LAKE SEDIMENT GEOCHEMICAL CHANGES IN RESPONSE TO LAND USE VARIATIONS IN THE CATCHMENTS OF LAKES VOLVI AND KORONIA, NORTHERN GREECE

by

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LAKE SEDIMENT GEOCHEMICAL CHANGES IN RESPONSE TO LAND USE VARIATIONS IN THE CATCHMENTS OF LAKE VOLVI AND LAKE KORONIA< NORTHERN GREECE

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Lakes Koronia and Volvi, located within the Mygdonia Basin in northern Greece, comprise an internationally protected wetland. The lakes support major industrial and agricultural activities, and a population of 45,000. Consequently, both sites have been greatly impacted by the conversion of marshland to farmland, water losses to irrigation, and pollution discharges including raw sewage, agricultural run-off, and industrial wastes. Sediment chronology and accumulation rates have been determined in cores from multiple sites within the lakes using ^{210}Pb dating techniques. Bulk sediment elemental composition (organic carbon content, C/N ratios, etc.) and trace metal concentrations have been measured to provide critical evidence for variations in land-use within watersheds. Stratigraphic variations in the carbon and nitrogen isotopic ratio of sedimented organic matter have been measured to determine changes in aquatic ecosystem productivity. The geochemical results will be compared to historical records to determine the relative importance of disturbances caused by urban, agricultural, and industrial activities.

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PREFACE

I would like to thank my committee members, Dr. Daniel Bain, Mr. Mark Collins, Dr. Mark Besonen, and especially Dr. Michael Rosenmeier. I would also like to thank Dr. George Zalidis, Vasilis Takavakoglou, Babatsikou Efrosini, Ourania Dionysiou, Thomas Alexandridis, and the Laboratory of Applied Soil Science, Aristotle University of Thessaloniki for facilitating fieldwork. I also thank Dr. Thomas Crisman, University of South Florida, for logistical assistance and thoughtful discussions. I am grateful to Benjamin Cavalari, Dr. Jason Curtis, Clayton Magill, Michael Rubinov, Janice Shook, and Marion Sikora for assistance in the field. Dr. Mark Brenner and William Kenney at the University of Florida's Land Use and Environmental Change Institute kindly provided ^{210}Pb and total phosphorus measurements. This work was funded in part by NSF grant ATM-0502216, grants from the University of Pittsburgh's University Honors College, University Center for International Studies, and Office of Experiential Learning, and an Undergraduate Student Research Grant from the Geological Society of America.

1.0 INTRODUCTION

Lakes Koronia and Volvi, located within the Mygdonian Basin in northern Greece, and their surrounding wetlands provide a critical water resource for agricultural, municipal, and industrial activities as well as a habitat for many rare and protected plant and animal species (Frasier, 1996). In 1995, massive fish kills, noxious algal blooms and water toxicity to birds plagued Lake Koronia, indicating large scale ecological shifts and overall environmental degradation within at least part of the basin. As early as 1974, international concern for the protection of the aquatic systems of the Mygdonian Basin became apparent when Lakes Koronia and Volvi were included in the Ramsar Convention on Wetlands (Frasier, 1996). In accordance with the Ramsar Convention, the European Union formulated a master plan for the environmental rehabilitation of Lake Koronia during the 1990s. Concerns have been raised about the economic and technological feasibility of this plan. For example, three solutions for restoring Lake Koronia are the diversion of winter flood discharge of the torrents that naturally drain into Lake Volvi, the transfer of water from the Aliakmon River, and the transfer of water from deep aquifers (Kolokytha, 2002). These could be harmful to Lake Volvi without successfully restoring Lake Koronia. Other main objectives of the plan lack funding, resources, and political will.

Although the wetland is internationally protected, the master plan and other conservation measures have been inadequate in protecting the remaining ecosystem. Water and land use is unregulated and intense farming and fishing activities have, in fact, been incentivized by the

Greek government, specifically through the District Authorities of the Ministry of Agriculture (Pyrovetsi 1997). Moreover, individuals residing within the watershed are generally uninformed about wetland conservation. Surveys conducted with both wetland and plains farmers within the region highlighted negative attitudes towards protected bird species, environmental policies, and the consequences of intensifying agriculture. Wetland farmers also had less awareness pertaining to the relationship between environment degradation and agriculture (Pyrovetsi and Daoutopoulos, 1997). No remediation efforts consider implementing sustainable farming initiatives as a primary goal.

The purpose of this study was to determine if recent (last ~100 years) changes in land use within the Mygdonia basin can be observed in sediment records of Lake Koronia and Volvi as well as to determine if there is evidence for longer-term (multi-century) human impacts on the lakes. Changes in lake productivity were reconstructed using stratigraphic variations in the carbon and nitrogen isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) of sediment core organic matter, sediment nutrient concentrations, and diatom and sponge spicule silica percentages. Bulk elemental concentrations were also used to reconstruct changes in sediment source. This record provided for the comparison of a heavily disturbed shallow lake and a relatively pristine deeper lake. Additionally, the record is used to determine whether older sediments in the lakes could be used to establish baseline conditions and whether geochemical results can provide insight into more effective remediation efforts.

2.0 STUDY SITE

The Mygdonia Basin, northern Greece has an area of about 16,400 hectares and is located 30 km northeast of the city of Thessaloniki. Lake Koronia (75 m above mean sea level) is located in the western portion of the basin (Figure 1). The lake is shallow (z_{avg}= 2 m) with a surface area of approximately 40 km^2 (Frasier, 1996). In contrast, the adjacent Lake Volvi (37 m a.m.s.l.), located in the eastern portion of the Mydgonia Basin, is much deeper (z_{avg} = 13.5 m) and more expansive, with a surface area nearing 70 km^2 (Frasier, 1996) (Figure 1).

The Koronia-Volvi watershed is occupied by ~45,000 people, with nearly 16,000 individuals concentrated in the town of Langadas, on the western shore of Lake Koronia (Frasier, 1996). Initially, this population expanded through refugee migrations into the watershed following the Ottoman-Habsburg Wars in the 1700s and after the Turkish War for

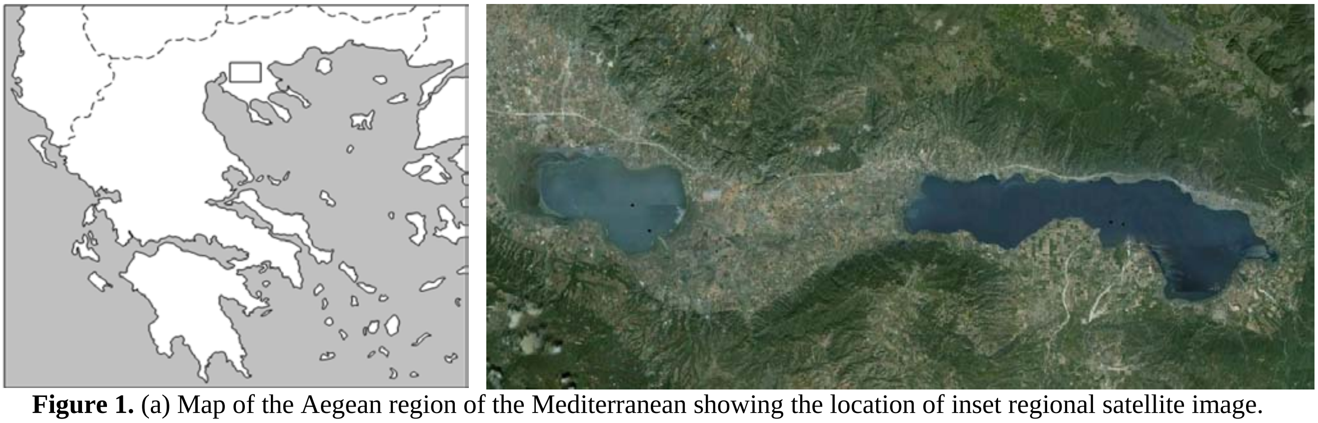

Figure 1. (a) Map of the Aegean region of the Mediterranean showing the location of inset regional satellite image. (b) Satellite image of the sediment coring sites at Lakes Koronia and Volvi, just east of the city of Thessaloniki.

Independence in the 1920s. Recent growth (since 1940) has been more dramatic along the western margins of the Koronia basin, largely as a result of the urban expansion of Thessaloniki (Frasier, 1996).

Although there are small scale industrial and municipal activities, land use in the Mygdonia Basin is primarily agricultural. Ninety percent of the basin lowland is cultivated with cereals, maize, tomatoes, and tobacco crops. Agricultural activities have been most intense to the northwest of Lake Koronia (Frasier, 1996). Advances in cultivation techniques became widespread in the 1940s and use of fertilizers began in the 1970s (Mitraki et. al, 2004). This agricultural expansion has affected the lakes (and surrounding wetlands) through the run-off of agrochemicals, conversion of marshland to farmland, and unsustainable water use, specifically the extraction of groundwater for irrigation. The effects of irrigation have become especially apparent in Lake Koronia, wherein l water levels have dropped progressively from 3.8 m in 1980 to <1 m in 1997 (Mitraki et, al, 2004).

The most important municipal environmental effect is the drainage of untreated sewage and industrial effluents into the lakes. Seventy small to medium sized industrial facilities are located on the western shore of Lake Koronia. The main industries are textile dyeing, dairy processing, metal finishing and fruit and vegetable canning (Tsiouris et. al., 2002). Commercial fishing was once a productive industry in both Lake Koronia and Volvi. However, over the last several decades, overfishing and degraded water quality have led to the depletion of fish stocks within the Koronia basin. Fishing is still productive in Lake Volvi, but overfishing is becoming an increasing threat (Frasier, 1996).

3.0 METHODS AND MATERIALS

In July 2005, four short (<1 meter) sediment cores were extracted from Lake Volvi and Lake Koronia (Figure 2, Table 1). Sediments were collected with a piston corer designed to retrieve undisturbed sediment-water interface profiles (Fisher et al., 1992). All cores were sectioned in the field at 1.0-cm intervals by upward extrusion into a sampling tray fitted to the top of the core barrel. Surface water samples (from a depth of ~30 cm) were also collected from the lakes.

Figure 2. Sediment core locations in Lakes Koronia and Volvi denotes by yellow dots

Sediment core chronologies from Koronia and Volvi were determined by ^{210}Pb and AMS ^{14}C dating. Radioisotope (^{210}Pb, ^{226}Ra, ^{137}Cs) activities were measured initially on a single core from Koronia (KOR-1-15-VII-05) and Volvi (VOL-1-16-VII-05) by direct gamma counting

Table 1. Sediment coring information for Lakes Koronia and Volvi

Core designation	Latitude and Longitude	Water depth	Total core length
KOR-1-15-VII-05	40°40’43.55” N 23°10’12.45” E	70 cm	90 cm
KOR-2-15-VII-05	40°39’56.67” N 23°10’53.75” E	70 cm	85 cm
VOL-1-16-VII-05	40°40’11.94” N 23°29’50.70” E	12.3 m	65 cm
VOL-2-16-VII-05	40°40’11.94” N 23°29’21.74” E	11.6 m	70 cm

(Appleby et al., 1986; Schelske et al., 1994) using an EG & G Ortec® GWL high purity germanium well detector at the University of Florida. Additional radioisotope activities in cores KOR-1-15-VII-05 and VOL-1-16-VII-05, as well as a second site in each of the lakes (KOR-2-15-VII-05 and VOL-2-16-VII-05) were measured at the University of Pittsburgh. In all cases, ^{226}Ra activity was measured at each depth to estimate supported ^{210}Pb activity. Unsupported ^{210}Pb activity was determined by subtraction of supported activity from the total activity measured at each level (Appleby & Oldfield, 1978). Radiocarbon ages were determined by accelerator mass spectrometry (AMS) at the University of California, Irvine W.M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory. Calibrated ages were calculated with the INTCAL09 on-line calibration (Reimer et al., 2009).

Total sediment organic carbon (TOC) and nitrogen (TN) concentrations were measured on acidified, carbonate-free samples using a EuroVector high temperature elemental analyzer. Inorganic carbon (IC) was measured by coulometric titration (Engleman et al., 1985) using a UIC/Coulometrics Model 5011 coulometer and coupled automated acidification preparation system (AutoMate FX, Inc.). Total phosphorus (TP) was measured at the University of Florida’s Land Use and Environmental Change Institute using a Technicon Autoanalyzer II with a singlechannel colorimeter, following digestion with H_2SO_4 and $K_2S_2O_8$ (Schelske et al., 1986). Biogenic silica from diatom frustules and sponge spicules was also measured at the University of Florida using the Technicon Autoanalyzer II and heteropoly blue method following digestion with Na_2CO_3 (Conley & Schelske, 1993).

Acidified, carbonate-free sediment samples for stable carbon and nitrogen isotope analyses were measured with a GV Instruments, Ltd. (now Isoprime, Ltd., a subsidiary of Elementar Analysensysteme) Isoprime™ stable isotope ratio mass spectrometer and coupled EuroVector high temperature elemental analyzer with a diluter kit for sequential isotope analyses. By international standard, $\delta^{13}C$ values are expressed in conventional delta (δ) notation as the per mil (‰) deviation from the Vienna PeeDee Belemnite (VPDB). Nitrogen isotope results are similarly expressed in conventional delta notation as the permil deviation from air.

Sediment core elemental analysis was performed by SGS Geochemical Services in Toronto. Concentrations of thirty-two metals were determined at 5-cm intervals within cores KOR-1-15-VII-05 and VOL-1-16-VII-05 by inductively coupled plasma mass spectrometry after a multi-acid digestion using HCl, HNO_3, HF, and $HClO_4$.

4.0 RESULTS

4.1 SEDIMENT CHRONOLOGY

Near-basal sediment core ages from Lakes Koronia and Volvi (Table 2) suggest the recovery of nearly 400 years of sediment from each basin. A direct basal date was indeterminable within VOL-2-16-VII-05, given the return of an ‘ultra-modern’ radiocarbon age, likely the result of some form of contamination.

Table 2. Near-basal radiocarbon ages from the Lake Koronia and Lake Volvi sediment cores.

Core	Depth	Accession numbers	Material	Radiocarbon age (BP)	±	Calibrated two sigma age ranges (AD)
Lake Koronia Core 1	84-85 cm	UCI76103	Wood	360	20	1560-1630
Lake Koronia Core 2	78-79 cm	UCI76104	Charcoal	270	120	1440-1710
Lake Volvi Core 1	64-65 cm	UCI76007	Charcoal	410	90	1390-1660
Lake Volvi Core 2	66-67 cm	UCI76008	Charcoal	-3800	100	Invalid Age

Pb-210 determinations, unfortunately, failed to provide any reliable sediment chronologies for the last ~100 years within both lakes. In core KOR-1-15-VII-05, for example, only two samples contained unsupported ^{210}Pb and no definitive monotonic decline in total ^{210}Pb activity was observed in VOL-1-16-VII-05 (Figure 3). Cesium-137 activities within all cores, however, provided some temporal constraints on near surface sediments. The first measurable

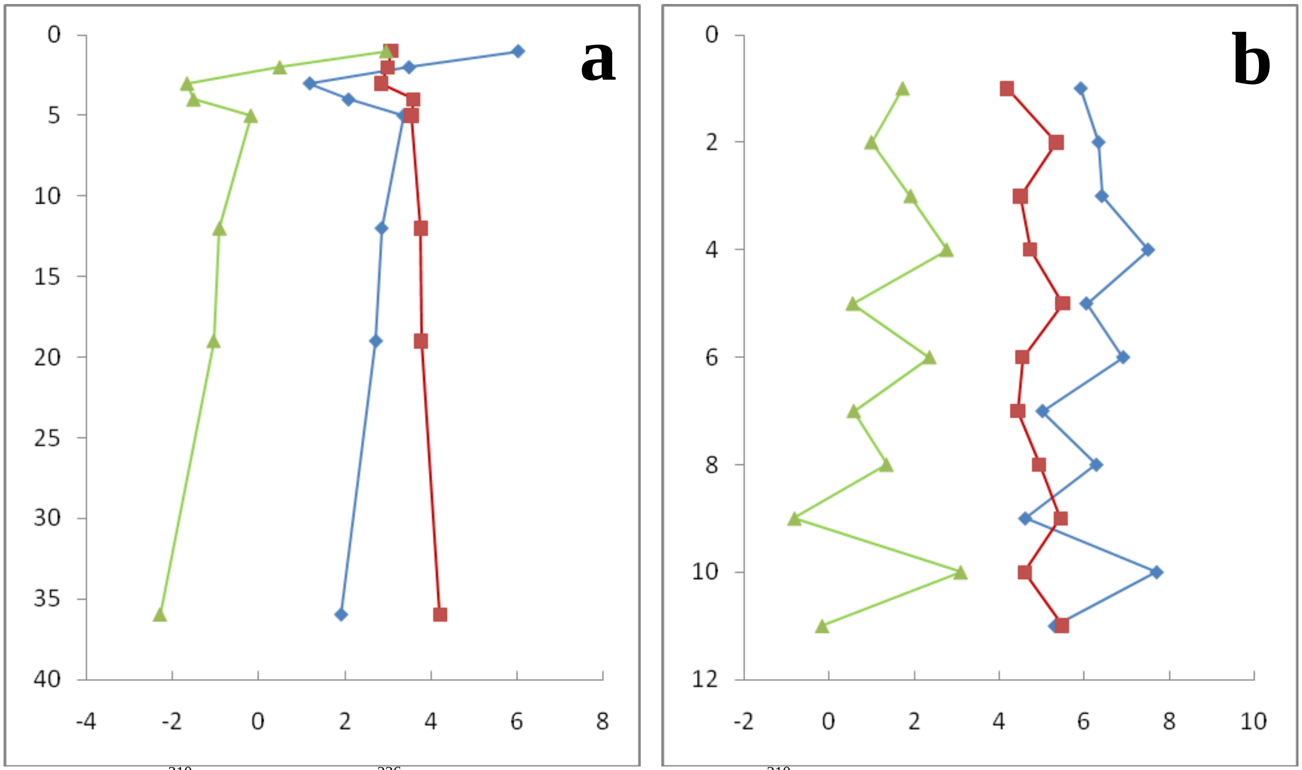

Figure 3. Total ^{210}Pb (filled circles), ^{226}Ra (filled squares), and unsupported ^{210}Pb (filled triangles) activities versus depth (a) KOR-1-15-VII-05 and (b) VOL-1-16-VII-05

^{137}Cs activity (equated with initial atmospheric nuclear weapons testing, *ca*. 1954) in Lake Koronia core KOR-1-15-VII-05 was observed at a depth of ~5 cm, and peak activity (corresponding to ~1964) occurred at a depth of ~2 cm (Figure 4). This near core top peak suggests that the uppermost sediments at the KOR-1-15-VII-05 site may be missing. At KOR-2-15-VII-05, located only 2 km southeast of KOR-2-15-VII-05, increased ^{137}Cs activity was noted at a depth of 27 cm, and maximum activity occurred at a depth of 14 cm. At Lake Volvi, ^{137}Cs activity increased beginning ~35 cm in core VOL-2-16-VII, and maximum activity was observed at 30 cm. A small peak in ^{137}Cs activity was also noted at a depth 17 cm in this core (attributed to fallout from the Chernobyl nuclear accident, *ca.* ~1986). Maximum ^{137}Cs activity was noted at ~25 cm and the smaller peak was observed at 14 cm within VOL-1-16-VII-05 (Figure 4).

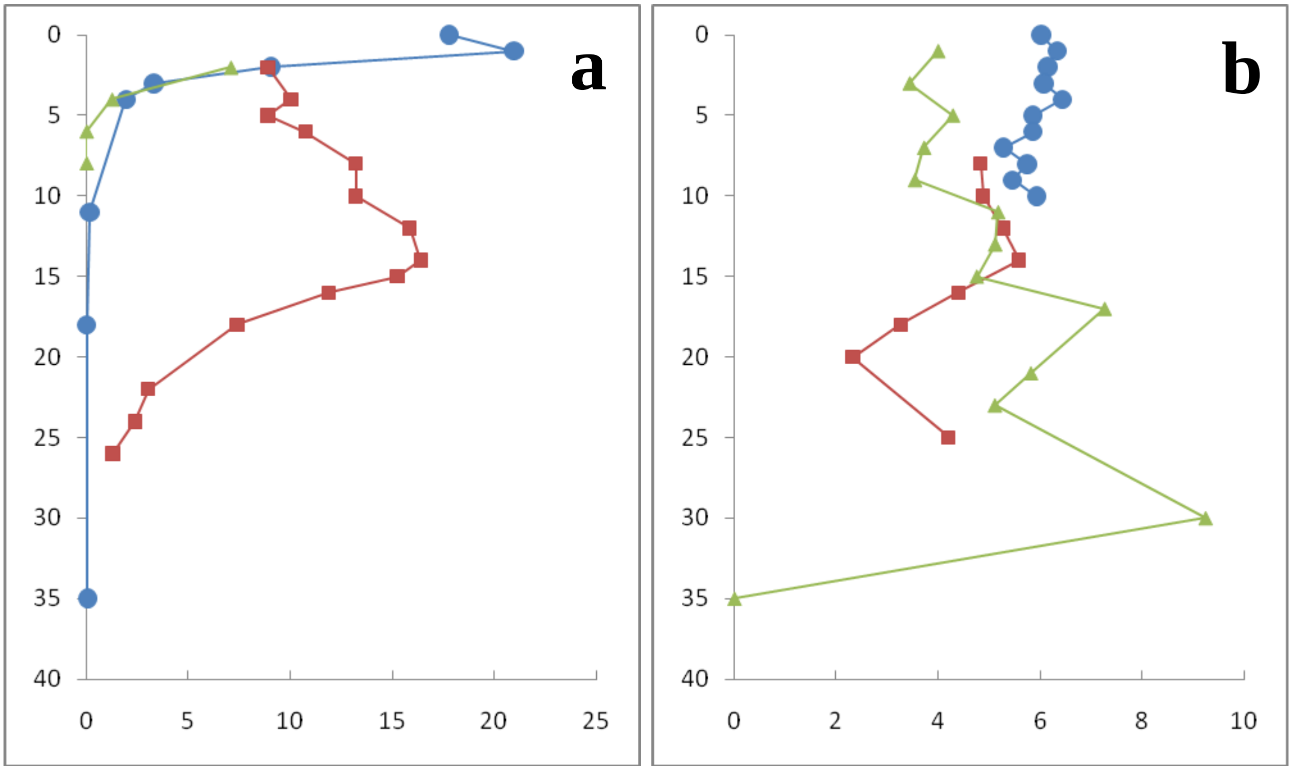

Figure 4. Cs-137 activity versus depth (a) KOR-1-15 VII-05 analyzed at the University of Florida and the University of Pittsburgh (filled circles and filled triangles) and KOR-2-15-VII-05 analyzed at the University of Pittsburgh (filled squares) and (b) VOL-1-16-VII-05 analyzed at the University of Florida and the University of Pittsburgh (filled circles and filled triangles) and VOL-2-16-VII-05 analyzed at the University of Pittsburgh (filled squares)

Calibrated AMS ^{14}C results and near-surface ages defined by Cs-137 were fit by a second order polynomial and extrapolated to the base of each sediment profile to provide age-depth relationships for each core (Figure 5). Surface ages of 2005 (the year of core acquisition) were assumed in the age models of all cores, with the exception of KOR-1-15-VII-05, as discussed above. The high degree of stratigraphic correlation in the lower horizons of VOL-1-16-VII-05 and VOL-2-16-VII-05 allowed the assignation of additional age-depth points within VOL-2-16-VII-05.

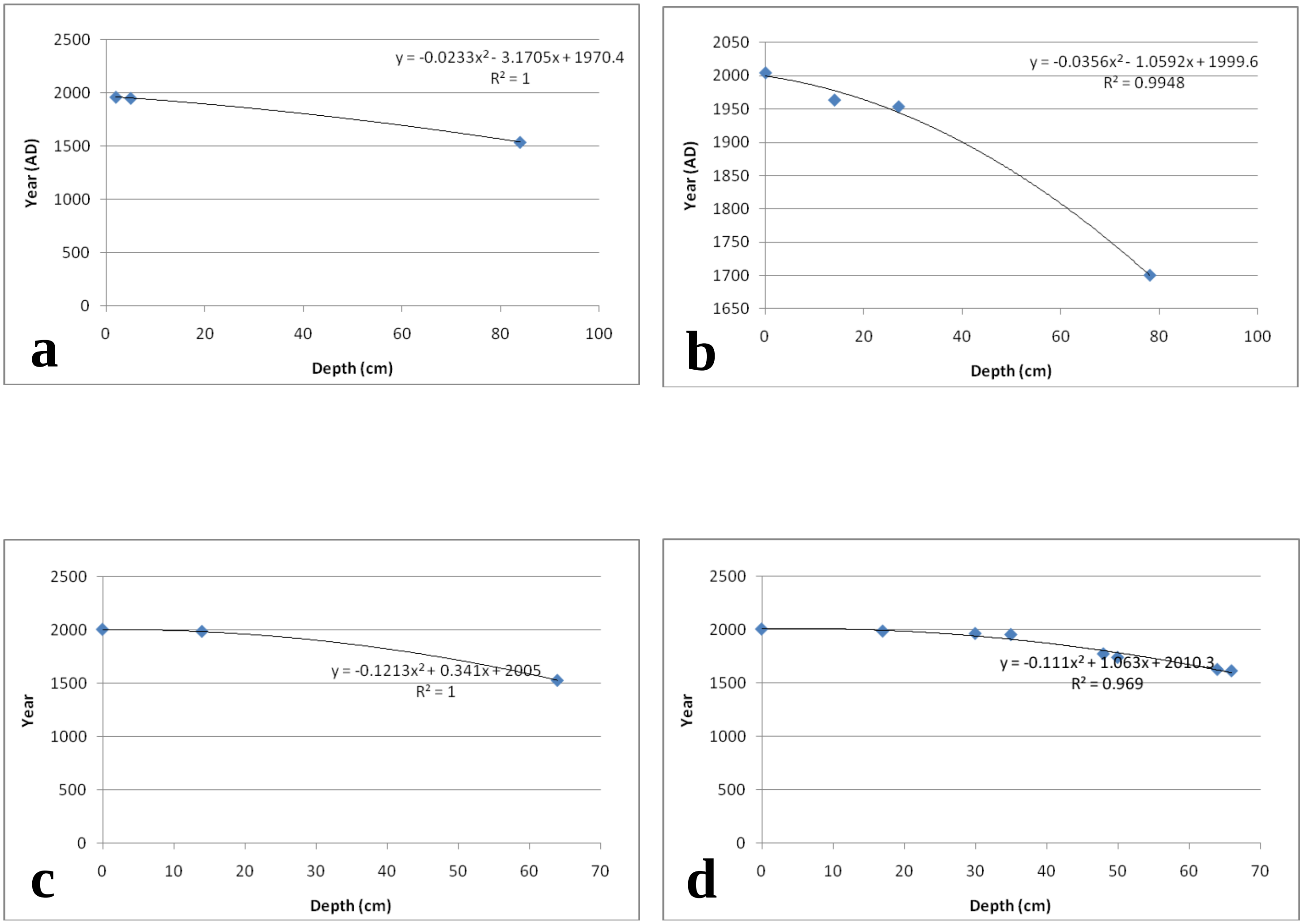

Figure 5. Age depth relationships a. KOR-1-15-VII-05 b. KOR-2-15-VII-05 c. VOL-1-16-VII-05 and d. VOL-2-16-VII-05

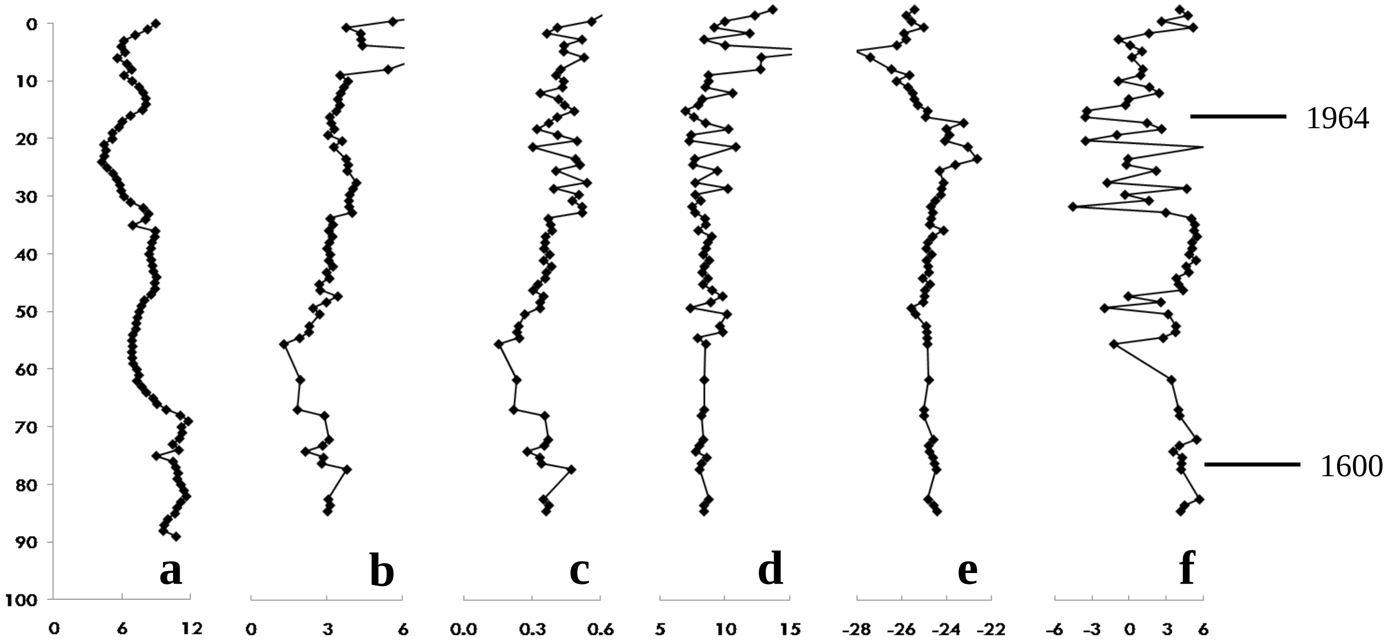

Figure 6. (a). Inorganic carbon, (b). organic carbon, (c). total nitrogen, (d). C:N ratios, (e). carbon and (f). nitrogen isotope values of KOR-1-15-VII-05

4.2 BULK SEDIMENT AND ISOTOPIC COMPOSITION

Paleoenvironmental proxies are plotted against depth. Results are discussed as a function of age. In Lake Koronia, at site KOR-1-15-VII-05, sediment organic carbon content averaged 3.2% and was relatively constant prior to ~1930 A.D. (Figure 6). After 1930 A.D., TOC was highly variable. Total nitrogen concentrations were highly variable throughout the core. Inorganic carbon concentrations decreased from the basal sediments to ~1950 A.D (from 5.7% to 3.3%). After 1950 A.D., IC content increased to a modern maximum value of ~9%. Carbon: nitrogen ratio values at core site KOR-1-15-VII-05 were relatively constant prior to ~1850 A.D. and averaged 8.5. After 1850 A.D., values were highly variable. The δ^{13}C of organic matter at KOR-1-15-VII-05 were relatively constant prior to 1880 AD (average of -24.6‰). After 1880,

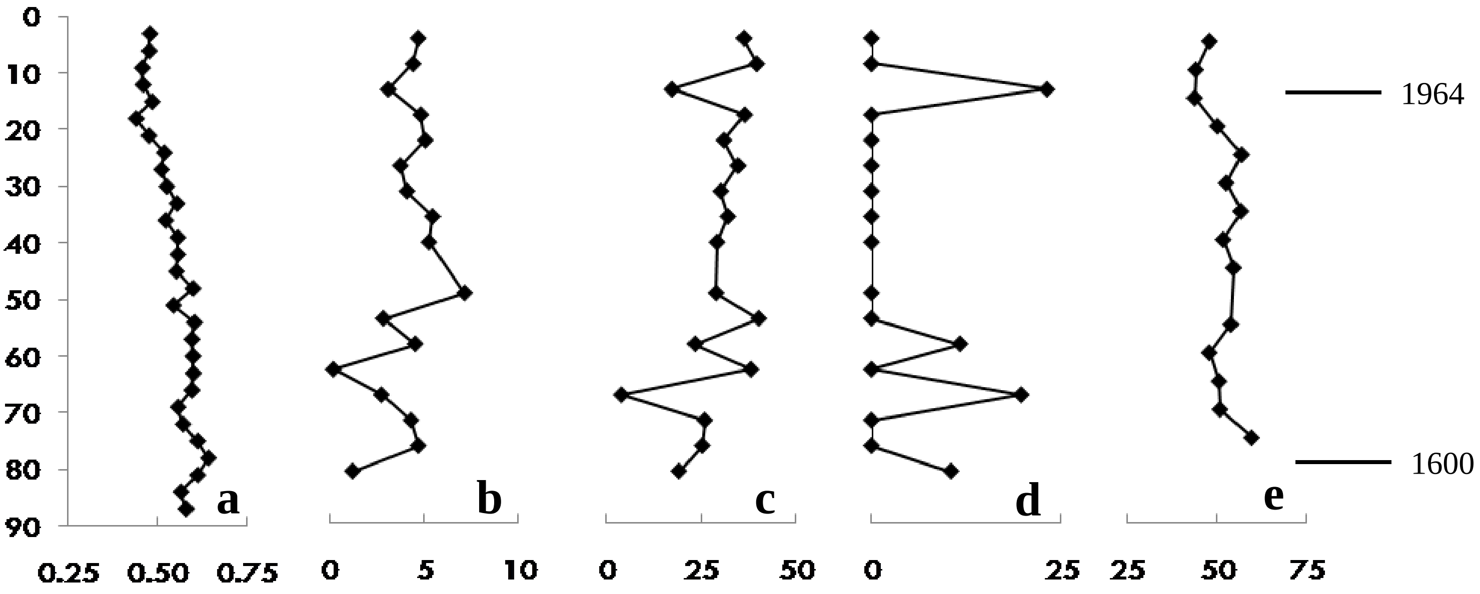

Figure 7. (a). Total phosphorous, (b). diatom silica concentrations, (c). sponge silica concentrations, (d). other silica concentrations, and (e). residual fraction in KOR-1-15-VII-05

δ^{13}C was more variable and generally decreased to -25.4‰. The organic matter δ^{15}N was highly variable throughout the core and averaged 2.3‰ (Figure 6).

Total phosphorus concentrations decreased at a relatively constant rate within the core, from 0.6% in the basal sediments to 0.5% at the near surface. Diatom and sponge spicule silica content was highly variable throughout the core. Sponge spicule silica generally increased throughout the core from a basal concentration of 19.2% to a surface (modern) concentration of 36.4%. Diatom silica was generally constant and averaged 4.0%. Peaks in concentrations of other silica forms (primarily minerogenic) occurred near 1630, 1700, and 1920 A.D. (Figure 7).

At core site KOR-2-15-VII-05, sediment organic carbon content averaged 2.6% and was relatively constant prior to ~1950 A.D. (Figure 8). After 1950 A.D., TOC increased (from ~2% to 5%). Total nitrogen concentrations were relatively constant until ~1950 A. D. After 1950

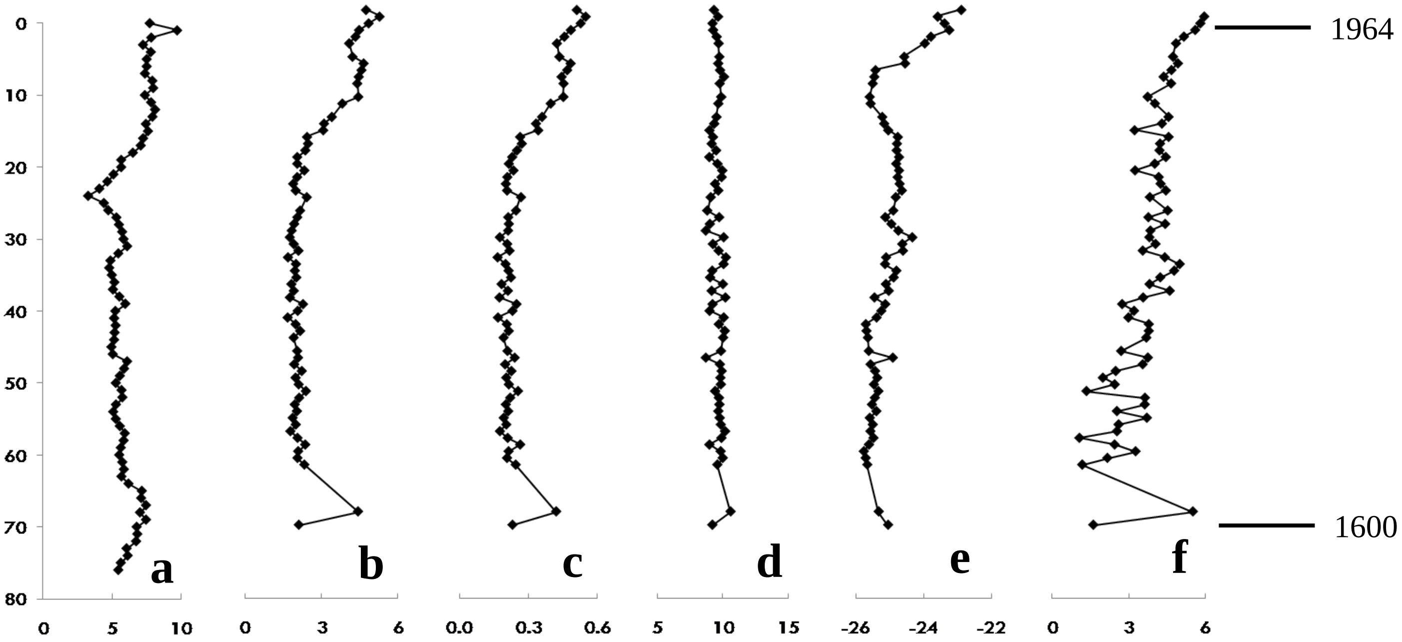

Figure 8. (a). Inorganic carbon, (b). organic carbon, (c). total nitrogen, (d). C:N ratios, (e). carbon and (f). nitrogen isotope values of KOR-2-15-VII-05

A.D. values increased from ~0.2% to 0.35%. Inorganic carbon concentrations were also relatively constant until ~1950 A.D. After 1950 A.D., IC content increased to a modern maximum value of ~9%. Carbon: nitrogen ratio values at core site KOR-2-15-VII-05 were relatively constant and averaged 10 (Figure 8).

The δ^{13}C of organic matter in core KOR-2-15-VII-05 was relatively constant prior to 1980 AD and averaged -25.2‰. After 1980, carbon isotopic values increased to -22.9‰ in modern sediments. Similarly prior to 1950 AD, the organic matter δ^{15}N averaged 3.4‰ then increased to 6.9‰ in modern sediments (Figure 8).

Organic carbon concentrations in core VOL-1-16-VII-05 were relatively constant prior to ~1780 A.D. and averaged 3.6%. Similarly, total nitrogen content in the core was relatively constant with an average of 0.42% prior to ~1780 A.D. Organic carbon and total nitrogen values peaked near 1800 A.D. and again *ca*. 1940 A.D, with organic carbon concentrations of over 7.6% and total nitrogen concentrations near 0.5%. Between 1800 and 1940 A.D., organic carbon

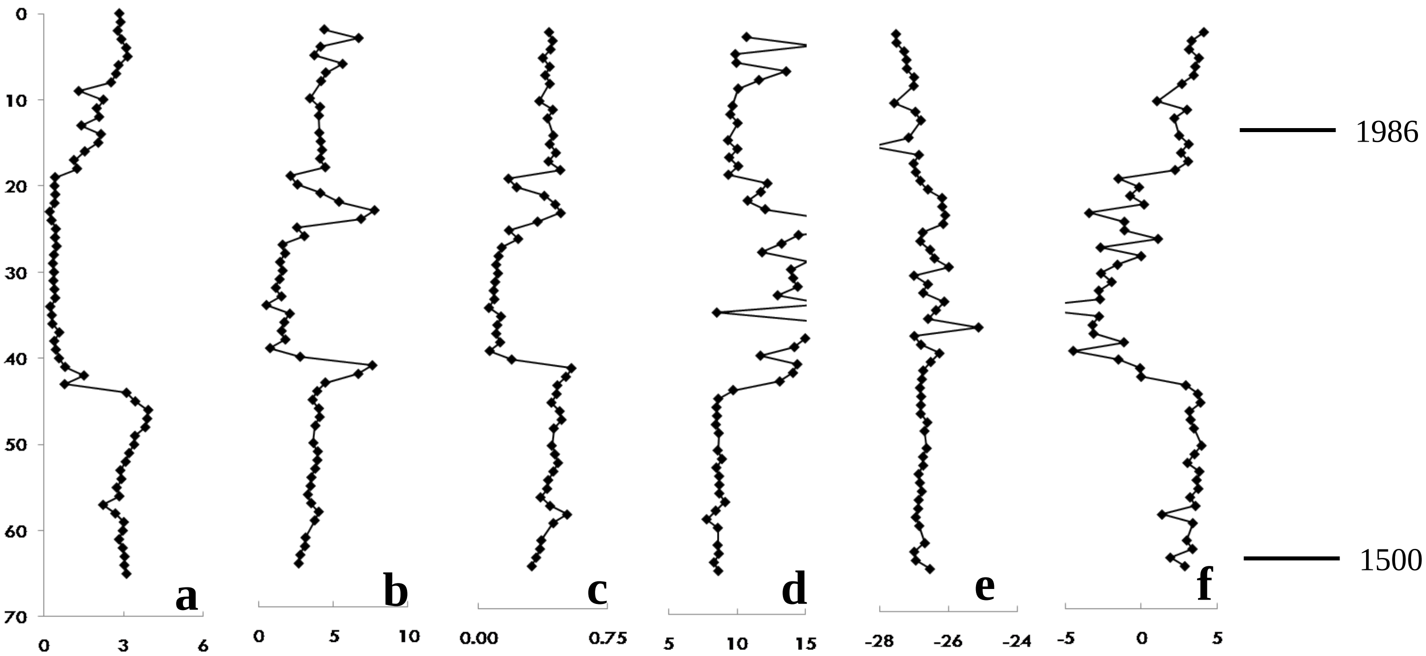

Figure 9. (a). Inorganic carbon, (b). organic carbon, (c). total nitrogen, (d). C:N ratios, (e). carbon and (f). nitrogen isotope values of VOL-1-16-VII-05

and total nitrogen concentrations were relatively low and unvaried. Organic carbon and total nitrogen concentrations during this interim period averaged 1.70% and 0.12%, respectively. After 1965 A.D., organic carbon content and total nitrogen concentrations were relatively constant, averaging 4.4% and 0.4%. Basal inorganic carbon concentrations were, similarly, constant prior to ~1780 A.D. Inorganic carbon content averaged 3.1% but decreased to <0.5% by 1800 A.D., remained relatively low prior to 1970 A.D., and then increased to a modern value near 3.0%. Carbon: nitrogen ratios in VOL-1-16-VII-05 were relatively constant prior to ~1780 A.D. and averaged 8.6. C:N values increased thereafter and remained elevated (at values between ~11.8 and 20) until ~1960 A.D. After 1960 A.D., C:N values decreased to an average value near 10.6 (Figure 9).

In Lake Volvi core VOL-1-16-VII-05, organic matter δ^{13}C values were relatively constant averaging -26.8‰. Organic matter δ^{15}N values were relatively constant prior to 1790

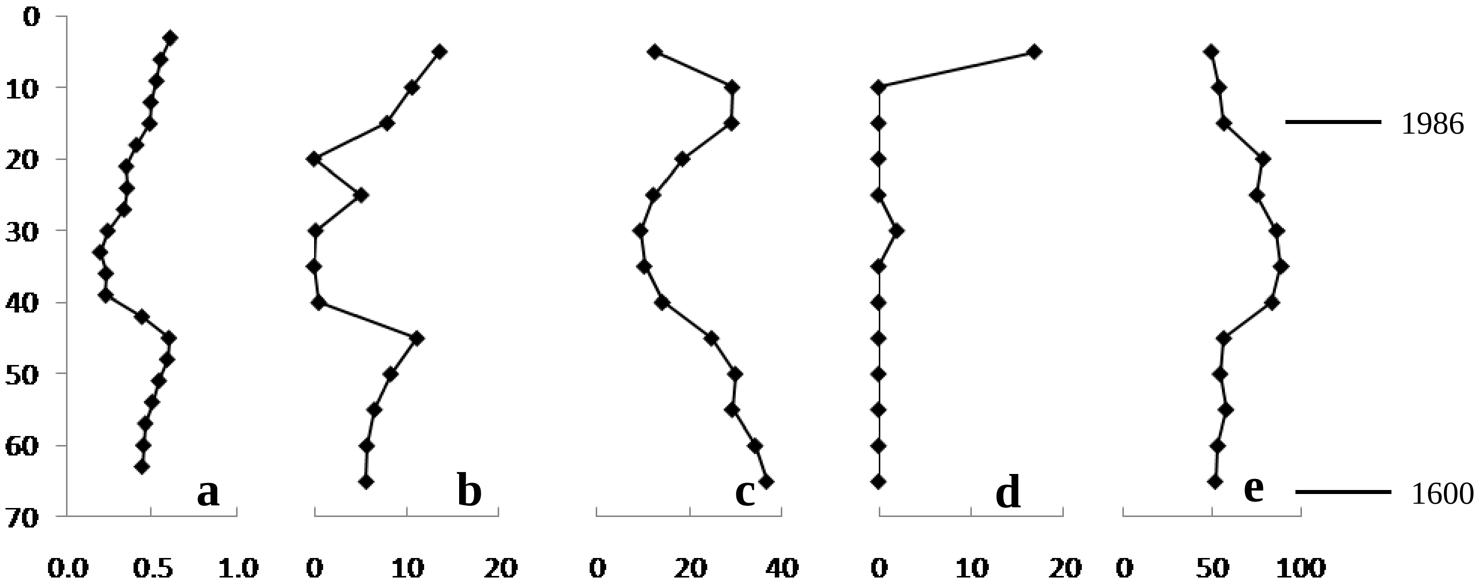

Figure 10. (a). Total phosphorous, (b). diatom silica concentrations, (c). sponge silica concentrations, (d). other silica concentrations, and (e). residual fraction in VOL-1-16-VII-05

A.D. and averaged 4.3‰. After 1790, nitrogen isotopic values decreased (to -4.5‰) until 1820 A.D. and then increased to values near 4.0‰ in modern sediments (Figure 9).

Total phosphorus concentrations in the basal sediments at Lake Volvi were relatively high (averaging ~0.6%). Total P content decreased after ~1780 A.D. to a minimum value near 0.2% at the turn of the following century. Phosphorus content then increased to a near surface (present day) concentration of 0.6%. Diatom silica content increased prior to ~1780 A.D. from 5.6% to 11.0%, whereas sponge spicule silica content decreased from 36.8% to 24.9%. Diatom and sponge silica concentrations decreased within the sediments after 1780 A.D. and remain relatively low until 1980 A.D. Diatom silica content increased after 1980 to a modern concentration of 13.5%. Sediment sponge silica content, in contrast, decreased to a modern concentration of 12.7%. High concentrations of other silica forms were noted centered near 1900 A.D. and in modern sediments (Figure 10).

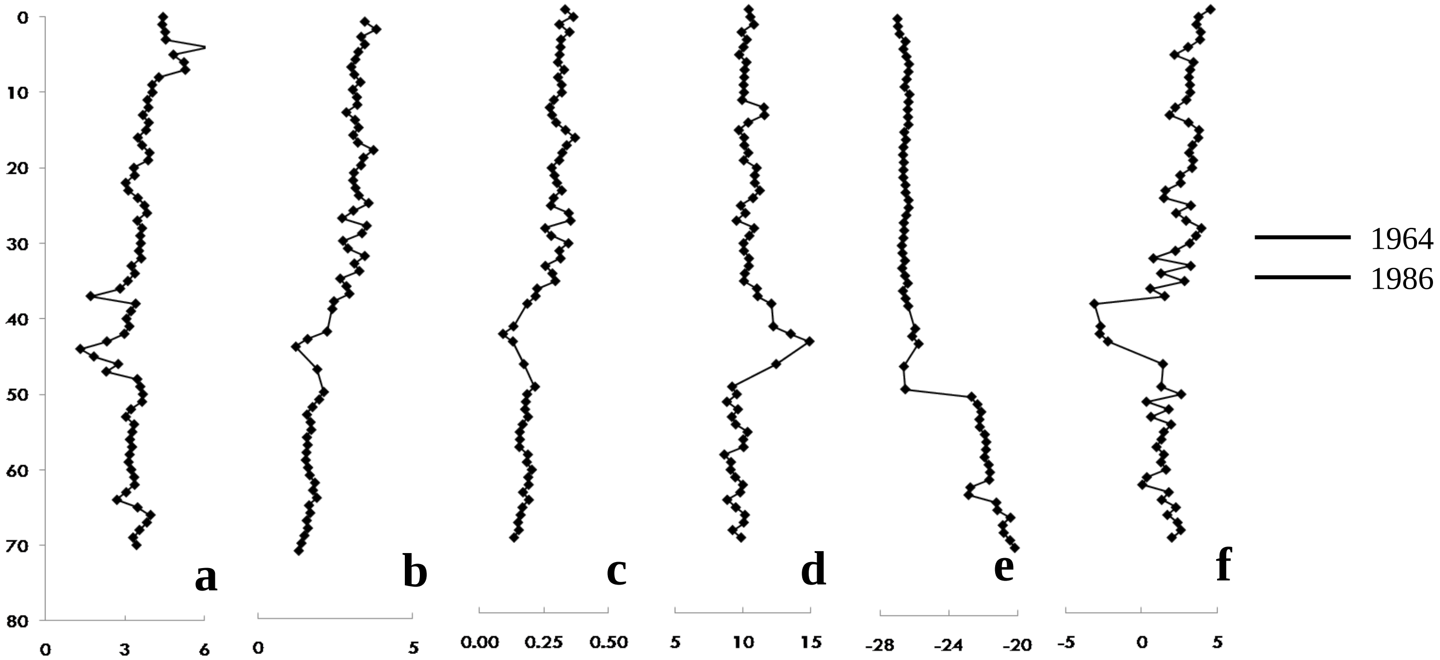

Figure 11. (a). Inorganic carbon, (b). organic carbon, (c). total nitrogen, (d). C:N ratios, (e). carbon and (f). nitrogen isotope values of VOL-2-16-VII-05

In Lake Volvi sediment core VOL-2-16-VII-05, organic carbon concentrations increased at a relatively constant rate from basal values (*ca*. 1525 A.D.) of 1.3% to a surface (modern) concentration of 3.8%, with the exception of a small shift to reduced TOC content (to values as low as 1.2%) between 1820 and 1860 A.D. Total nitrogen in the core similarly increased from basal concentrations (averaging 0.13%) to a near surface maximum value (0.36%). Low values (<0.1%) were also noted between 1785 and 1900 A.D. Inorganic carbon concentrations were relatively constant (averaging ~3%) prior to 1800 A.D. Low IC values (as low as 1.3%) were noted throughout the mid-1800s, followed by an increase to a modern values near 6.2% (Figure 11). Carbon/nitrogen ratio values were relatively constant throughout the core with values near 10, with the exception of a shift between 1780 and 1900 A.D. to values >15 (Figure 11).

The $\delta^{13}C$ of organic matter in core VOL-2-16-VII-05 decreased at a relatively constant rate from -20.2‰ to -27.7‰ between basal and surface sediments, respectively with the exception of one large shift to more negative values in 1780 A.D. In contrast, organic matter

$\delta^{15}N$ increased at a relatively constant rate from 2.0‰ in the core base to 4.6‰ in modern sediments. Nitrogen isotopic values also shift to more negative values in the late 1700s (Figure 11).

4.3 ELEMENTAL COMPOSITION

Small shifts in bulk sediment elemental and trace metal concentrations were noted in KOR-1-15-VII-05 in 1780 and 1900 A.D. But values were relatively constant throughout the rest of the core with the exception of sodium which increased throughout the core (from 0.9% to 1.6%) (Figure 12, Table 3).

Bulk elemental concentrations in VOL-1-16-VII-05 were relatively constant prior to 1770 A.D.. A shift occurred between 1770 A.D. and 1820 A.D. when concentrations drastically decreased of arsenic (shifted to 11 ppm), calcium (shifted to 2.3%), chromium (shifted to 58 ppm), copper (shifted to 2.8 ppm), iron (shifted to 2.8%), magnesium (shifted to 1.2%), manganese (shifted to 600 ppm), and lead (shifted to 27 ppm). Sodium (shifted to 3.1%) and titanium (shifted to 0.55%) increased over this same period (Figure 13, Table 3).

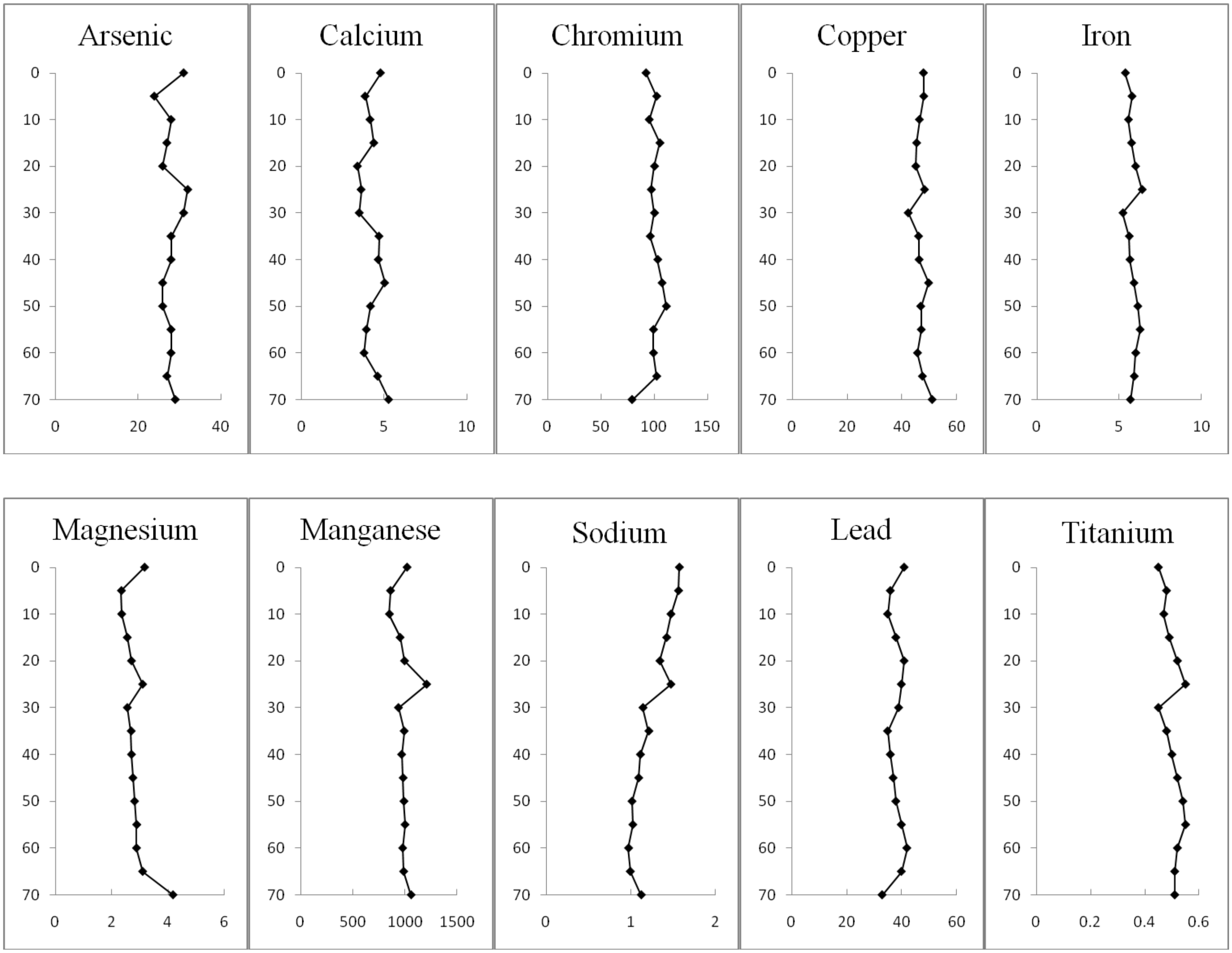

Figure 12. Bulk elemental composition of KOR-1-15-VII-05

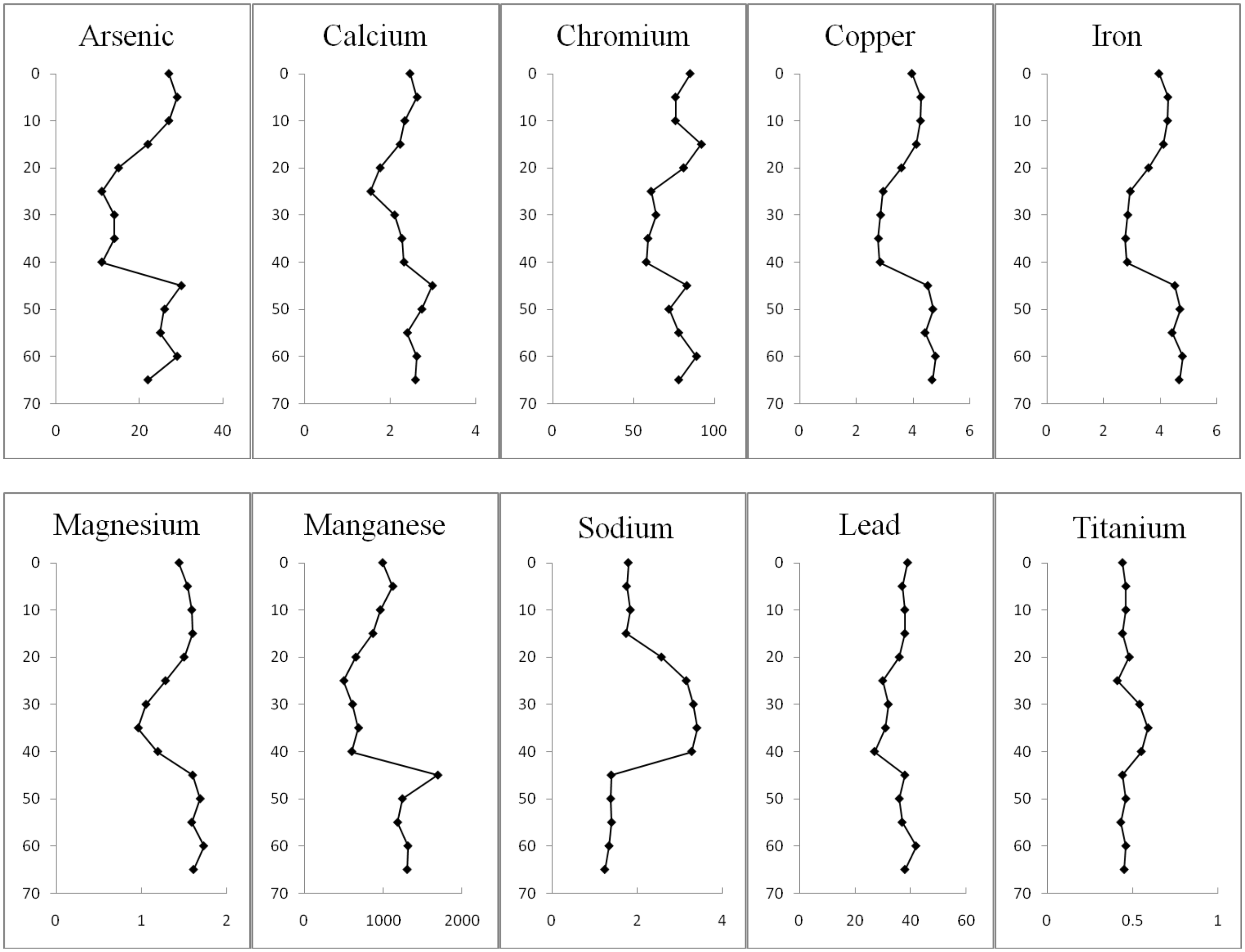

Figure 13. Bulk elemental composition of VOL-1-16-VII-05

Table 3. Elemental composition for KOR-1-15-VII-05 and VOL-1-16-VII-05.

KOR-1-15-VII-05		
Metal	Maximum value	Average value
Arsenic	32	27.8
Calcium	59400	45000
Chromium	111	98.7
Copper	51.2	46.8
Iron	62700	58000
Magnesium	41800	29000
Manganese	1210	992
Sodium	15700	12500
Lead	42	38.2
Titanium	5500	5000

VOL-1-16-VII-05		
Metal	Maximum value	Average value
Arsenic	11.2	10.0
Calcium	29900	23600
Chromium	92	75.1
Copper	38.4	29.2
Iron	47900	39000
Magnesium	17300	14600
Manganese	1310	978
Sodium	33200	21100
Lead	42	3.32
Titanium	5900	4720

5.0 PROXY INTERPRETATIONS

Changes in lake water chemistry and sediment geochemistry result primarily from variations in material output from the surrounding catchment, often due to land-use changes. For example, deforestation and increased agricultural production enhance the transport of soil nutrients and organic and inorganic matter to a lake, which is in turn reflected in sediment lithologic composition (Deevey, 1984; Binford et al., 1987). Land clearance accelerates alleviation and colluviation, and increases in sediment accumulation may reflect intensified watershed erosion. Carbon to nitrogen nutrient ratios can also be used to evaluate the relative contributions to sediments of terrestrial and aquatic organic matter sources (Kemp et al., 1977; Meybeck, 1982; Håkannson, 1985; Krishnamurthy & Bhattacharya, 1986; Nakai, 1986; Hassan et al., 1997). Moreover, sedimentary biogenic silica measurements provide insights into trophic state changes and shifts in the algal community composition (Stoermer et al., 1985; Schelske et al., 1986;Whitmore, 1989, 1991; Anderson et al., 1993).

Variations in the carbon and nitrogen isotopic ratio ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) of sediment organic matter also indicate changes in lake primary productivity (Stuiver, 1975; McKenzie, 1982, 1985; Hollander & McKenzie, 1991; Hollander et al., 1992; Schelske & Hodell, 1991, 1995; Hodell & Schelske, 1998). Phytoplankton preferentially remove the lighter ^{12}C and ^{14}N from the dissolved inorganic carbon and nitrogen of surface waters during photosynthetic uptake. As supplies of CO_2 and NO_{-3} are depleted, phytoplankton discriminate less against the heavier

$^{13}CO_2$ and $^{15}NO_{-3}$ and sinking organic matter is progressively enriched in ^{13}C and ^{15}N. Changes in the $\delta^{13}C$ and $\delta^{15}N$ of organic matter can therefore be used to reconstruct productivity in surface waters.

Additional factors may influence the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ of lacustrine organic matter. Changes in pH, temperature, species composition, nitrogen limitation or fixation, and growth rate can affect the $\delta^{13}C$ and $\delta^{15}N$ of phytoplankton (Hinga et al., 1994; Goericke et al., 1994; Laws et al., 1995). The isotopic signature of sedimented organic matter may be further altered by relative shifts in the organic matter source material (i.e., terrestrial vs. aquatic) contributed to the sediment pool and changes in the relative abundance of macrophytes and phytoplankton. Lastly, the stable isotopic signature of sedimented organic matter may be influenced by differential, post-depositional preservation of the various components of the organic matter pool, each of which may possess a distinctive isotopic value.

Elemental composition can be used to determine the extent of major and trace metal loading to the lake associated with industrial activities. Changing elemental concentration can also indicate changes in watershed erosion. Elevated titanium and sodium concentrations, for example, have been used to indicate periods of heavy erosion (Mackereth, 1966; Engstrom and Wright, 1984; Jones, 1984; Young and King, 1989).

6.0 DISCUSSION

The top of core KOR-1-15-VII-05 appears to be missing and this is not an artifact of coring.

Although C:N values throughout the core indicate that the core has been plankton-dominated since at least ~1550 A.D, geochemical records from sediment core KOR-2-15-VII-05 suggest nutrient enrichment and increased algal productivity within Lake Koronia over the last fifty years. For example, total nitrogen content increased after 1940 A.D. and organic carbon content increased markedly after 1950 A.D. Run-off from urban areas and agricultural fields would enhance nutrient loading to the lake, causing increased algal productivity.

Organic matter $\delta^{13}C$ values in the Koronia sediments increased markedly after 1980 indicating that the lake was more productive than at any other time since ~1550 A.D. The increase in $\delta^{15}N$ of organic matter from 1950 A.D. to the present may be related to an increase in the $\delta^{15}N$ of the dissolved inorganic nitrogen delivered to the lake. The $\delta^{15}N$ of sewage-derived ammonium and nitrate is ^{15}N-enriched with measured values typically +10 to +20‰ (Heaton, 1986; Aravena et al., 1993; Spaulding et al., 1993). Soil nitrate also tends to be relatively enriched in ^{15}N (measured values +3 to +12‰). Increased nitrate loading from sewage and soils may have contributed to the increased $\delta^{15}N$ of the sediment organic matter.

At Lake Volvi, C:N ratios in sediment core VOL-1-16-VII-05 and VOL-2-16-VII-05 suggest that the lake has been algal-dominated over (at least) the last ~400 years. Total phosphorus values generally increase in sediments from VOL-1-16-VII-05 suggesting increased nutrient loading that is likely associated with the intensification of agriculture. After 1980 A.D. diatom silica concentrations increase while sponge spicule concentrations decrease suggesting an increasing population of algae and decreasing population of macrophytes in the lake.

Organic carbon and total nitrogen concentrations and nitrogen isotopic values generally increase throughout core VOL-2-16-VII-05, suggesting increasing aquatic productivity within Lake Volvi over the last several hundred years. However, organic matter $\delta^{13}C$ values decreases from basal to modern sediments within the core. With increased primary productivity (as suggested by other sediment indicators) ^{13}C in organic matter would be expected to increase. Therefore, the influx of a source of ^{13}C depleted organic matter is necessary to reconcile the relatively low carbon isotopic values within the most recent sediments. Sewage, like other terrestrial organic matter sources, is depleted in ^{13}C relative to organic matter produced by phytoplankton (Burnett and Schaeffer, 1980; Gearing et al., 1991). The relatively light $\delta^{13}C$ values of organic matter in recent sediments from Lake Volvi could reflect an increasing contributions to the sediment organic matter pool from sewage effluent as the watershed lacks sewage treatment and functioning septic tanks (Frasier, 1996).

From 1780-1950 A.D., the geochemical record from VOL-1-16-VII-05 suggests a drastic change in sediment source. This shift coincided with increased population growth due to refugee migrations after 1780 A. D. and could reflect intensified agricultural activity within the basin. The period of 1780-1830 A. D. was one of the wettest of the Little Ice Age in the Southern Balkans (Xoplaki et. al, 2001). Deluges in Northern Greece associated with this increased precipitation during the Little Ice Age could have led to increased soil erosion. Decreased nitrogen and organic carbon content can be attributed to reduced lake productivity and dilution by inorganic fluvial sediment loading (Brown et al., 2000; Wolfe et al., 2006). Diatom silica and sponge spicule silica content both markedly decrease over the same period indicating a reduction in aquatic productivity, perhaps as a result of persistent increases in lake water siltation and water column shading. A dilution in total phosphorus and most metal concentrations (with the exception of titanium) is also noted over the same time period. Elevated titanium and sodium concentrations can be attributed to increased basin erosion. High C:N values, similarly, indicate a substantial influx of terrestrial organic debris. Decreased organic carbon and nitrogen content and increased C:N values also occur in VOL-2-16-VII-05. However, although VOL-2-16-VII-05 is only ~ a km to the west of VOL-1-16-VII-05, this shift is far less pronounced in VOL-2-16-VII-05.

Trace metal concentrations in sediments from both lakes indicate that heavy metal loading has not occurred in the last ~400 years. Sediment elemental composition from core site KOR-1-15-VII-05 remained relatively constant, suggesting that there have been no significant changes in heavy metal loading. However, major industrial expansion within the Koronia watershed occurred after ~1970 A.D., and this time frame is missing within the analyzed sediment core. It should be noted, however, that sodium concentrations within the sediment increased continually through time, perhaps indicative of a long-term increase in lake water salinity. Alternatively, increasing sodium concentration may simply reflect a diffusion gradient within the sediment (Haskell et al., 1996). Surface sediment elemental composition from VOL-1-16-VII-05 is not elevated from basal concentrations, suggesting that metal loading did not occur, even after industrial expansion beginning in the 1970s.

7.0 CONCLUSIONS

Sediment geochemistry suggests that aquatic productivity has increased in both lakes over the last 50 years, due to agricultural nutrient loading. This trend appears more pronounced in Lake Koronia cores than in Lake Volvi sediments. Sediments in Lake Volvi suggest a source of depleted ^{13}C organic matter to the lake that could possibly be sewage. This would suggest that the lack of sewage treatment facilities near Lake Volvi is of considerable concern. Metal pollution does not appear to have been significant to either lake but it must be considered that Lake Koronia sediments after 1970 A.D. were not analyzed. The Lake Volvi sediment cores provide evidence for intensified erosion between 1800 and 1950 A.D. possibly associated with intensified anthropogenic activities in the watershed and/or increased precipitation associated with natural climate variability. Geochemical results suggest that catchment agricultural activities have been detrimental to the lakes while industrial activities have not had large scale effects.

Basal sediments in all four cores provided baseline ecological values that should be included in discussions of wetland remediation plans. These values do not represent conditions of the watershed before humans occupied the region but can provide information from when human activities were less intense.

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