$ values of -23.8±0.2‰ and

-26.3±0.9‰ in the fresh and decomposed samples, respectively (Table 3-4). The measured δ^{15}N was 2.3±0.5‰ and 5.3±1.4‰ in the fresh and decomposed samples, respectively.

Table 3-4. Stable isotopic composition of different organic matter sources

Sample	δ^{13}C (‰ vs. VPDB)	δ^{15}N (‰ vs. Air N_2)
SOM, Decayed	-26.3±0.9	5.3±1.4
SOM, Fresh	-23.8 ±0.2	2.3±0.5

.

Sediment

At Site 1, $\delta^{13}C$ was highly variable from the bottom of the cores until about 10 cm (2002) (Figure 3-9a). At 10 cm, it shifted to more negative values and then remained relatively constant (with minor fluctuations) in the top 10 cm of the cores. Sedimentary $\delta^{15}N$ was constant with depth at 3‰ (Figure 3-9b).

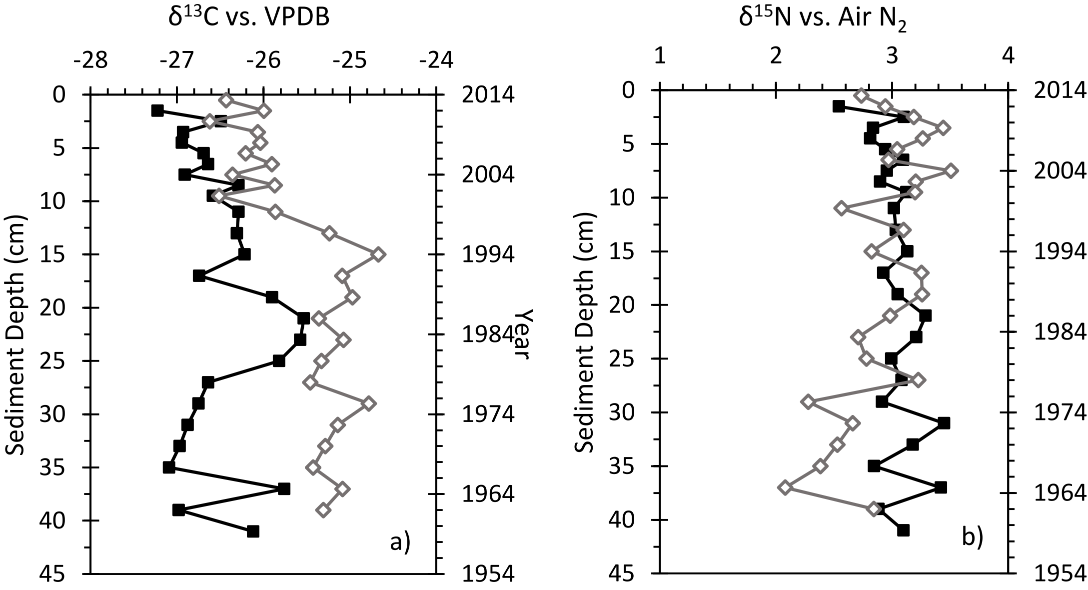

Figure 3-9. Sedimentary $\delta^{13}C$ composition (a) and $\delta^{15}N$ composition (b) at Site 1. Solid, black squares represent data points in core 1-A. Open, grey diamonds represent data points in core 1-B.

At Site 6, δ^{13}C gradually increased from -27.5‰ at 15 cm then at 10 cm, it leveled out around -25‰ in core 6-A and -26 in core 6-B (Figure 3-10 a). The δ^{13}C signature of sediment is significantly negatively correlated with depth (r=-0.91) and with organic carbon content (r=-0.92) and nitrogen content (r=-0.93) (Table 3-3). Sedimentary δ^{15}N increased from 1.5~2‰ at the bottom of the cores to 3‰ at the top of the cores (Figure 3-10b).

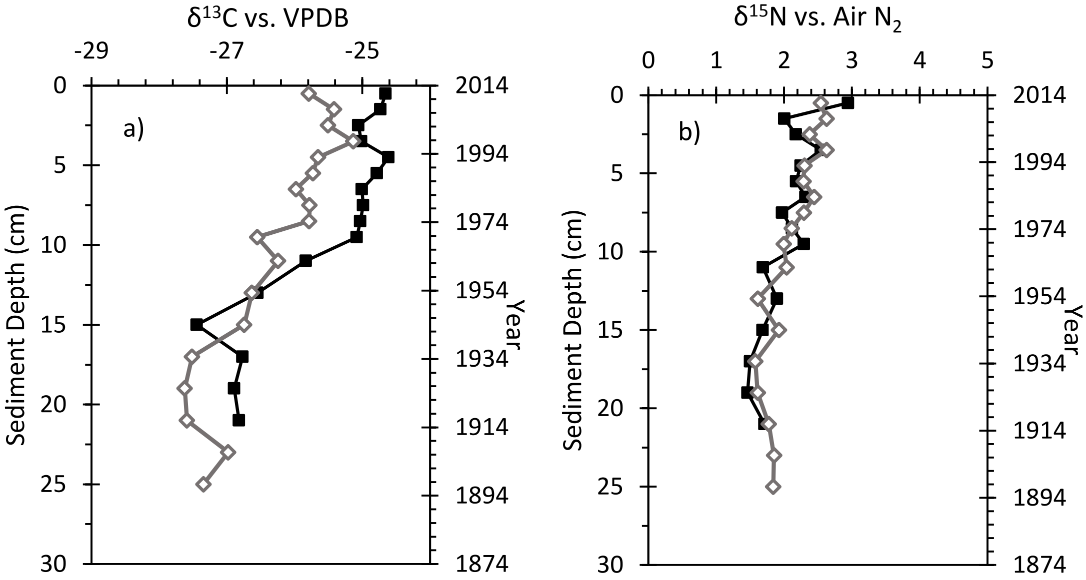

Figure 3-10. δ^{13}C composition (a) and δ^{15}N composition (b) at Site 6. Solid, black squares represent data points in core 6-A. Open, grey diamonds represent data points in core 6-B.

Discussion

Correlation analysis between the measured sediment properties with hydrologic properties of the lake corresponding to the same time period (average precipitation, lake level, etc.) resulted in the finding of no significant relationships. The lack of significant correlations between measured sediment properties with supplemental hydrologic data suggests that for a given sediment property, there is a combination of biogeochemical processes contributing to its variance---no one factor has a significant impact on a given sediment property. In addition, the processes that affect each sediment property are not constant over time due to changes occurring in the watershed and implementation of different management practices (Figure 3-1). With each shift in lake processes due to watershed events or management strategies, the interactions between constituents in the water column and sediment would have changed drastically and processes that previously contributed to the variation in one sediment property may no longer have a direct influence on its value.

Water Content

The water content at Site 1 increased with decreasing depth because sediment at the top of the core is less compacted than sediment towards the bottom, under the weight of the overlying sediment. Water content is greater at Site 1 than Site 6 which is consistent with previous analyses of Big Bear Lake sediment that concluded Site 1 contained the greatest clay content, which has higher porosity than sand or silt (Dyal, 2003).

Water content at Site 6 decreased from the bottom of the cores to a depth of about 9.5 cm, corresponding to the year 1974 (Figure 3-2b). The depth 9.5 cm represents the median depth for the sediment interval from 8 cm to 9 cm which corresponds to the time frame from 1969 to 1979. In 1977, lake level stabilization would have increased the depth of the water column at Site 6. Increases in lake level at a particular site result in the reduction of larger sediment particle input (sand) and increases in smaller sediment particles which have greater porosity, and thus greater water content (Rothenberg et al., 2010). Kirby (2005) observed a transition from sandy-silts below 8 cm at TMDL 6 to silty clay in top sediments from a sediment core extracted in 2003.

Elemental Composition

Site 1

Organic carbon and nitrogen were constant with depth from the bottom of the cores to 5 cm (Figure 3-3a, b). The data fit slightly better to an exponential function (r=0.954) than a linear function (r=0.952) for OC, and N content also fit slightly better to an exponential function (r=0.983) than a linear function (r=0.981), which is indicative of organic matter decomposition in top sediments (Wetzel, 2001). Rate constants and half-lives were calculated and are presented in Table 3-5.

Table 3-5. Rate constants and half-lives (with 95% confidence intervals) for organic carbon and total nitrogen in Big Bear Lake sediment from Site 1.

	k_r (yr^{-1})	$t_{1/2}$ (yr^{-1})	Lower 95% C.I.	Upper 95% C.I.
Organic Carbon	0.019±0.004	36.5	24.2	73.9
Total Nitrogen	0.033±0.004	21.0	15.4	33.7

Organic carbon and nitrogen half-lives in Big Bear Lake sediment are relatively short compared to deeper lakes such as Lake Superior (half-lives 54-180 years) but longer than half-lives of OC and N in Lake Elsinore, a shallower eutrophic lake also located in southern California (Johnson et al., 1982).

Below 5 cm, the OC and N concentrations were constant with depth which suggests that only the top 5 cm is involved in active decomposition. Organic matter is normally better preserved in deeper water due to increased stratification limiting the amount of O_2 that reaches sediment and bottom waters. However, OC and N content were lower at Site 1 than the shallower Site 6. This discrepancy can be explained by the presence of macrophytes at Site 6, which have very recalcitrant OM constituents that decay much more slowly than algae (Wetzel, 2001; Kirby et al., 2012). Average OC:N at Site 1 was 8, reflecting algal biomass input which typically has an OC:N value less than 9 (Kapanen, 2012). OC:N commonly increases with sediment depth as N is preferentially utilized during microbial decomposition (Lehmann et al., 2002). At Site 1, OC:N was constant with depth which suggests that organic matter is highly recycled in the water column, prior to permanent sedimentation (Hiriart-Baer et al., 2011).

Typically, total phosphorus decreases with increasing depth, due to mineralization of organic matter and conversion of organic phosphorus to inorganic P (Rydin, 2000). This trend was reflected in both replicate cores, although in core 1-A, TP increased up-core in the top 5 cm and in core 1-B, TP increased up-core in the top 10 cm (Figure 3-4d). Therefore, it is difficult to make any conclusive assumptions about the depth that sediment contributes to active P recycling. Generally, it is considered to be the top 10 cm (Kapanen, 2012). Average TP concentrations at Site 1 were about 1,200 µg/g dry weight which is similar to TP concentrations in other moderately eutrophic and mesotrophic lakes. For example, Lake Simcoe, a mesotrophic lake in Canada, has an average TP of 1,500 µg/g (Dittrich et al., 2013) and Lake Erken, also a mesotrophic lake located in Sweden, has an average TP of 1,100 µg/g (Rydin, 2000).

Inorganic elements, specifically aluminum, potassium, and silicon exhibited a brief increase in influx to the sediment around the year 1984, which was more pronounced in core 1-A than 1-B and also corresponded with a decrease in sulfur and calcium (Figure 3-3d; Figure 3-4a, b, c; Figure 3-5). 1983 was an extremely wet year in this region, and increases in precipitation would have increased runoff and input of inorganic materials to lake sediments (Figure 3-1c). The molar ratio of silicon to aluminum (approximately 2.73) suggests the influx of alumino-silicates with a molar ratio of 3, such as albite, to the sediment. The influx of inorganics likely diluted other constituent concentrations (sulfur and calcium).

Sulfur began decreasing in the sediment in 2004, suggesting that aeration has reduced the production of metal sulfides which precipitate under conditions of low dissolved oxygen (Wetzel, 2001).

Calcium displayed increasing concentrations from 1984 to about 2004, where it stabilized (Figure 3-5). With the successful alum treatment in 2004 and the start of aeration on the west side of the lake, the presumed decline in algal productivity with reduction in internal loading may have reduced the precipitation of $CaCO_{3,}$ which is induced by photosynthesis.

The variability in other bulk elemental concentrations in the replicates cores from Site 1 and lack of significant correlations (Table 3-2) between elements hinders the interpretation of biogeochemical processes occurring in profundal sediment near the dam.

Site 6

Elemental depth profiles at TMDL Site 6 exhibited significant correlations with each other as well as significant increases (or decreases) in concentrations from about 15 cm to 10 cm (Figure 3-6a, b; Figure 3-7). The pronounced changes began at sediment depth corresponding to 1940 (1935-1945) and continued until about 1974 (1969-1979). These trends are arguably largely the result of changes in lake levels as well as proliferation of macrophytes and subsequent in-lake management strategies to control macrophyte growth.

Organic carbon and nitrogen decreased drastically from the bottom of the cores to about 10 cm, corresponding to the time interval 1969-1979 (Figure 3-6a, b). During this interval, the prolonged 15-year drought of the 1950s and 1960s came to an end and the in-lieu stabilization program began which prevented significant reductions in lake level (Kirby, 2005) (Figure 3-1a, b). The maintenance of deeper water at Site 6 presumably allowed for greater preservation of organic matter. Prior to this time period, decreasing lake level and shallower waters would have increased oxygen content of bottom waters, increasing decomposition and decreasing OC and N preservation. The early 1980s also mark the beginning of mechanical harvesting of macrophytes. Prior to that time, macrophytes were increasing in abundance. The epiphytic algae community associated with macrophytes mineralize a majority of OC and N and recycle it within the epiphytic/macrophyte complex, reducing the OC and N that is permanently buried in the sediment (Wetzel, 2001). In addition, the dominant macrophytes in Big Bear Lake, coontail and milfoil, are perennial and during winter dormancy, only leaves and shoots senesce while roots persist (Wetzel, 2001). The OC and N accumulated in macrophyte roots and the attached periphyton community would have been removed during mechanical harvesting, representing a permanent removal of the OC and N stored in macrophyte biomass.

OC:N at Site 6 is greater than at Site 1 due to the contribution of macrophyte biomass which has a higher OC:N ratio than algal biomass (Wetzel, 2001). The decline in OC:N with decreasing depth (Figure 3-6c) can be explained by a shift in OM source or may indicate preferential utilization of N during decomposition. OC:N content decreased from 13 at the bottom of the cores to 10 at the top of the core. However, comparison of OC:N profiles with organic carbon and nitrogen depth profiles reveals that OC:N does not reflect the same trend as OC and N. If substantial decomposition was occurring in sediment, OC and N would be expected to decrease with depth in addition to the change in OC:N ratio, which suggests that the increase in OC:N with depth is not due to diagenetic processes. The average OC:N content measured from terrestrial vegetation was 84.5 which is much greater than the OC:N content of aquatic vegetation, with a mean value of 23 (Table 3-1). Since terrestrial plants have a greater OC:N content than macrophytes, the decrease in sedimentary OC:N over time could be attributed to increasing aquatic plant biomass relative to terrestrial.

Metals and other inorganic elements exhibited a drastic increase between 1934 and 1974 (Figure 3-7a, b). Delivery of inorganics to sediment can result from increased erosion in the watershed as well as a decrease in distance from source (eroded soils) and sink (bottom sediment) (Rothenberg et al., 2010). Increases in urbanization and resort-development during the 1930s and 1940s would have resulted in extensive land-clearing and erosion. The increase in inorganic elements at Site 6 is consistent with the period of development and urbanization within Bear Valley watershed which would be expected to increase erosion and thus the delivery of metals to the sediment. However, Site 1 does not exhibit this same drastic increase (Figure 3-4a, b), therefore the increase is most likely due to declining in lake level during this period and decreased distance that inorganics had to travel before settling on bottom of the lake at Site 6. According to Kirby (2005), during the 1950s and 1960s drought which lasted about 15 years, TMDL 6 was likely at or above lake level, so changes in lake level would have had more drastic consequences on depositional processes at Site 6 than they would at Site 1. The increase in metal concentrations subsided around 1974 when deeper lake depths were maintained due to the implementation of the in-lieu water program.

Although total phosphorus is not significantly correlated with water content, the two properties reflect similar trends which are related to changes in lake level (Figure 3-2b; Figure 3-6d). Like water content, TP began to increase at 10 cm (Figure 3-6d) because prior to this period of time, sediments were comprised of larger-sized particles which reduce the amount of P stored in sediments because it is easily leached to the water (Kapanen, 2012). In addition, macrophytes absorb P directly from sediment. P releases from the senescence of macrophyte biomass are readily utilized by the attached periphytic community through direct assimilation or adsorption onto $CaCO_3$ (Wetzel, 2001).

Phosphorus Species

Redox-sensitive P made up 20% of TP in Big Bear Lake which is consistent with studies of other mesotrophic lakes such as Lake Simcoe in Ontario, Canada, in which Fe-P made up 20% of total P in the main basin and 42% of total P in Kempenfelt Bay. However, in both basins, Fe-P decreased with sediment depth reflecting its mobility within the sediment (Dittrich et al., 2013). In Big Bear Lake, Fe-P and mobile-P remained fairly constant with depth (Figure 3-8) which may be the result of aeration which prevents P release from the Fe-P fraction. Low concentrations of loosely-adsorbed/pore-water P throughout the entire length of the cores indicates that the majority of organic P is mineralized in the water column, prior to sedimentation (mineralization of OM is the main source of pore-water P). Any P that is mobilized with depth may be immediately adsorbed onto aluminum or calcium in the sediment. In both replicates, Fe-P experienced the lowest values at about 7 cm, corresponding to the year 2004. Iron does not exhibit this same trend and is not correlated with Fe-P, implying a decoupling of the Fe and P cycles. The minimum in Fe-P concentration during 2004 may be due to the effects of the herbicide in the two years prior which increased nutrient concentrations in the water column and depleted dissolved oxygen, leading to a release of P from redox-sensitive fractions in the sediment. Although not significantly correlated, Al-P and bulk aluminum concentration both exhibited an increase around 25 cm (1984 in core 1-A), immediately following the wet year of 1983 which would have increased aluminum flux from the watershed to lake sediments (Figure 3-1; Figure 3-4a; Figure 3-8).

Stable Isotopic Composition

Variations in $\delta^{13}C$ with sediment depth have been attributed to diagenetic processes occurring in the sediment, a shift in dominant source of organic matter (allochthonous vs. autochthonous), and changing lake productivity (Hodell & Schelske, 1998; Terranes & Bernasconi, 2000; Dean, 2006; Machiwa, 2010; Hiriart-Baer et al., 2011; Torres et al., 2012).

Decomposition of organic matter typically results in a decrease in $\delta^{13}C$ of 1.6 to 1.8‰ with depth due to preferential decay of more labile compounds which are also more enriched than recalcitrant compounds, as well as contribution of depleted microbial biomass (Lehmann et al., 2002). The $\delta^{13}C$ value of decomposed SOM in epilimnetic water was 2.5‰ depleted compared to fresh SOM which indicates that decomposition results in a 3‰ decrease (Table 3-4). These results are consistent with previous studies that have observed 2-3‰ decreases in settling particulate organic matter and organic matter in the sediment under anoxic conditions (Lehmann et al., 2002; Dean, 2006). In recently deposited sediments of eutrophic Lake Mendota, values of $\delta^{13}C$ were 2-3‰ lower than the POC produced in the epilimnion due to the addition of OC produced by methanotrophic bacteria in the hypolimnion (Dean, 2006). The lower $\delta^{13}C$ value of decomposed SOM compared to initial SOM, and the similarity between decomposed SOM and sediment core-top $\delta^{13}C$ values (Figure 3-9a) suggest significant recycling occurring in the water column, prior to permanent sedimentation, otherwise it would be expected that the surficial sediment values would reflect $\delta^{13}C$ of fresh SOM (-23.8‰). While changes in $\delta^{13}C$ may be occurring in the water column, there was no evidence of diagenesis occurring on $\delta^{13}C$ within the sediment at Site 1. In the top 10 cm, $\delta^{13}C$ was constant (Figure 3-9a), while OC decreased in the top 5 cm (Figure 3-3a). This suggests that as OC is depleted due to decomposition, $\delta^{13}C$ does not change. In Lake Ontario, sedimentary diagenesis of OC in oxic pore waters was observed to reduce OC in top sediments without changing the $\delta^{13}C$ composition (Hodell & Schelske, 1998). The lack of a significant change in $\delta^{13}C$ with increasing diagenesis allows for the utilization of $\delta^{13}C$ in inferring historic changes in productivity or organic matter deposition within Big Bear Lake.

Due to the differences in $\delta^{13}C$ signatures between terrestrial and aquatic vegetation, variations in $\delta^{13}C$ in sediment can also occur due to shifts in relative contribution of allochthonous vs. autochthonous OM. Terrestrial vegetation collected from Big Bear Lake's watershed had an average $\delta^{13}C$ of -27.3‰ which is consistent with values reported for terrestrial plants in other studies, between -26 and -28‰ (Dean, 2006). Aquatic vegetation and suspended organic matter had slightly more enriched values, which is expected due to CO_2 limitation in lakes (Torres et al., 2012). The decrease in $\delta^{13}C$ values at Site 1 therefore suggests a shift to greater terrestrial vegetation input relative to autochthonous organic matter.

Increasing productivity typically results in more positive $\delta^{13}C$ values due to CO_2 depletion in epilimnetic water during phytoplankton blooms. As CO_2 becomes depleted, it also becomes progressively enriched in ^{13}C because of the fractionation algae exert against ^{13}C. As the pool becomes more enriched, algae utilize increasing amounts of ^{13}C, leading to an enrichment in $\delta^{13}C$ in the sediment (Torres et al., 2012). However, at Site 1, $\delta^{13}C$ exhibits a negative shift rather than positive which may reflect decreasing productivity due to successful in-lake management strategies implemented to reduce phytoplankton blooms. The shift to more negative values occurred around 2004, when alum treatment was implemented in the western region of the lake. The immobilization of phosphorus lowered P concentrations in the water column, and suppressed P release from the sediment, making it less available to phytoplankton. This decrease in P availability may have reduced autochthonous productivity, causing a greater relative contribution of terrestrial vegetation, and a corresponding decrease in $\delta^{13}C$ in the sediment.

Site 6 exhibited more positive $\delta^{13}C$ compared to Site 1, due to shallower water and more eutrophic conditions (Figure 3-10a). $\delta^{13}C$ increased drastically from 15-20 cm to 10 cm which may be indicative of diagenetic processes, however, since $\delta^{13}C$ is significantly correlated with other constituents, including inorganic elements, the increase with decreasing sediment depth is likely not a result diagenetic processes and actually reflects lake level changes that specifically impact Site 6 sediment. The fact that $\delta^{13}C$, OC, and N concentrations (Figure 3-6; Figure 3-10) were constant in the top 10 cm implies that the OM is already highly mineralized in the water column or that diagenesis is not a prominent process occurring in the top sediment at Site 6, probably due to the highly recalcitrant OM that comprises macrophyte biomass. The increase in $\delta^{13}C$ from

1934 to 1974 could also have resulted from the increasing contribution of autochthonous OM (macrophytes) relative to terrestrial OM. The rapid increase subsides when the mechanical harvesting program was implemented and macrophyte biomass contributions were stabilized.

Changes in $\delta^{15}N$ of sediment have been found to occur due to diagenetic processes, denitrification, and changes in productivity (if N is a limiting nutrient) (Terranes et al., 2000; Torres et al., 2012). Diagenetic changes are due to a balance between addition of depleted microbial biomass and substrate degradation which results in enrichment of residual OM (Lehmann et al., 2002). As suspended organic matter settles in the water column, decomposition results in preferential mineralization and release of ^{14}N ammonium, leaving residual OM enriched in ^{15}N (Lehmann et al., 2002). The $\delta^{15}N$ of SOM in Big Bear Lake reflects this process with 3‰ enrichment of decomposed SOM in Big Bear Lake surface water relative to the initial SOM signature (Table 3-4). Once SOM reaches the anoxic hypolimnion and/or sediment, chemotrophic processes contribute depleted microbial biomass, lowering the $\delta^{15}N$. This explains why $\delta^{15}N$ at the sediment surface at both sites does not reflect the decomposed SOM because contribution of depleted microbial biomass offsets the enrichment due to mineralization of ammonium (Figure 3-9 b; Figure 3-10 b; Table 3-4).

Increases in denitrification with the onset of anoxic conditions in bottom water have also been attributed to enrichment of $\delta^{15}N$ due to the preferential reduction of ^{14}N-nitrate, leaving residual nitrate enriched in ^{15}N (Teranes & Bernasconi, 2000; Lu et al., 2010). In Lake Erie, from 1960 to 1985, $\delta^{15}N$ values were relatively constant despite large changes in epilimnetic nitrate concentrations during this period. The fact that $\delta^{15}N$ increased until 1960 and then remained constant was correlated with the history of anoxia in the basin (Hodell & Schelske, 1998). Similarly, $\delta^{15}N$ of Site 1 sediment remained constant with depth through-out the entire length of the core despite fluctuations in N loads to Big Bear Lake over the past 50 years.

If N is limiting, increasing $\delta^{15}N$ often reflects increased productivity and more eutrophic conditions as phytoplankton (or aquatic plants) compete for limited N and use progressively more ^{15}N relative to ^{14}N as the epilimnetic CO_2 pool becomes more enriched in ^{15}N (Lehmann et al., 2002). In Lake Simcoe, Canada, $\delta^{15}N$ increased from 4.5‰ to 7.3‰ in the main basin. This increase was attributed to increasing productivity due to its correlation with $\delta^{13}C$ as well as TP concentrations which also increased up-core. C:N of OM decreased up-core, signifying increasing autochthonous primary productivity (Hiriart-Baer et al., 2011). Site 6 sediment in Big Bear Lake demonstrated similar trends, with increases in $\delta^{15}N$ up-core corresponding to increased TP concentration and decreased OC:N values (Figure 3-6c, d; Figure 3-10b). These multiple lines of evidence point to increasing productivity at Site 6.

Conclusion

Phosphorus concentration, stable isotopic and elemental composition of Big Bear Lake sediment reflect changes in depositional processes within the lake in response to changes in productivity as well as historical in-lake management activities. Lake level stabilization has had a significant effect on biogeochemical processes operating at TMDL Site 6, including organic matter preservation, total phosphorus burial, and deposition of metals and inorganics in the sediment. The proliferation of macrophytes at Site 6 has resulted in a drastic difference between OM processes and biogeochemical processes occurring at Site 1 and Site 6. Comprehensive interpretation of the differences in sediment processes occurring at Site 1 and Site 6 and how they have varied over time provides a framework for interpreting how future watershed events will affect sedimentary and lake-wide processes.

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