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Abstract

Ancient lakes, which are important centres of biodiversity and endemism, are threatened by a wide variety of human impacts. To assess environmental impact on ancient Lake Ohrid we have taken short sediment cores from two contrasting site locations, comprising a site of urban pollution and an apparently pristine area. Recent impacts on water quality and ecology were assessed using sediment, geochemical, ostracode, and diatom data derived from analysis of two ^{210}Pb-dated sediment cores spanning the period from 1918 to 2009. According to the index of geoaccumulation, sediments were often moderately contaminated with As. Fe and Ni concentrations often exceeded reported maximum limits above which harmful effects on sediment-dwelling organisms are expected. Productivity in the (pristine) south-eastern part of Lake Ohrid (Sveti Naum) is generally lower than in the north, probably due to the strong influence of spring discharge. Low ostracode and diatom concentrations, low abundance of the epilimnetic diatom *Cyclotella ocellata*, and low values of TOC and TIC indicate a lower productivity from the early 1920s to the late 1980s. Since the mid 1970s, increased relative abundance of *C. ocellata* and increasing diatom concentration indicate increasing productivity in the south-eastern part. Rising numbers of ostracode valves and higher TIC and TOC contents in both sediment cores indicate an increase in productivity during the late 1980s. A slight increase in productivity near Sveti Naum continued from the early 1990s until 2009, witnessed by rising TC, TIC, and TOC content and a generally high number of ostracode valves and ostracode diversity. The area near the City of Struga (site of urban pollution) is also characterized by rising TOC and TIC contents and, furthermore, by increasing Cu, Fe, Pb, and Zn concentrations since the early 1990s. The recent reduction in the number of ostracode valves and ostracode diversity is probably caused by a higher heavy metal load into the lake. This suggests that living conditions for the endemic species in Lake Ohrid have become less favourable in the northern part of the lake, which might threaten the unique flora and fauna of Lake Ohrid.

Keywords (separated by '-') Lake Ohrid - Palaeolimnology - Eutrophication - Geochemistry - Ostracodes - Diatoms

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ORIGINAL PAPER

Recent anthropogenic impact in ancient Lake Ohrid (Macedonia/Albania): a palaeolimnological approach

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Abstract Ancient lakes, which are important centres of biodiversity and endemism, are threatened by a wide variety of human impacts. To assess environmental impact on ancient Lake Ohrid we have taken short sediment cores from two contrasting site locations, comprising a site of urban pollution and an apparently pristine area. Recent impacts on water quality and ecology were assessed using sediment, geochemical, ostracode, and diatom data derived from analysis of two ^{210}Pb-dated sediment cores spanning the period from 1918 to 2009. According to the index of geoaccumulation, sediments were often moderately contaminated with As. Fe and Ni concentrations often exceeded reported maximum limits above which harmful effects on sediment-dwelling organisms are expected. Productivity in the (pristine) south-eastern part of Lake Ohrid (Sveti Naum) is generally lower than in the north, probably due to the strong influence of spring discharge. Low ostracode and diatom concentrations, low abundance of the epilimnetic diatom *Cyclotella ocellata*, and low values of TOC and TIC indicate a lower productivity from the early 1920s to the late 1980s. Since the mid 1970s, increased relative abundance of *C. ocellata* and increasing diatom concentration indicate increasing productivity in the south-eastern part. Rising numbers of ostracode valves and higher TIC and TOC contents in both sediment cores indicate an increase in productivity

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during the late 1980s. A slight increase in productivity near Sveti Naum continued from the early 1990s until 2009, witnessed by rising TC, TIC, and TOC content and a generally high number of ostracode valves and ostracode diversity. The area near the City of Struga (site of urban pollution) is also characterized by rising TOC and TIC contents and, furthermore, by increasing Cu, Fe, Pb, and Zn concentrations since the early 1990s. The recent reduction in the number of ostracode valves and ostracode diversity is probably caused by a higher heavy metal load into the lake. This suggests that living conditions for the endemic species in Lake Ohrid have become less favourable in the northern part of the lake, which might threaten the unique flora and fauna of Lake Ohrid.

Keywords Lake Ohrid · Palaeolimnology · Eutrophication · Geochemistry · Ostracodes · Diatoms

Introduction

Lakes respond chemically and biologically to human impact. Commonly used proxies, such as ostracodes, diatoms, and geochemical parameters, have been used effectively to reconstruct anthropogenic influence through time on lakes from analysis of lake sediment cores (Reed et al. 2008; Pérez et al. 2010). Aquatic ecosystems such as lakes (Löffler et al. 1998; Matzinger et al. 2006a; Patceva et al. 2006) and rivers (Patceva et al. 2004; Veljanoska-Sarafiloska et al. 2004; Bilali et al. 2012) in Macedonia and Albania are under increasing human impact and this also applies to some ancient lakes in the world. Lakes Baikal, Biwa, and Tanganyika are examples. The lakes are influenced by lake level changes (mainly due to irrigation) and particularly the littoral areas are affected by sediment loading which leads to a disturbance of microhabitats and, as a result, to a drop in the number of animal and plant species (Cohen et al. 1999; Alin et al. 1999; Asaeda and Shinohara 2012; Touchart 2012). However, so far there is no evidence that a tipping point is imminent. The biodiversity hotspot of deep, ancient Lake Ohrid may equally be threatened (Matzinger 2006b). Recently, concern has been raised related to a "creeping biodiversity crisis" in Lake Ohrid (Kostoski et al. 2010), which poses a serious threat to the endemic species (Albrecht and Wilke 2008) whose extinction would cause an irreversible loss. To date the potential of palaeolimnological techniques to assess the influence of accelerated human impact on the ecology of the lake has not been explored.

The town of Ohrid is one of the oldest human settlements in Europe (UNESCO ROSTE 2004), and the shores of the adjacent lake have been inhabited since prehistoric times. Archaeological investigations have documented settlements from as early as 6,000 BC (Ministry of Environment and Physical Planning, undated). The first evidence of settled human communities and domesticated animals at about 8.5 ka BP is indicated by the presence of coprostanol, a biomarker for human and animal faeces, in a sediment core taken in Lake Ohrid (Holtvoeth et al. 2010). Wagner et al. (2009) identified the onset of human impact on catchment vegetation at about 5,000 BP and a distinct increase at 2,400 BP. After the end of World War II the population increased 5–6 times. Today, 106,000 people live in the Macedonian part of the watershed, about 61,000 residents in the Albanian part, and about 25,600 residents in the Greek part (Avramoski et al. 2003). Agriculture is one of the most important economic sectors in the region (Spirkovski et al. 2001), and run-off from cultivated land and pastures is an important source of total phosphorus (TP) input into Lake Ohrid (Spirkovski et al. 2001). Besides agriculture, households are the main anthropogenic source of phosphorus (Matzinger et al. 2004). Avramoski et al. (2003) and Matzinger et al. (2004) documented that phosphorus concentration has increased at least fourfold over the past 100 years and Matzinger et al. (2004) found an increase in sediment carbonate content over the last 50 years which is indicative of the early stages of eutrophication. To date, the TP concentration in the centre of Lake Ohrid is still low enough to consider the lake as "oligotrophic", but there are major concerns over water quality in the littoral zone. Veljanoska-Sarafiloska et al. (2004) showed that certain areas of the shoreline are in an alarming condition, in particular where rivers enter the lake, and suggested that much of the littoral zone was mesotrophic. The River Velgoska, for example, flows through industrial zones, is exposed to sources of untreated sewage, and is classed as eutrophic. The mesotrophic River Koselska flows through rural and agricultural areas and during heavy rains sometimes receives overflow sewage water from

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the sewage system. The River Sateska, diverted into Lake Ohrid in 1962, flows through agricultural and urban areas and carries a high load of sediment, drainage water, and communal wastewater which is deposited in the littoral zone. From evidence for a switch to more organic sediment character in the littoral zone, Matter et al. (2010) estimated that major impact in the shallow-water zone had persisted since ca. 1955. Other pollution sources are metal component factories in Pogradec, which discharge untreated waste into the lake, and old mines, north-west of Pogradec (Avramoski et al. 2003). The two chromium mines, three nickel–iron mines and one coal mine went out of use at the turn of the century, but many piles of waste material remain and are a permanent pollution source (Spirkovski et al. 2001). To improve the water quality of Lake Ohrid, major improvements to the sewage treatment system have been carried out recently. Since June 1988 the Regional Sewerage System for the Protection of Lake Ohrid collects wastewater from about 65 % of the Ohrid-Struga region. After treatment, the water is discharged into the River Crni Drim. Two additional construction phases should allow treatment of most of the shoreline on the Macedonian part of the lake (UNESCO ROSTE 2004), although several households in the City of Ohrid and nearby settlements are still not connected to any sewage system (Lokoska 2012). In Pogradec, three wastewater treatment plants have been opened in the last 5 years, but some unconnected areas remain (Neugebauer and Vallerien 2012).

The focus of this study is to explore past impacts on Lake Ohrid caused by anthropogenic pollution using selected proxies comprising ostracodes and diatoms, representing both water column and lake-bottom conditions, as well as geochemical parameters. To achieve the aim, we used ^{210}Pb and ^{137}Cs dated sediment cores taken from localities with contrasting degrees of human impact.

Site description

Lake Ohrid (Fig. 1) straddles the border between Macedonia and Albania and is located at 695 m a.s.l. It has a surface area of 358.2 km^2 (230 km^2 belongs to Macedonia and 128.2 km^2 to Albania). The length of the shoreline is 87.5 km, the maximum length of the lake is 30.8 km, and its maximum width is 14.8 km. The lake has a maximum depth of 289 m and an average depth of 164 m. The total watershed incorporates its sister lake, Prespa, and covers an area of 2,340 km^2 (Dodeva 2012) extending into Greece (Watzin 2003). Lake Ohrid is directly connected with Lake Prespa via underground karstic channels and these springs contribute ~53 % to Ohrid's inflow. Only a small proportion of the inflow originates from rivers (~23 %) and direct precipitation (~23 %) (Albrecht and Wilke 2008). The main tributaries are the rivers Velgoska (mean annual inflow 0.4 m^3 s^{-1}), Sateska (5.5 m^3 s^{-1}), Koselska (1.3 m^3 s^{-1}), and Čerava (0.2 m^3 s^{-1}) (Patceva et al. 2004; Matzinger et al. 2007). The only outlet is the River Crni Drim (Dodeva 2012). Lake Ohrid is a Quaternary graben-shaped lake formed by a combination of post-Pliocene uplift and gradual subsidence (Aliaj et al. 2001). West of the lake, the landscape is characterized by the "Mokra" mountain chain, which reaches ~1,500 m a.s.l. and in the east, by the "Galičica" mountain chain (1,750 m a.s.l) (Wagner et al. 2009). The Mokra is composed of serpentine (peridotites) overlain by Triassic limestone and the Galičica consists mainly of Triassic limestone (Stankovič 1960). The catchment of Lake Ohrid is characterized by continental climate. Between 1961 and 1990, average annual air temperature was 11.1 °C in the City of Ohrid. The maximum air temperature was 31.5 °C, the minimum −5.7 °C, and the lake never freezes (Popovska and Bonacci 2007). Maximum precipitation occurs in December and March, and the late summer is dry (Salemaa 1994). Mean annual precipitation averages ~750 mm (Wagner et al. 2009).

Materials and methods

Sediment cores were collected in September 2009 from 50 m water depth in Lake Ohrid (Fig. 1). The sampling depth was chosen because Mikulić and Pljakić (1970) reported maximum candonid ostracode diversity at this depth. The northern sampling location offshore from the City of Struga (core St09) (41°09.411′N, 20°40.986′E) represented a site of high urban pollution, being the largest town on the Macedonian shoreline of Lake Ohrid (63,376 residents in 2002) (GeoHive). The south-eastern area near the springs of Sveti Naum represented a relatively pristine location (core Sv09) (40°55.760′N, 20°45.175′E),

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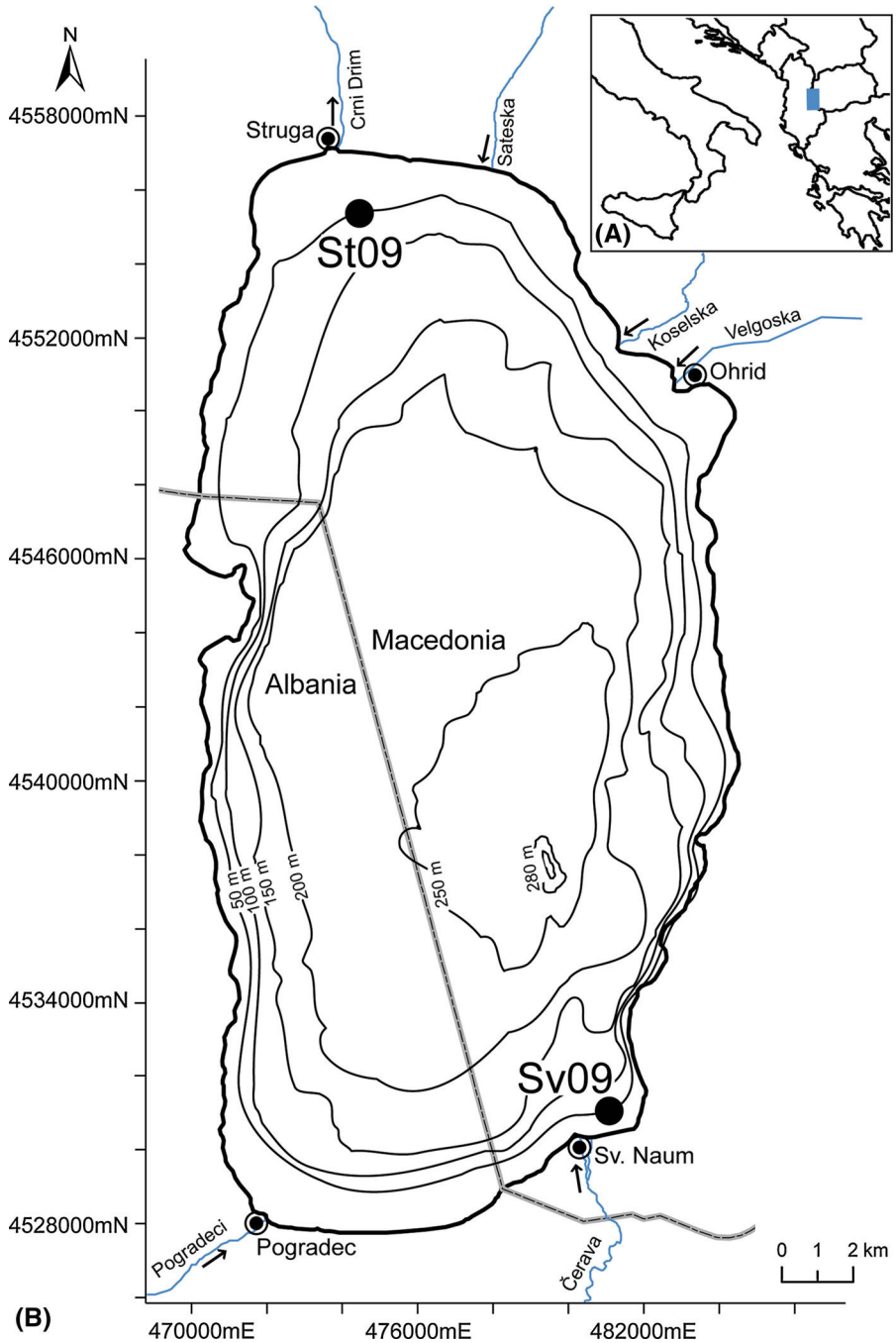

Fig. 1 Location of Lake Ohrid (*square*) on the border of Macedonia/Albania (**a**) and a bathymetric map of Lake Ohrid showing coring locations and cities and rivers discussed in the text (**b**)

with low intensity tourism and scattered domestic dwellings. At each location, three parallel cores, with a diameter of 11 cm, were retrieved 36 cm apart with a gravity multicorer. One core per location was subsampled for ^{210}Pb and ^{137}Cs dating in the field. The top 15 cm were subsampled every 0.5 cm and below 15 cm down to the base of the core every 1 cm. The cores taken for ostracode, diatom, and geochemical analyses were sampled in the field every 1 cm throughout. Cores for sediment description and photography were split in two halves at the Institut für Seenforschung, Langenargen.

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Chronology

^{137}Cs, ^{226}Ra, and ^{210}Pb activities (Bq kg^{-1} (dry weight)) were measured through gamma spectroscopy in freeze-dried and pulverized samples at the Eawag, Swiss Federal Institute of Aquatic Science and Technology Dübendorf, Switzerland with high-purity germanium well detectors. Unsupported ^{210}Pb activities were obtained by level by level subtraction of ^{226}Ra activities from total activities. Chronologies were established using the Constant Flux and Constant Sedimentation rate model (CFCS model) (Appleby and Oldfield 1992) for ^{210}Pb as well as the beginning of ^{137}Cs production in 1955, the fall-out 'bomb' peak in 1963, and the Chernobyl accident of 1986.

Sediment description and inorganic sediment components

A Munsell soil colour chart was used to describe sediment colour. To measure the water content, 10 g sediment were weighed before and after oven drying at 105 °C for 24 h. The loss on ignition (LOI) method was performed after Heiri et al. (2001) with 2–3 g sediment to estimate content of organic matter, carbonate, and siliciclastics. Samples were freeze-dried, homogenized, and analyzed for the major and trace elements arsenic, copper, iron, lead, nickel, zinc, and zirconium using an energy-dispersive XRF miniprobe multi-element analyzer (EMMA) (Cheburkin and Shotyk 1996). Mercury content was obtained by a direct mercury analyzer (DMA-80). Contents of sulphur were measured with an elemental analyzer (HEKAtech GmbH, EuroEA 3000). Analyses were carried out at the Institut für Umweltgeologie, Technische Universität Braunschweig. The contents of organic carbon and nitrogen were quantified at the NERC Isotope Geosciences Laboratory, British Geological Survey, Nottingham and both contents were used for the calculation of C/N ratios. The C/N atomic ratios were calculated by multiplied the C/N ratios by 1.167 (the ratio of atomic weights of nitrogen and carbon) (Meyers and Teranes 2001). Concentrations of total carbon (TC) and total inorganic carbon (TIC) were determined with a DIMATOC 200 (DIMATEC Co.) at the Institut für Geologie und Mineralogie, Universität zu Köln. Total organic carbon (TOC) was quantified from the difference between TC and TIC. All concentrations were compared with mass accumulation rates (MARs) of single elements (Meyers and Teranes 2001). To assess the pollution of the sediment, the Index of Geoaccumulation (I_{geo}) was used (Müller 1986). The index consists of six descriptive pollution classes: <0 = practically uncontaminated; 0–1 = uncontaminated to slightly contaminated; 1–2 = moderately contaminated; 2–3 = moderately to strongly contaminated; 3–4 = strongly contaminated; 4–5 = strongly to very strongly contaminated; >5 = very strongly contaminated. To assess ecological impact, measured major and trace elements were compared with the probable effect concentrations (PECs) above which harmful effects on sediment-dwelling organisms are expected (Jaagumagi 1993; MacDonald et al. 2000).

Ostracodes

For ostracode analyses, 50 g wet sediment was immersed in a 3 % H_2O_2 solution for 1–3 h and thereafter sieved through plastic sieves (63, 125, and 250 µm). Because earlier instars in the 63 µm fraction were not identifiable to the species and sometimes to the genera level, this fraction was excluded from analyses. Ostracode valves and carapaces were sorted with fine brushes under a Leica MZ 7.5 stereomicroscope. Ostracode carapaces were counted as two valves and species relative abundances were calculated as percentages (50 g wet sediment). Stratigraphic zone boundaries were defined using constrained incremental sum of squares cluster analysis (CONISS; Grimm 1987). We used Past to calculate the Shannon index (H□) (Krebs 1989), the Heip's index of evenness (E) (Heip 1974), and two indices of turnover (Bray–Curtis dissimilarity (BC) (Bray and Curtis 1957) and Jaccard similarity coefficient (J) (Magurran 2004)). To illustrate the Bray–Curtis dissimilarity and the Jaccard similarity we compared the ostracode assemblages of the youngest core sample (2009 AD) in each case with the respective corresponding sample, i.e. the first sample with the second sample, the first sample with the third sample, etc.

Diatoms

Diatom slides were prepared from 32 sediment samples of the core Sv09, using standard procedures (Battarbee et al. 2001). ~0.1 g equivalent dry

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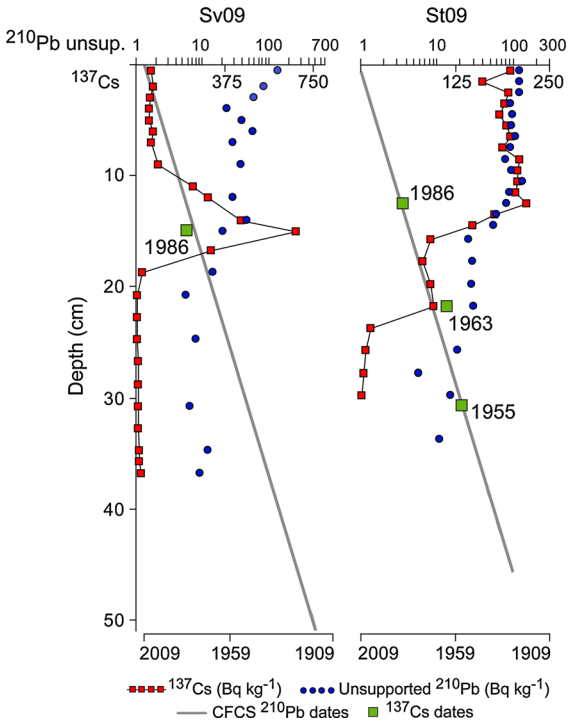

Fig. 2 ^{137}Cs and total and unsupported ^{210}Pb (Bq kg^{-1}) concentrations plotted on log scale in sediment cores Sv09 and St09 and the respective CFCS model with 1955, 1963, and 1986 fallout maxima determined by ^{137}Cs

sediment weight per sample, calculated from wet weight and water content, was heated in 25–30 ml 30 % H_2O_2 to oxidize organic material, and then a few drops of conc. HCl were added to remove carbonates and remaining H_2O_2. The residue was suspended in distilled water and centrifuged 4–5 times to wash away clay and remaining HCl. The suspension was diluted to the appropriate concentration, and known quantities of microspheres were added for the calculation of absolute diatom concentration. Slides were prepared using Naphrax™ as a mountant. Diatoms were counted along transects at 1000× magnification under oil immersion with an OLYMPUS BX51 light microscope. At least 300 valves were counted where possible, and 100 valves or so for poorly preserved assemblages. Diatom identification was based on Krammer and Lange-Bertalot (1986, 1988; 1991a, 1991b); Lange-Bertalot (2001); Krammer (2002); Levkov et al. (2007); Levkov (2009); Levkov and Williams (2011), adopting the nomenclature of the Catalogue of Diatom Names (online version) (California Academy of Sciences 2011) with the exception of the species *Cyclotella radiosa* (Grunow in Van Heurck) Lemmermann 1900, the genus name for which should revert to *Cyclotella* rather than *Puncticulata* (Houk et al. 2010). The F index of the endemic *Cyclotella fottii* Hustedt in Huber-Pestalozzi 1942 was estimated based on the ratio of pristine valves to all valves (sum of pristine and partially dissolved valves), where F = 1 implies valves preserved well while F = 0 shows valves are appreciably dissolved (Ryves et al. 2001). Biostratigraphic zone boundaries were defined using constrained incremental sum of squares cluster analysis (CONISS; Grimm 1987).

Results

Chronology

^{137}Cs peaks (1955, 1963, and 1986) were first identified independently and then compared with results from sedimentation rates based on the ^{210}Pb data so that the three marker ages could be assigned to the ^{137}Cs curve. For both cores, the differences of these ages to the averaged CFCS age line (constant sedimentation rate) are minimal (Fig. 2) so a linear age-depth model based on the ^{210}Pb data was appropriate.

The total ^{210}Pb activities in core St09 (Fig. 2) ranged between 155 Bq kg^{-1} (2.25 cm) and 26 Bq kg^{-1} (39.50 cm). Unsupported ^{210}Pb activity was highest at 10.25 cm (131 Bq kg^{-1}) and minimum activity (6 Bq kg^{-1}) was found at a depth of 27.50 cm. Using the CFCS ^{210}Pb model, an average sedimentation rate of 0.40 cm year^{-1} has been determined. Maximum ^{137}Cs activities were 220 and 97 Bq kg^{-1} at 12.25 and 21.50 cm, respectively, and correspond to the Chernobyl peak from 1986 and the nuclear weapons testing ^{137}Cs maximum in 1963. The onset of ^{137}Cs activities around the year 1955 was identified at 30.5 cm. According to the CFCS model, the total age of the sediment core is ~80 years (~1928).

In core Sv09, total ^{210}Pb activity was highest at the top of core (174 Bq kg^{-1}) and declined relatively evenly down to the base of the core, with a minimum at 35.50 cm (33 Bq kg^{-1}) (Fig. 2). Unsupported ^{210}Pb activities ranged from 138 Bq kg^{-1} (0.25 cm) to 6 Bq kg^{-1} (20.50 cm). Using the CFCS ^{210}Pb model, an average sedimentation rate of 0.47 cm year^{-1} was

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determined. ^{137}Cs activities in core Sv09 failed to display a sharp peak that might identify the onset of ^{137}Cs production in 1955 and the maximum fallout of 1963, nevertheless, the ^{137}Cs maximum of 676 Bq kg^{-1} at 14.75 cm indicates the 1986 Chernobyl peak. According to the CFCS model, the base of Sv09 is dated to ~1918.

A reason for the difference in absolute values of ^{137}Cs and ^{210}Pb activities in cores Sv09 and St09 could be the different lithologies: St09 has a higher carbonate content than Sv09, which mostly consists of siliciclastics. That could result in different affinities of the sediment to take up the radionuclides and a varying degree of reworking.

Sedimentology and geochemistry

Sediments from core St09 (Fig. 3) were relatively homogenous with a dark greyish brown colour. From the base of the core to 37.5 cm, sandy silt occurred, which was overlaid by clayey silt. Organic matter was low and fluctuated between 3.5 and 6.4 %. Carbonate content was higher from the core base to 7 cm depth with only slightly varying content (minimum of 18.5 % at 35 cm; maximum 23.2 %). Above, the content decreased to 12.8 %, rose again to 16.7 % at 2 cm. The water content was lowest (44.5 %) at the core base and increased towards the top (61.0 %). Ni and Zr decreased slightly upcore and fluctuated irregularly (Fig. 4). These fluctuations were also shown in the concentrations of As, Cu, Fe, Hg, Pb, and Zn but these elements show a slight increased upcore trend. C/N ratios increased to the core top and fluctuated to a greater or lesser extent. The maximum Hg concentration (0.08 mg kg^{-1}) was measured close to the base of the core between 48 and 49 cm. According to the Index of Geoaccumulation (I_{geo}) (Müller 1986) this corresponds to the pollution class, "moderately contaminated". However, this sample is a single peak with a value much higher than the rest of the St09 sequence, and may be an outlier. Arsenic concentrations correspond in 17 samples to the pollution class "moderately contaminated" and in one sample (29–28 cm) to the pollution class "moderately to strongly contaminated" (34.74 mg kg^{-1}). The probable effect concentrations (PECs) of Ni (48.6 mg kg^{-1}) (MacDonald et al. 2000) were exceeded in a total of 26 samples, mostly in the upper part of the core, and As concentration exceeded the PEC (33.0 mg kg^{-1}) (MacDonald et al. 2000) between 1957 and 1959 AD (29–28 cm) (34.74 mg kg^{-1}).

From the base of core Sv09 to 22.5 cm, the sediment consisted of silty clay with an upcore decreasing clay content (Fig. 3). Between 22.5 and 17.5 cm, a sand–silt–clay unit occurred that was overlaid by silty clay up to 12.5 cm. The uppermost 12.5 cm were characterized by clayey silt. The sediment colour was olive brown at the base of the core, dark greyish brown above 33 cm, and brown in the uppermost 12.5 cm. Organic matter and carbonate content were generally low and fluctuating. The maximum organic content (7.0 %) occurred at 10 cm depth and the minimum (1.6 %) at 21 cm. Maximum carbonate content (7.5 %) was measured at 7 cm and minimum (1 %) at 25 cm depth. Between the base of the core and 13 cm, water content fluctuated between 27.0 and 33.2 %. Above, the content increased with some fluctuations to 43.8 % at the core top. As and Hg show an increasing trend over time in Sv09 (Fig. 5), and concentrations of Cu, Fe, Ni, Zn, and Zr fluctuated irregularly throughout the core. Pb is the only element in Sv09 which shows an upcore decrease. The C/N ratios fluctuated throughout the sediment profile and vary between 9.90 and 17.70. According to the I_{geo}, As concentrations in core Sv09 correspond in nine samples to the pollution class "moderately contaminated", mostly in the upper core sequence. Fe concentrations exceed the PEC (43.77 g kg^{-1}) (Jaagumagi 1993) in three samples [1969–1972 AD (58.04 g kg^{-1}), 1986–1989 AD (47.81 g kg^{-1}), and 2003–2005 AD cm (54.32 g kg^{-1})] and Ni concentrations exceed the PEC (48.6 mg kg^{-1}) (MacDonald et al. 2000) in all samples.

TIC and TOC contents in both cores were similar to the LOI values and show matching patterns (Figs. 4, 5). TIC content in St09 fluctuated between 4.29 % (6–5 cm) and 6.71 % (32–31 cm), TOC between 0.66 % (32–31 cm) and 2.16 % (4–3 cm). Lowest TIC (0.19 %) and TOC (0.59 %) contents in core Sv09 occurred at a depth of 22–21 cm. Highest TOC (1.74 %) and TIC values (1.36 %) occurred between 1–0 and 3–2 cm, respectively.

Ostracodes

A total of 19 ostracode species was found in core St09 (Fig. 6; ESM 1), with a relatively high number of

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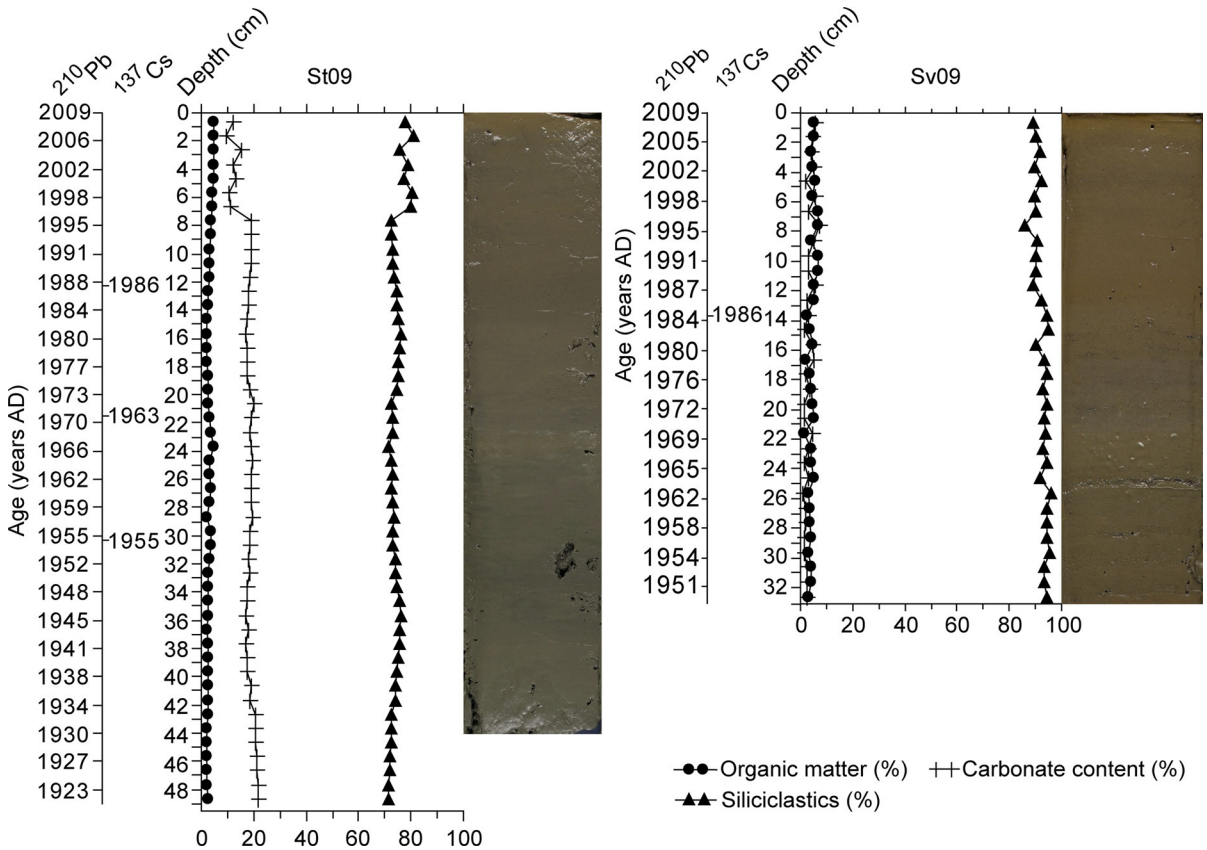

Fig. 3 Core photographs, organic matter, carbonate content, and siliciclastics in cores Sv09 and St09

juvenile candonids. Dominant species are *Candona media* Klie 1939 (up to 54 %) and *Cypria lacustris* Sars 1890 (up to 43 %). The Shannon index and the Evenness do not show any distinct patterns. The highest Shannon (1.96) occurred in 16–15 cm, the lowest (0.75) in 14–13 cm. Evenness ranged between 0.19 in 23–22 cm and 0.71 in 16–15 cm. The Bray–Curtis dissimilarity shows the highest value in 36–35 cm (0.63) and the lowest in 12–11 cm (0.08). The sample from 6 to 5 cm is, with a Jaccard similarity of 0.86, most similar to the core top sample. The lowest similarity occurred in 37–36 cm (0.25). Cluster analysis yielded four major zones in core St09: In Zone O-I (49–36 cm, 1922–1945 AD) 14 ostracode species and juvenile candonids occurred. The juvenile candonids show a high dominance (31–77 %), whereas the other species were relatively rare. In Zone O-II (36–23 cm, 1945–1968 AD) the number of species was 16 and in Zone O-III (23–15 cm, 1968–1982 AD) the number of species dropped down to 14. Zone O-IV (15–0 cm, 1982–2009 AD) yields the highest number of valves (3,001 valves) in 12–11 cm depth (1988–1990 AD) throughout the core.

In core Sv09, a total of 15 ostracode taxa was identified (Fig. 7; ESM 1). Furthermore, juvenile individuals of the family Candonidae, of the genera *Cypria*, and of the species *Prionocypris zenkeri* (Chyzer and Toth 1858) as well as *Cyclocypris* sp. (juv.?), were found. Mostly, *Candona trapeziformis* Klie 1939 is the dominant species in core Sv09 (up to 60 %). Only in the upper core part (3–0 cm; 2004–2009 AD) *Cypria obliqua* Klie 1939 dominates the assemblage (13–23 %). The total number of valves in core Sv09 was rather low. Highest abundance is reached in 12–11 cm (406 valves). The Shannon index increased upcore and the Evenness decreased. The Bray–Curtis dissimilarity ranged between 0.17 (23–22 cm) and 0.67 (15–14 cm). Jaccard similarity was lowest in 22–21 cm (0.09) and highest in 2–1 cm (0.58). Cluster analysis yielded five major assemblage zones: Zone O-I (34–26 cm, 1947–1962 AD) comprised six ostracode species and juvenile candonids.

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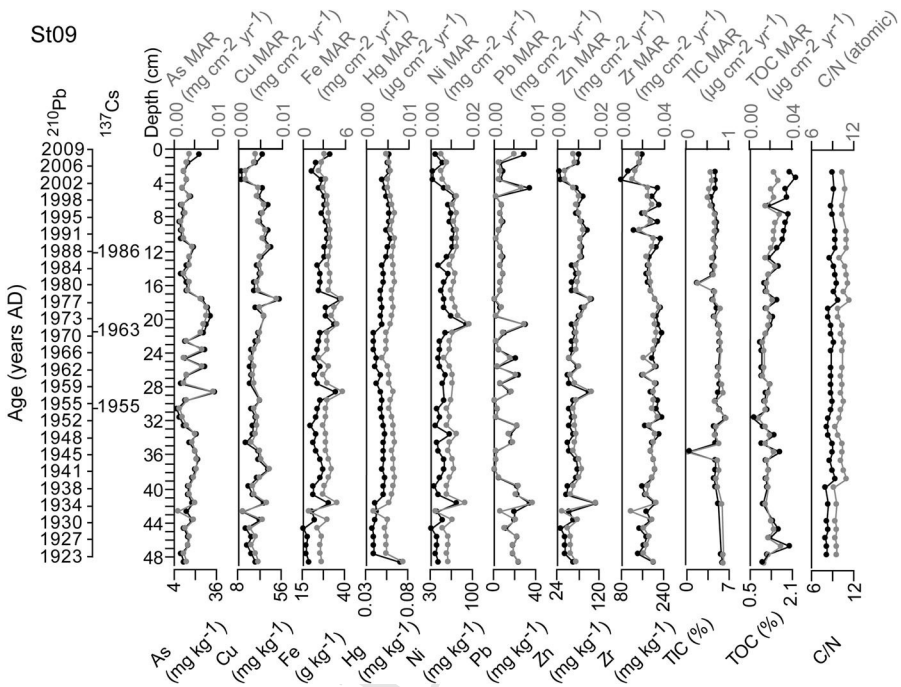

Fig. 4 Summary of geochemical concentrations (*black dots* and *lines*) as well as mass accumulation rates (MAR) and C/N atomic ratios [C/N (atomic)] (*grey dots* and *lines*) measured in core St09

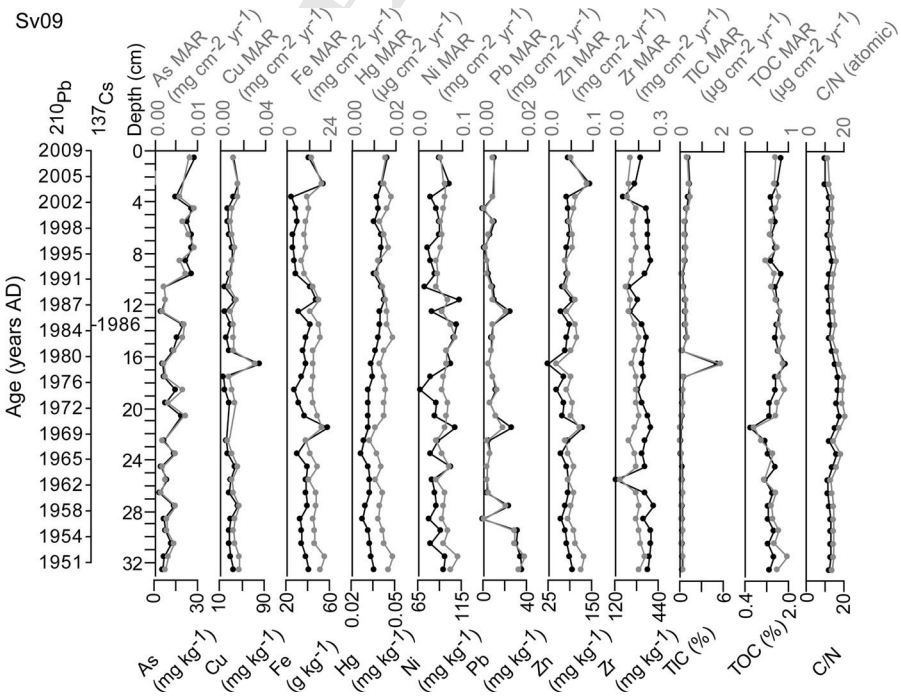

Fig. 5 Summary of geochemical concentrations (*black dots and lines*) as well as mass accumulation rates (MAR) and C/N atomic ratios [C/N (atomic)] (*grey dots* and *lines*) measured in core Sv09

The total number of valves was low; with a maximum of 45 valves in 31–30 cm and 27–26 cm. In Zone O-II (26–17 cm, 1962–1978 AD) seven species and juvenile candonids were found and in Zone O-III (17–13 cm, 1978–1986 AD) seven species and juvenile candonids occurred. The abundance increased slightly. Zone O-IV (13–3 cm, 1986–2004 AD) revealed the highest number of valves in the core (maximum in 12–11 cm with 406 valves). In Zone O-V (3–0 cm, 2004–2009 AD) ostracode abundance

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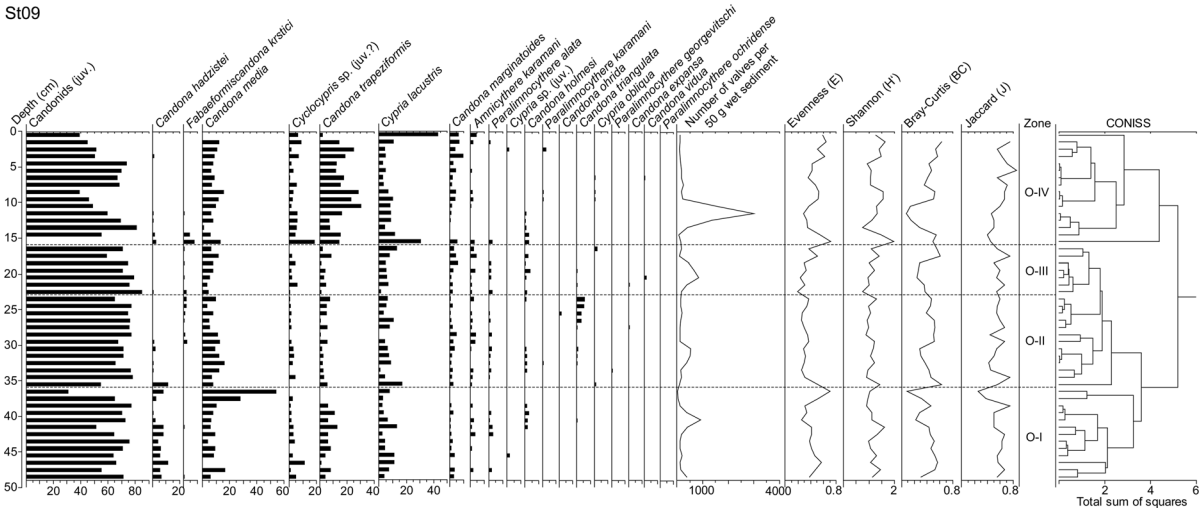

Fig. 6 Ostracode species assemblages, Heip's index of evenness, Shannon index, Bray–Curtis dissimilarity, and Jaccard similarity coefficient in core St09

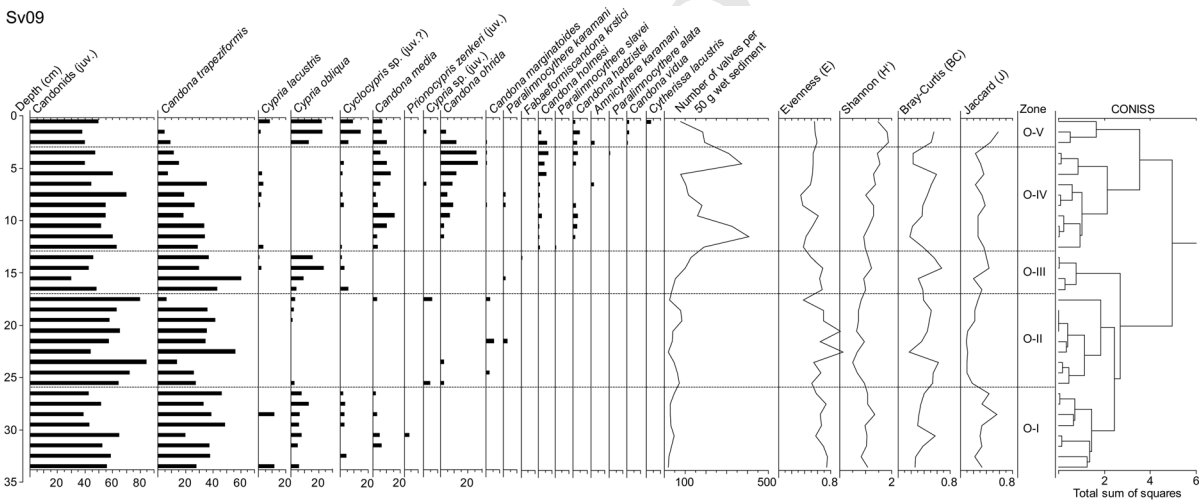

Fig. 7 Ostracode species assemblages, Heip's index of evenness, Shannon index, Bray–Curtis dissimilarity, and Jaccard similarity coefficient in core Sv09

was lower compared to Zone O-IV. The maximum number of valves was 193 in 3–2 cm and dropped down to 76 valves in 1–0 cm. This zone included the highest number of species in the entire core (13 species; exclusively juvenile candonids).

Diatoms

A total of 274 diatom species was identified in core Sv09. The majority are only found in Lake Ohrid, Sveti Naum and the hydrologically-connected Lake Prespa, underlining the high level of biodiversity and endemism in the lake. 24 groups and complexes (Fig. 8; ESM 2) were established through combination of species with similar morphological features and apparent ecological preferences. Four main zones (Fig. 8) can be recognised. In Zone D-I (33–24 cm, 1949–1965 AD), the endemic planktonic *Cyclotella fottii* was dominant (20–40 %), while the planktonic *Cyclotella ocellata* Pantocsek 1902 occurred at relatively low abundances (5–10 %). The benthic *Amphora pediculus* (Kützing) Grunow in Schmidt

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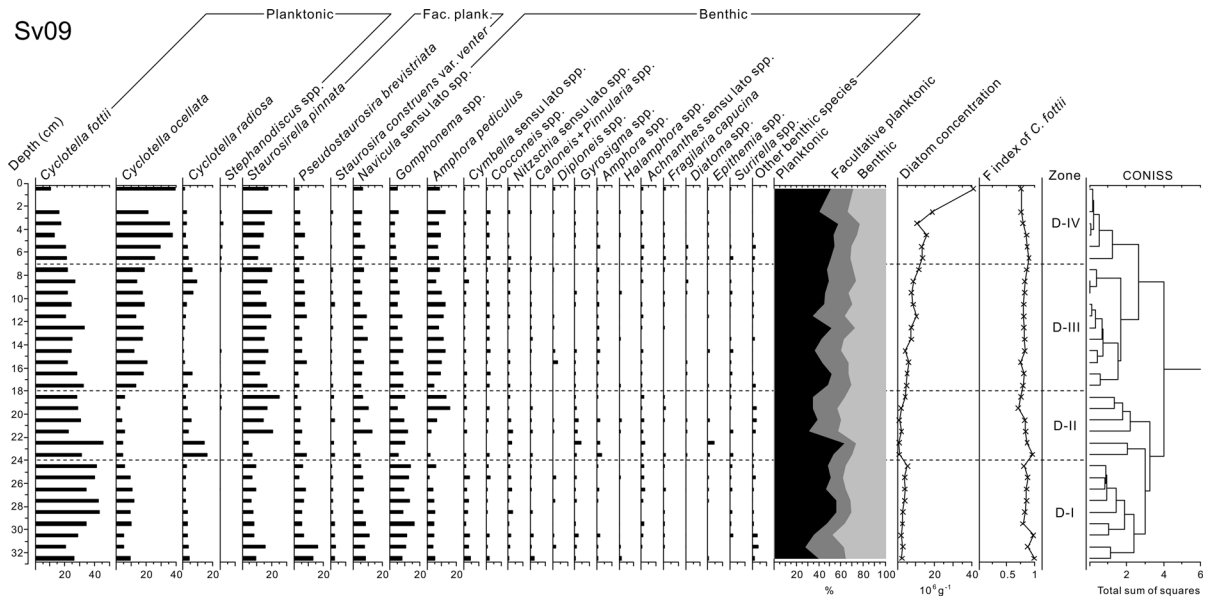

Fig. 8 Summary diatom assemblages, concentration, and F index of the endemic species *C. fottii* in core Sv09

et al. 1875 was present consistently at low abundance (5 %). Zone D-II (24–18 cm, 1965–1976 AD) exhibited very low diatom concentrations. A minor peak in the planktonic *Cyclotella radiosa* occurred at 24–22 cm depth, at the expense of benthic taxa, and was followed by an increase in the relative abundance of *A. pediculus*, *Staurosirella pinnata*, and *Navicula* sensu lato species with an associated reduction in the abundance of *C. fottii*. Zone D-III (18–7 cm, 1976–1996 AD) exhibited a gradually increasing concentration, and an increase to 10–20 % throughout in *C. ocellata*. Zone D-IV (7–0 cm, 1996–2009 AD) is marked by a trend towards the increasing abundance of *C. ocellata* at the expense of *C. fottii*, and there was an abrupt increase in diatom concentration towards the top. The higher relative abundance of *A. pediculus* and *Staurosira pinnata* Ehrenberg 1843 is maintained throughout the depth of 22–0 cm. The common effect of diatom valve deformation due to high toxic metal pollution (Cattaneo et al. 2004) was not observed in core Sv09.

Discussion

The combination of geochemical and biological proxies used here provides evidence by which to assess changes in toxic metal pollution and eutrophication over time linked to accelerated anthropogenic impact on Lake Ohrid. The exceeded PECs of Fe and Ni in cores St09 and Sv09 throughout the period, and without any notable increases over the last decades, indicate that the source is natural and derived from catchment geology. The south-west and west of Lake Ohrid consists of ultramafic extrusive rocks with associated weathering crusts containing chromium and iron-nickel ore deposits (Vogel et al. 2010). Higher concentrations of Fe and Ni in core Sv09 (Sveti Naum) could result from the closer proximity of the south-eastern part of the lake these deposits and to the piles of waste and ore dump sites of disused mines. Furthermore, the observed counterclockwise rotating surface water current in Lake Ohrid (Vogel et al. 2010) would transport these elements from the western to the eastern part of the lake. Malaj et al. (2011) found that concentrations of heavy metals in sediments are 100 times higher at sample locations in the Albanian sector of the lake, which are also closer to the mining sites than those from the Macedonian area. Many samples were also moderately contaminated (and in one case, moderately to strongly contaminated) with arsenic. The most common sources for As, for over a 100 years, are pesticides and wood preservatives (Alloway 1995), presumably derived from agricultural activity in the catchment as agriculture is one of the most important economic sectors around Lake Ohrid

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(Spirkovski et al. 2001) and natural source of As do not exist around Lake Ohrid.

The generally higher abundance of ostracode valves and species diversity near Struga, in comparison to Sveti Naum correlates with slightly higher TOC and TIC values near Struga, indicating higher productivity in the northern part of the lake. C/N ratios near Sveti Naum are higher than near the City of Struga. Such higher ratios were also observed by Vogel et al. (2010) in the south-eastern part of Lake Ohrid near to the river mouth of Čerava, which passes through agricultural and populated areas. Ratios above 10 indicate that most of the organic matter comes from autochthonous production (Meyers and Ishiwatari 1993).

Near the City of Struga, the low ostracode abundance correlates with some peaks in the concentration of As, Cu, Fe, Ni, Zn, and Zr. The number of ostracode valves increases during time intervals when the heavy metal concentrations are low and vice versa. Since species composition does not shift in parallel, these fluctuations may be explained simply by changes in precipitation or amount of snow melt and a subsequently higher sediment load into the lake, rather than being a direct indicator of ecological impact.

The period between the early 1920s and the late 1980s is characterized by low ostracode abundance and low Shannon diversity in both sequences. The low numbers of valves near Sveti Naum could be explained by very low values of TOC and TIC, which indicate a low productivity near the spring discharge. This is confirmed by the low diatom concentration in Zone D–I, and a low abundance of mesotrophic *Cyclotella ocellata* indicating lower productivity in the south-eastern part of Lake Ohrid, with little nutrient input from Lake Prespa in the 1950s and early 1960s. Lake Prespa underwent a relatively high lake-level phase from 1950 to 1962 (Popovska and Bonacci 2007; Popovska 2011), which reduced nutrient enrichment in Lake Prespa. This decreased nutrient input to Lake Ohrid could have been amplified by the retention of nutrients within the karst aquifer (Matzinger et al. 2006a) and by the dilution of Lake Prespa subterranean outflow by mountain range precipitation (Popovska and Bonacci 2007). Only juvenile valves of the ostracode *P. zenkeri* were found in core Sv09. This species prefers waters connected to springs (Meisch 2000) and was probably imported from the springs of Sveti Naum into the lake.

The peak in the diatom species *Cyclotella radiosa* corresponds to a low diatom concentration, correlating with an abrupt lake-level increase in Lake Prespa in 1963 (Popovska and Bonacci 2007; Popovska 2011). This would have, increased the subterranean flow into Lake Ohrid, decreased the nutrient concentration (Matzinger et al. 2006a) and would be likely to have an impact on sediment accumulation rate. The age model does not show a clear change of sediment accumulation rate. Since, the F index of *Cyclotella fottii* does not show evidence of increased diatom dissolution, the low concentration of diatom valves supports a reduction in productivity, supported also by low ostracode abundance. While small forms of diatoms such as *Amphora pediculus* and *Staurosirella pinnata* are known to be vulnerable to sediment focusing processes on steep slopes in boreal lakes (Biskaborn et al. 2012), their abundance decreases rather than increases in this part of the record, which is dominated by planktonic taxa. Instead, the increased subterranean inflow may have resulted in small forms being less likely to settle out of the water column.

Matter et al. (2010) analyzed sediment cores, taken near the north-western shore in Lake Ohrid from ~5 to 10 m and at 53 m water depth. In the cores from shallower water they found a boundary between two distinct stratigraphic units, dated to ~1955. The sediment above this boundary was darker and characterized by lower carbonate content bit higher TOC, Fe, Si, and diatom contents. Moreover, a sewage smell was noticeable during core opening. Matter et al. (2010) related this change to increasing anthropogenic impact at that time, but there was no evidence for a similar boundary in the deep water core, other than a slight increase in TOC. Our results show a similar pattern at 50 m depth, with a slight increase in TOC but no evidence for dramatic eutrophication. It appears that the shallow waters in Lake Ohrid show a faster and more drastic response to anthropogenic influences than the deeper water areas (Matter et al. 2010).

Since the mid 1970s, there has been an accelerated, zigzag lake-level decline in Lake Prespa due to the usage of water for irrigation. The most dramatic drop occurred between 1987 and 1995 with a decrease of 5–6 m (Popovska 2011). A lake-level lowering of Lake Prespa by <20 m can increase the nutrient concentration of the lake and thus lead to increased nutrient input via springs to Lake Ohrid, in spite of a decrease in underground flow. Lake Prespa was

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undergoing eutrophication at the time due to intensified agriculture and associated water abstraction, fertilizer utilization, and enhanced soil erosion (Matzinger et al. 2006a), which amplified the effects of the lake-level decrease. The increase in the abundance of *Cyclotella ocellata* corresponds to the accelerated nutrient input to Lake Ohrid during this period, and may represent a response to productivity. The diatom record does not show an oscillation of nutrient input linked to the renewed lake-level rise in Lake Prespa between 1979 and 1986 and the dramatic decline between 1987 and 1995, however. An alternate explanation may be that the increase relates instead to associated warming, resulting in an increase in epilimnetic taxa with stronger summer thermal stratification, as appears to be the case in longer term transitions between glacial and interglacial phases (Reed et al. 2010). However, the ostracode data do provides evidence of this lake-level decline in Lake Prespa as the number of valves near the City of Struga and near Sveti Naum increased. This increase resulted in the highest valve concentration in the entire core St09 (maximum = 3,001 valves per 50 g wet sediment). In Sv09, high ostracode abundance (406 and 327 valves per 50 g wet sediment) was also reached during this time. In both cores, this period is characterized by low Shannon species diversity. Increasing productivity in Lake Ohrid is confirmed by high concentrations of TIC and TOC in St09 during this time span and a slight increase near Sveti Naum. It seems that in the highly oligotrophic condition of Lake Ohrid, subtle changes in nutrients have no clear effect on the endemic planktonic diatom *C. fottii* which inhabits the deep, open waters.

After ~1996 AD, the further increase in the epilimnetic diatom *C. ocellata* is mainly the result of the overall decreasing trend of the Prespa lake level (Popovska 2011) and increasing nutrient input into Lake Ohrid (Matzinger et al. 2006a). Between 1991 and 2009 AD, the area next to Sveti Naum was characterized by the highest As concentrations in the entire core. TIC and TOC increased slightly, pointing to increased productivity. This increase could be the reason for the upward increase of the total number of ostracode valves in comparison to the period between the early 1920s and the mid 1980s. Furthermore, the total number of species reached a maximum (13 species), which was the highest number in the entire core. This high biodiversity is also apparent in the coinciding high Shannon index.

The diatom record in core Sv09 does not show the clear changes for the major eutrophication, but there has been an increasing trend in nutrient concentration and productivity in south-eastern Lake Ohrid since the mid 1960s, in spite of its consistent oligotrophic condition. The measured average total phosphorus (TP) concentration in 2002–2004 was 4.6 g l^{-1}, and a simple linear model may estimate the Ohrid TP concentration increasing from ~3.7 g l^{-1} in the mid 1960s to ~4.8 g l^{-1} in the late 2000s (Matzinger et al. 2006b). The productivity in this part of Lake Ohrid is strongly influenced by the subterranean inflow and its nutrient supply, which are directly linked to the trophic status and water level of Lake Prespa (Matzinger et al. 2006a; Wagner et al. 2009). If closely connected, the shifts of diatom flora in Sv09 occur 1–2 years later than the changes of water level in Lake Prespa, maybe because the average drainage time from Lake Prespa to the springs near Lake Ohrid is 18 months (Popovska and Bonacci 2007). But a more detailed analysis of the basin-wide diatom response would be necessary to test whether the influence of Prespa has an impact on diatom ecology across the lake as a whole.

In 1988, the first sewage-water treatment system started to operate in the Ohrid-Struga region (UNESCO ROSTE 2004), and Watzin (2003) reported that after the system was completed, an improvement in the water quality in the Ohrid Bay was visible, namely the number of bacteria decreased one thousand fold. However, this positive effect is not clearly visible near the City of Struga. The concentrations of As, Cu, Fe, Hg, Ni, Pb, Zn, and Zr show a downward trend after the water-treatment plant came into operation but the concentrations fluctuated during the time and in the last years, mostly all concentrations show an increase. TIC concentrations were relatively stable and TOC shows a strong upcore increase reaching the maximum concentration between 2002 and 2004 AD. The number of ostracode valves and the total number of species decreased, which could point to the fact that the living conditions in this part of the lake became less favourable.

Conclusions

This multi-proxy approach using sediment records with a high sample resolution from Lake Ohrid provide a detailed insight into the environmental history of the lake. Geochemical analysis reveal

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relatively high As concentrations in the northern and south-eastern part of the lake. In core St09 from the northern part, evenly distributed throughout the core, the concentrations correspond to the I_{geo} class "moderately contaminated" and in one sample from the late 1950s to the class "moderately to strongly contaminated". Sediments from the upper core part (Sv09), taken in the south-eastern sector, were according to the I_{geo} "moderately contaminated" with As. These high concentrations may have been originated from pesticides and wood preservatives used in agriculture around Lake Ohrid. Furthermore, Fe and Ni concentrations often exceeded the PEC levels in both sediment cores, which could have been caused by the ultramafic extrusive rocks with associated weathering crust containing chromium and iron-nickel ore deposits in the west and south-west of Lake Ohrid (Vogel et al. 2010).

Between the early 1920s and the late 1980s, the lake shows generally a low productivity in the northern and south-eastern part, which is indicated by low numbers of ostracode valves, low abundance of the mesotrophic diatom *Cyclotella ocellata*, a general low diatom concentration, as well as low values of TOC and TIC. Furthermore, the low numbers of ostracode valves correlated near the City of Struga with some high concentrations of As, Cu, Fe, Ni, Zn, and Zr. Since the mid 1970s, the increase of *C. ocellata* and an increasing diatom concentration corresponds to rising productivity in the south-eastern lake area. A high number of ostracode valves, the highest number in both cores, indicate an increasing productivity in the late 1980s. This was also confirmed by higher concentrations of TIC, and TOC. A slight increasing productivity trend in the south-eastern part of Lake Ohrid continued from the early 1990s until 2009, which is visible in the increasing TIC and TOC values. During this time, the total number of ostracode valves and the number of ostracode species are also generally high in this area. However, since the early 1990s, the area near the City of Struga in the northern part of the lake is characterized by a decreasing trend in the number of ostracode valves and in the total number of species. This corresponds to an increase of, e.g., TIC, TOC, As, Cu, Fe, Pb, and Zn. This might be an indication that the conditions in the northern lake part became less favourable for ostracodes, which might have dramatic consequences as a loss of the endemic Ohrid ostracode species would be irrevocable.

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