THE UNIVERSITY OF HULL

Diatom-based reconstruction of multi-timescale climate and environmental change from Lakes Dojran and Ohrid in the northeastern Mediterranean region

A thesis submitted for the Degree of Doctor of Philosophy in the University of Hull

by

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ABSTRACT

The southern Balkans is located at the juncture between the west-east and north-south contrasting hydroclimatic domains across the Mediterranean, and this study focuses on diatoms as indicators of late Quaternary climate change and recent human impact in Lakes Dojran and Ohrid. Lake Dojran (Macedonia/Greece) is a shallow and currently hypereutrophic lake controlled by a classic Mediterranean climate. The Lake Dojran diatom data provide a new insight into changes in lake level and trophic status during the Younger Dryas and Holocene in the northeastern Mediterranean region, and are also important in disentangling regional climate effects from local catchment dynamics during the Holocene. The pigment data from the upper part of the sequence provide clear evidence for accelerated eutrophication of Lake Dojran due to water abstraction and intensified agriculture during the recent several centuries. Ancient lakes in Europe are restricted to the southern Balkan region, and Lake Ohrid (Macedonia/Albania), under the influence of Mediterranean and somewhat continental climates, is a rare example with a high degree of biodiversity and endemism. In deep and highly oligotrophic Lake Ohrid, the diatom data provide a clear picture of Lateglacial and Holocene changes in temperature and lake productivity which is primarily modulated through stratification or mixing regime and associated nutrient redistribution in the water column, and comparison with the data from Lake Dojran reveals different responses of diatoms to climate in the contrasting types of lakes. Diatom analysis of a short core in the southeastern part of Lake Ohrid reveals human-induced eutrophication of Lake Ohrid in the recent several decades influenced by nutrient transfer through springs from hydraulically-linked Lake Prespa. Preliminary diatom analysis of the ICDP deep core in Lake Ohrid generates a preliminary interpretation of the response of diatoms to glacial-interglacial cycles and the evolution of endemic diatom species during the past more than one million years.

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Chapter 1 Introduction

The Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) confirms that human activity has changed the climate system, with a high risk of impacts on terrestrial and freshwater ecosystems and their biodiversity (Settele et al., 2014). Climate change also has a tendency to exacerbate existing impacts (e.g. water abstraction, eutrophication) from human activities in catchment areas (Moss, 2012). Developing a deeper understanding of the character and drivers of climate change on long-term timescales is fundamental to our ability to model future climate change (Herold et al., 2012). The understanding of terrestrial and ecosystem response to climate change is also directly relevant to modern conservation (Froyd and Willis, 2008).

Palaeoenvironmental studies of biological, geochemical and mineralogical remains preserved in continental sedimentary archives such as lake sediment cores can offer unrivalled insights into ecosystem response to climate change on a variety of timescales from decades to millennia, and into the character of accelerating human impacts such as freshwater eutrophication during the Holocene and its acceleration in the recent decades. Across Europe, most studies have focused on the Holocene epoch simply because the sedimentary archives (primarily lakes and peat bogs) only formed after Lateglacial ice retreat at the Marine Isotope Stage (MIS) 2–1 transition (Roberts and Reed, 2009). Longer Quaternary continental records >500 ka in age from ancient tectonic lakes (Mackay et al., 2010) are of global importance for palaeoclimate reconstruction over multiple glacial–interglacial timescales and in the absence of human impact, but are rare (Lang and Wolff, 2011).

The Mediterranean region is an important transitional zone between temperate areas under the climatic influence of mid-latitude westerlies and arid areas under the Subtropical High pressure system. Most of the region is dominated by a semi-arid or semi-humid, Mediterranean-type climate of summer drought and mild, wet winters. Natural climate variability and intensified human impact make this region particularly vulnerable to future climate change. In this context, palaeoclimate reconstruction becomes a key issue for

understanding patterns and processes of climate change and for predicting future climate scenarios and possible impacts on human societies (Lionello et al., 2006; Lionello, 2012). In spite of a marked increase in research effort on late Quaternary lake records over the last two decades (e.g. Harrison and Digerfeldt, 1993; Roberts et al., 2008, 2011a; Magny et al., 2013), our understanding of climate variability and ecosystem response is still limited. Similarly, the potential for palaeolimnological research focused on recent water quality degradation (Reed et al., 2008; Bennion et al., 2011; Battarbee et al., 2012) is largely untapped across the Mediteranean.

1.1 Current understanding of Holocene climatic forcing

Palaeoenvironmental analysis offers potential to improve understanding of Mediterranean climate change, but the clear definition of regional contrasts is still elusive. An early review of lake-level reconstruction proposed an east-west contrast during the Holocene (Harrison and Digerfeldt, 1993). More recently, Roberts et al. (2008, 2011a) confirmed this, defining a marked contrast during the Holocene to the east and west of a line running through the Balkans, southern Italy and Tunisia, based on stable isotope data and model output. On a centennial-decadal timescale, the complexity of regional patterns was also demonstrated in an east-west contrast between the northern Iberian Peninsula and central Turkey (Roberts et al., 2012), and this is coherent with an east-west contrast in the growth variability of Mediterranean pines (Seim et al., 2014). In contrast, Magny et al. (2013) proposed a north-south divide around ca. 40°N during the Holocene in the central Mediterranean from carbonate-based lake-level reconstruction. Peyron et al. (2013) supported this from pollen-based quantitative reconstruction of summer precipitation, and also proposed a similar pattern in the Aegean Sea. This is coherent with a north-south contrast in fire activity in the western Mediterranean (Vannière et al., 2011). The southern Balkans is a key location for understanding Mediterranean climate change, being located at the juncture of the proposed boundaries between west-east and north-south contrasting climate and hydrological domains. The southern Balkans is particularly complex, and patterns and mechanisms of climate and environmental change are still poorly understood. The

complexity of palaeoenvironments is indicated, for example, by discrepancies in vegetation reconstruction between adjacent sites such as Lake Ioannina (northwestern Greece) and Nisi Fen (northern Greece) (Lawson et al., 2004, 2005).

1.1.1 Summer climate mode and the Subtropical High pressure

The character and influence of the Holocene summer insolation maximum across the Mediterranean is a topic for vigorous ongoing debate (Tzedakis, 2007). In a major review, Tzedakis (2007) argued that the enhanced African monsoon did not extend to the Mediterranean, and the monsoonal effect has been mainly indirect in terms of Nile discharge and runoff along the North African coast. On the other hand, the northward-migrated, strengthened North Atlantic Subtropical High pressure in response to high summer insolation blocked westerly moisture penetration into the Mediterranean (Magny et al., 2013; Desprat et al., 2013). Tzedakis (2007) also suggested that the enhanced Indian monsoon may have accentuated summer aridity in the eastern Mediterranean. Modelling experiments show little sign of summer precipitation in spite of high summer insolation (Brayshaw et al., 2011). Magny et al. (2013) discussed the influence of ice sheets in the Northern Hemisphere on humidity in the Mediterranean, and suggested that the rapid melting of ice sheets and associated fresh water forcing in the North Atlantic Ocean contribute to summer aridity during the earliest Holocene in the south-central Mediterranean.

Davis and Brewer (2009) reconstructed Holocene changes in the latitudinal temperature gradient (LTG) based on differences in pollen-based area-average temperatures between northern (55–70°N) and southern Europe (35–45°N). The LTG reflects combined effects of the differential heating of insolation (the latitudinal insolation gradient, LIG) and the high-latitude cooling influence of remnant ice sheets (Davis and Brewer, 2009). The Subtropical High pressure is located at ca. 36°N when the summer LTG is zero (Davis and Brewer, 2009). A weaker (more positive) summer LTG drives a northern position of the Subtropical High pressure (Davis and Brewer, 2009), and the tendency would be towards much drier summers than today. The quantitative reconstruction of the Subtropical High pressure may be relevant to moisture change in the northeastern Mediterranean. The

additional, area-average temperature reconstruction for southeastern Europe (Davis et al., 2003), supported by other regional syntheses (Finné et al., 2011; Abrantes et al., 2012), may be relevant in terms of evaporation and its effect on moisture balance.

1.1.2 Winter climate mode and the Arctic Oscillation (AO)

Modelling experiments show high winter precipitation during the early Holocene (Brayshaw et al., 2011), which is coherent with a southward-shifted storm track and responds to weak winter insolation (Desprat et al., 2013). Desprat et al. (2013) also suggested that the rapid melting of ice sheets in the Northern Hemisphere and associated reorganisation of atmospheric circulation contribute to high winter precipitation during the early Holocene in the south-central Mediterranean. Roberts et al. (2008, 2011a) and Magny et al. (2013) suggested that this is probably attributed to winter cyclogenesis and local precipitation. However, it is inconsistent with the positive AO/NAO and resultant aridity in the north-central Mediterranean (Magny et al., 2013). Data-model comparison shows that models underestimate the role of AO/NAO (Gladstone et al., 2005; Brewer et al., 2007; Mauri et al., 2014), and Davis and Brewer (2009) proposed that models overestimate low-latitude warming in summer and high-latitude warming in winter.

The Mediterranean exhibits a dry climate during the positive phase of AO/NAO and more precipitation during their negative phase (Martinson et al., 2000; Wanner et al., 2001). However, AO has a larger horizontal scale (Thompson and Wallace, 1998), and NAO alone cannot account for changes in winter precipitation in Turkey (Jones et al., 2006). In terms of precipitation, the northeastern Mediterranean is distinguished from the Levant and southeastern Mediterranean (Felis and Rimbu, 2010), and from the NAO-highly related Iberia and western Mediterranean (Roberts et al., 2012). The prominent role of AO/NAO in influencing Holocene hydroclimatic change across the Mediterranean is revealed not only at the centennial scale (e.g. Lamy et al., 2006) but also at the millennial scale (e.g. Davis and Stevenson, 2007; Fletcher et al., 2013). The AO index is zero when the winter LTG is zero (Davis and Brewer, 2009). A weaker (more positive) winter LTG drives a more positive AO, and the tendency would be towards dry winters. The AO quantitative reconstruction (Davis

and Brewer, 2009) may be more relevant than the NAO in interpretation of northeastern Mediterranean climatic records.

1.2 The strength of diatom analysis in palaeolimnological research

The potential to strengthen palaeoenvironmental interpretation by the analysis of multiple proxies is well recognised in palaeolimnological research. Proxies include a variety of biotic indicators (pollen, plant microfossils, diatoms, ostracods, chironomids, cladocerans, etc.) and sedimentological/geochemical variables (stable isotopes, organic and inorganic geochemistry, grain size, magnetic sediment properties, etc.). Among abiotic climatic proxies, the δ^{18} O signal of authigenic and biogenic carbonates (Leng and Marshall, 2004) and the abundance of organic matter and carbonates (Birks and Birks, 2006) play a prominent role. Very often biotic climatic proxies represent an indirect response to climate, whereby limnological changes such as shifts in nutrient availability or lake-habitat characteristics at the coring site, for example, are responses to climate-induced changes in lake level, length of ice cover, mixing regime or anoxia. They may also represent a response to changes in the catchment such as vegetation cover, erosion and nutrient export. Diatoms (single-celled siliceous algae, Bacillariophyceae) are abundant, diverse and, being at the bottom of the food chain, sensitive to a wide range of water chemistry variables (Battarbee, 2000). Their silica frustules often preserve well in lake sediment cores, and they play an important role in providing information on a wide spectrum of past environmental and ecological changes (Table 1.1). They are regarded as the strongest palaeoindicators of lake-level change and nutrient concentration in particular, by virtue of which they also offer excellent potential for reconstructing recent human-induced water quality degradation (Korhola, 2007; Wolin and Stone, 2010; Hall and Smol, 2010; Bennion et al., 2010).

1.2.1 Lake level

Planktonic diatoms often dominate open-water environments, while benthic and facultative planktonic (tychoplanktonic) diatoms typically dominate littoral habitats. Shallow-water conditions expand benthic habitat and macrophyte growth, producing a larger percentage of

benthic and facultative planktonic forms preserved at the coring site (usually the deepest, central part of lakes). Conversely, during deeper lake phases, benthic substrates are often reduced, producing a larger proportion of plankton preserved at the coring site. Thus, the ratio of planktonic to non-planktonic diatom taxa has been usually used to infer water-level changes (Wolin and Stone, 2010). An increase in the relative abundance of plankton at the coring site would indicate a lake-level increase, but a similar response might also be driven by an increase in lake productivity, since planktonic diatoms respond more directly to water-column nutrient enrichment (Hall and Smol, 2010).

1.2.2 Ice cover

Under clear or snow-free ice, thermal heating and convective mixing allow heavily-silicified planktonic diatoms to be supported. Thick or snow-coved ice restricts light penetration, inhibiting diatom growth, and also plays a major role in the stratification of the water column, which in turn has an influence on lake mixing and nutrient recycling processes (Battarbee et al., 2001; Mackay et al., 2003a). If lakes are permanently covered by ice, the productivity is low; if ice cover partially thaws around the margins in summer, an increased area of littoral habitat is opened up for benthic production; if the whole lake becomes ice free during summer months and providing that the lake is deep enough, planktonic taxa would become more abundant. Ice cover acts to inhibit plankton development, while prolonged periods of ice cover tend to favour the growth of *Fragilaria* species (Mackay et al., 2003a).

1.2.3 Nutrient availability

Nutrient availability plays a major role in structuring diatom composition and driving lake productivity. Increased nutrient availability usually causes most alteration to plankton communities, and benthic communities can also be affected as a result of changing habitat availability and though increased shading by plankton crops (Battarbee et al., 2001). Nutrient enrichment may thus be reflected in diatom records by increases in diatom concentration, in the relative abundance of planktonic taxa, and/or in diatom-inferred total phosphorus (DI-TP) concentration (Lowe and Walker, 1997), which may result from climatic and anthropogenic forcings on external nutrient input as well as from mixing-induced nutrient redistribution in

the water column. Individual diatom species have distinct TP optimum and tolerance estimates in the European Diatom Database Initiative (EDDI) (Juggins, 2001), and some specific diatom taxa or assemblages may be good indicators of trophic status. Planktonic diatom composition is also influenced by the ratios of nutrient elements (i.e. resource competition theory); for example, *Stephanodiscus minutulus* prefers high P concentration, while *Asterionella formosa* and *Fragilaria crotonensis* prefer high Si concentration (Kilham et al., 1996). Diatoms are a strong proxy for indicating anthropogenic eutrophication and subsequent re-oligotrophication in the recent past (e. g. Marchetto et al., 2004; Anderson et al., 2012; Berthon et al., 2014).

1.2.4 Mixing regime

Lake mixing and stratification regimes are driven by temperature and/or wind intensity and thus are intimately linked to climate. Whilst mixing influences the composition of benthic taxa and is responsible for resuspending facultative planktonic and benthic taxa into the water column, its main influence is on the composition of the plankton (Battarbee et al., 2001). Planktonic diatoms are more abundant during periods of lake mixing and different taxa have evolved competitive physiological, morphological and life-cycle strategies to cope with buoyancy problems (Battarbee et al., 2001). Heavily-silicified *Aulacoseira* species are favoured by mixing over other planktonic species, and small-sized *Cyclotella* species and longer *Fragilaria* species with lower sinking rates benefit from stratification (Winder et al., 2009; Wolin and Stone, 2010).

1.2.5 Salinity

Salinity reconstruction is of specific relevance to closed-basin, saline lakes, whereby climate-induced shifts in lake level may be registered by brine concentration and dilution (Fritz et al., 2010). Ionic concentration is expressed as salinity, and conductivity is used to represent salinity due to the direct linkage of conductivity to total dissolved solids (TDS) and the approximate relationship between salinity and TDS (Reed, 1996). Many diatoms tolerant of oligosaline chemistry are generally tolerant of relatively high ionic concentration (>0.5 g l⁻¹), so can also occur in eutrophic fresh water with high nitrate and/or phosphate

concentration. Thus, many diatoms are eutrophic and halotelerant, and this may make it difficult to disentangle salinity change from nutrient shifts in attempting to infer lake-level change. However, some diatoms appear to be obligate saline taxa which do not occur in eutrophic fresh water, presumably because they have a specific preference for elevated chloride, sulphate or carbonate concentration. These rare obligate saline taxa represent the strongest indicators for palaeosalinity in lakes which may be subject to aridity and nutrient enrichment. Although the mechanisms that link diatoms and salinity are not well understood, many salinity training sets show that salinity optima of diatom taxa are evenly distributed, and tolerances do not exhibit any maxima or minima (Fritz et al., 2010; Potapova, 2011). Thus, diatom-inferred conductivity (DI-Cond) reconstruction is more robust than DI-TP reconstruction over extended time periods such as the Holocene (Juggins, personal communication).

1.2.6 Temperature

Lake-water temperature clearly regulates the rates of many metabolic processes, and thus climate warming may favour larger diatom species (Berthon et al., 2014) and/or improve lake productivity which is reflected by high absolute diatom concentration. Temperature also has a major influence on other physical and chemical variables in the lake system, such as ice cover, stratification or mixing regime, and nutrient availability, and thus it is likely that most of the influences exerted by temperature on diatom composition are indirect rather than temperature alone (Anderson, 2000; Battarbee et al., 2001; Mackay et al., 2003a).

As discussed above, in some cases equifinality may occur, in that a similar diatom response could be exhibited as a result of different causal mechanisms. In the southern Balkans, shifts of *Cyclotella ocellata* during the last glacial–interglacial cycle reveal changes in temperature and resultant productivity in deep Lake Ohrid (Reed et al., 2010), while lake-level change is indicated by the shifts of *C. ocellata* in shallower Lake Prespa (Cvetkoska et al., 2014a, 2015) and Lake Ioannina (Wilson et al., 2008; Jones et al., 2013). Thus, all techniques have strengths and weaknesses, underlining the value of the multi-proxy approach.

Species	Ecological and environmental preferences	References
Fragilaria crotonensis		
Kitton 1869	Deep waters, high nitrogen and silica	Bailey-Watts (1986); Saros
Asterionella formosa	concentrations	et al. (2005)
Hassall 1850		
Stephanodiscus minutulus		
(Kützing) Cleve & Möller		
1882	High phosphorus concentration, eutrophic and	Bennion (1995); Kilham et
Stephanodiscus parvus	halotolerant	al. (1996); Fritz et al. (1993)
Stoermer & Håkansson		
1984		
Cyclotella meneghiniana	Shallow to deep waters, fresh waters of high	Gasse (2002); Saros and
Kützing 1844	conductivity to saline conditions	Fritz (2000)
Pseudostaurosira		
<i>brevistriata</i> (Grunow)		
Williams & Round 1987	Facultative planktonic disturbed environments	
Staurosira construens var.	Facultative planktonic, disturbed environments,	Battarbee et al. (2001);
<i>venter</i> (Ehrenberg)	initiability sediment surfaces and/or the base of	Anderson (2000); Sayer
Hamilton 1992	emergent macrophytes, cold waters and lake ice	(2001); Schmidt et al. (2004)
Staurosirella pinnata	cover	
(Ehrenberg) Williams &		
Round 1987		
Aulacoseira granulata		
(Ehrenberg) Simonsen	Planktonic and deep, eutrophic and turbid,	
1979	mixing and turbulent (larger and	
Stephanodiscus medius	heavily-silicified planktonic diatoms sink rapidly	Bennion (1995); Bennion et
Håkansson 1986	in the absence of mixing, even in a deep lake	al. (2010); Wolin and Stone
Stephanodiscus hantzschii	with a long settling distance, and in a shallow	(2010)
Grunow 1984	lake there is insufficient mixing to suspend	
Cyclostephanos dubius	these taxa for long growth periods)	
(Fricke) Round 1982		
Cyclotella fottii Hustedt	Endemic, hypolimnetic, oligothermic and	Stanković (1060)
1942	oligophotic	Stalikovic (1960)
Cuclotalla acallata	Epilimpotic ouruthormic oligotrophisto	Stanković (1960); Wagner et
Cyclotella ocellata	epinimietic, eurythermic, oligotrophic to	al. (2009); Lorenschat et al.
Pantocsek 1902	mesotrophic	(2014)
Stephanodiscus		Stanković (1960): Wagner et
transylvanicus Pantocsek	Hypolimnetic, mesotrophic	al (2000): Pood at al (2010)
1892		ai. (2009), Reeu et al. (2010)
		Krammer and
Cyclotella iris Brun &	Fossil hypolimpetic oligotrophic	Lange-Bertalot (1991a);
Héribaud 1893		Houk et al. (2010); Wagner
		et al. (2014)

 Table 1.1 Ecological and environmental preferences for main diatom species in the thesis.

Small-sized planktonic	High surface area to volume ratios, low nutrient	Winder et al. (2009); Finkel
	and light availability, low sinking velocities (high	et al. (2009); Catalan et al.
ulatori species	stratification and shallow mixing)	(2013)

1.3 The importance of deep, ancient lakes in palaeoclimate research

Deep, ancient lakes are of global importance for palaeoclimate research, as they are situated within active graben basins and contain long, continuous sedimentary records spanning the Quaternary, such as Lake Baikal (Williams et al., 2001) and Lake Malawi (Scholz et al., 2011); they are also of great potential for evolutionary studies, as they are renowned as hotspots of biodiversity with very high levels of endemism (Albrecht and Wilke, 2008; Cohen, 2012). In these lakes, diatom records provide powerful insights into mechanisms of environmental change over glacial–interglacial timescales, and also provide useful insights into biodiversity, endemism and evolution of diatoms over long timescales (Mackay et al., 2010). Thus, long-term palaeoclimate reconstruction and evolutionary processes draw much attention to the study of deep, ancient lakes. In the long diatom records from deep, ancient lakes, ecological and limnological interpretations of shifts in planktonic diatom composition and relative abundance are challenging and complex (Mackay et al., 2010), while shifts in biogenic silica content and absolute diatom concentration are related to changes of overall in-lake productivity (Mackay, 2007) as a result of the domination of open-water planktonic taxa.

Across the Mediterranean, only one long pollen record at Tenaghi Philippon (northeastern Greece) provides the opportunity to date to examine the response of vegetation change to glacial–interglacial cycles during the past more than one million years (Tzedakis et al., 2006). Lake Ohrid (Macedonia/Albania) is a rare example of a deep, ancient lake across the Mediterranean, and compared to well-studied Lake Baikal that spans a distinct climate gradient of over 4° latitude and that possesses a vast catchment of several vegetation zones (Mackay et al., 2002), Lake Ohrid, due to its small size, is a key site for studying past climate change in the northeastern Mediterranean. Lake Ohrid is probably the most diverse lake in the world taking surface area into account (Albrecht and Wilke 2008). Compared to Lake

Baikal, whose complex lake morphology and heterogenous sedimentary environments cause spatial variability of diatom distributions (Mackay et al., 2003b, 2006), Lake Ohrid has a very simple, tub-shaped morphology and is therefore an excellent archive to test the response of diatoms in deep, ancient lakes to long-term climate and limnological change. Previous research has focused on the response to the last glacial-interglacial cycle (Reed et al., 2010) and future planned research will focus on glacial-interglacial cycles over the last more than one million years (Wagner et al., 2014), but Holocene diatom response in Lake Ohrid is still worth investigating, which offers potential both to examine the hypothesis of diatom response to temperature-induced productivity (Reed et al., 2010) and to assess the influence of human activity. During previous two low-resolution analyses of diatoms, the Lateglacial and early-Holocene sedimentation is absent in core Lz1120 (southeastern Lake Ohrid) (Wagner et al., 2009) and the early-Holocene climatic signal is most likely compromised in core Co1202 (northeastern Lake Ohrid) (Reed et al., 2010), and high-resolution analysis of the Holocene has not yet been achieved. A new core Co1262 (western Lake Ohrid) has a 150 cm-longer Holocene sedimentary record than the DEEP core (central Lake Ohrid) and thus offers the greatest potential for high-resolution diatom analysis of all the sediment cores retrieved to date (Table 1.2). Moreover, compared to significant shifts of diatoms in shallow Lake Dojran (Macedonia/Greece) in response to changes in lake level and trophic status during the Lateglacial and Holocene in the northeastern Mediterranean (Zhang et al., 2014), Holocene diatom behaviour in deep, ancient Lake Ohrid is valuable to be assessed in detail.

1.4 Aims

The thesis has a primary focus on diatom-based Quaternary palaeoclimate reconstruction in the northeastern Mediterranean. It also addresses issues of human impact on the natural environment during the late Quaternary. The research links to the major International Continental Scientific Drilling Program (ICDP) project SCOPSCO (Scientific Collaboration on Past Speciation Conditions in Lake Ohrid) and associated studies of Lakes Dojran and Prespa in Macedonia/Albania/Greece. It thus benefits from considerable multi-proxy data generated from palaeolimnological research by collaborators in Germany and other European states.

The primary aims of past climate and environmental change in the thesis are threefold: 1) to improve understanding of Holocene climate change in the northeastern Mediterranean which is a region still poorly understood; 2) to test whether accelerated human impact in the recent past threatens the high conservation status of Balkan lakes; and 3) to generate a preliminary >1.2 Ma diatom record from a deep, ancient Balkan lake. An overall aim of diatom research is to test diatom response to climate and environmental change in contrasting types of lakes but also at different timescales in a deep, ancient Balkan lake.

1.5 Objectives

- 1. Diatom-based Lateglacial and Holocene climate and environmental reconstruction in shallow, currently eutrophic Lake Dojran (Macedonia/Greece): this study uses diatoms as a strong proxy for lake levels and trophic status to strengthen previous interpretation based on sedimentological and geochemical data from core Co1260 (spanning the past ca. 12,500 years) (Table 1.2; Francke et al., 2013). In interpretation of Holocene limnological change in terms of palaeoclimate shifts versus the influence of local catchment dynamics, this study exploits extant regional palynological data for vegetation change, comprising late-Holocene pollen data from a separate littoral Dojran sequence (Athanasiadis et al., 2000) and chronologically-robust Holocene pollen data from the highlands (in southwestern Bulgaria) and lowlands (in northern Aegean Sea) (Kotthoff et al., 2008a; Tonkov et al., 2008, 2013). Adopting a novel approach, the importance of seasonality in driving Holocene climate change is assessed by reference to the summer and winter latitudinal temperature gradient (LTG) model (Davis and Brewer, 2009), which incorporates variation in the Subtropical High pressure and Arctic Oscillation (AO). This study also compares with various hydroclimatic proxy data from the Balkans, Italy and Anatolia.
- Diatom response to Lateglacial and Holocene climate and environmental change in deep, highly oligotrophic Lake Ohrid (Macedonia/Albania): this study uses the relative abundance and absolute concentration data of planktonic diatom taxa from core 1262

(spanning the past ca. 12,300 years) in western Lake Ohrid (near the Lini Peninsula) to test diatom response to Holocene climate, environmental and limnological change, and compares with sedimentological and geochemical data from the same core (Table 1.2; Lacey et al., 2014). This study also compares with extant low-resolution diatom data from cores Lz1120 (southeastern Lake Ohrid; Wagner et al., 2009) and Co1202 (northeastern Lake Ohrid; Reed et al., 2010), and catchment vegetation change from pollen records in core Lz1120 (Wagner et al., 2009) and hydraulically-linked Lake Prespa core Co1215 (Aufgebauer et al., 2012; Panagiotopoulos et al., 2012).

- 3. Recent anthropogenic impact on Lakes Dojran and Ohrid: this study uses diatoms from a short sediment core Sv09 (spanning the last ca. 60 years) near Sveti Naum springs in southeastern Lake Ohrid and compares with ostracod data from the same core (Table 1.2; Lorenschat et al., 2014) to assess the influence of nutrient supply through springs from Lake Prespa on changes of productivity in the southeastern part of Lake Ohrid. This study also compares with monitoring data for water-level change in Lake Prespa (Popovska and Bonacci, 2007; Popovska, 2011) and its eutrophication due to human activity. In Lake Dojran, this study combines diatom and pigment data from the top 55 cm section (spanning the past ca. 480 years) of core Co1260 to assess changes of productivity in Lake Dojran under the influence of human activity, and takes into consideration human-induced Dojran lake-level changes (Stojov, 2012) and anthropogenic deforestation in the catchment (Athanasiadis et al., 2000).
- 4. Diatom response to glacial-interglacial cycles during the past more than one million years in Lake Ohrid: this study uses the preliminary diatom data from core catcher samples in the DEEP site Hole 1B and compares with shifts of total inorganic matter (TIC) content and borehole logging spectral gamma ray data (Table 1.2; Wagner et al., 2014) to generate a preliminary interpretation of diatom response to glacial-interglacial climate change on an orbital timescale.

Core code	Core code Core length Age Water depth		Water depth	Proxies and existing papers
				sedimentological and geochemical proxies,
Dojran Co1260*	717 cm	ca. 12,500 a	6.7 m	isotopes (Francke et al., 2013), diatoms
				(Zhang et al., 2014)
Doirani-1/2	550 cm	ca. 5,000 a	littoral (0 m)	pollen (Athanasiadis et al., 2000)
Doiran DOI978	47 cm	unknown	4 m	organic matter, carbonate, diatoms, ostracod
	47 CIII	unknown	4 111	and isotopes (Griffiths et al., 2002)
Obrid Core 9	8 850 cm	ca 30.000 a	210 m	organic matter, carbonate and diatoms
	8,850 cm	ca. 50,000 a	210111	(Roelofs and Kilham, 1983)
				sedimentological and geochemical proxies,
Ohrid Lz1120	1,075 cm	ca. 39,500 a	105 m	diatoms, ostracod and pollen (Wagner et al.,
				2009), isotopes (Leng et al., 2010)
				sedimentological and geochemical proxies
Ohrid Co1202	1,494 cm	ca. 136,000 a	145 m	(Vogel et al., 2009), diatoms (Reed et al.,
				2010), isotopes (Leng et al., 2010)
				sedimentological and geochemical proxies,
Ohrid Co1262*	1,006 cm	ca. 12,300 a	260 m	isotopes (Wagner et al., 2014a; Lacey et al.,
				2014)
				sedimentological and geochemical proxies,
Ohrid Sv09*	33 cm	ca. 60 a	50 m	diatoms and ostracod (Lorenschat et al.,
				2014)
Obrid St00	40 cm	co. 00 o	F0 m	sedimentological and geochemical proxies,
Onna Sto9	49 011	Ca. 90 a	50 M	ostracod (Lorenschat et al., 2014)
	maximum			organic matter carbonate magnetic
	drilling			organic matter, carbonate, magnetic
Ohrid DEEP*	depth: 569	>1.36 Ma	243 m	susceptibility, borenoie logging spectral
	m; field core			gamma ray data and diatoms (wagner et al.,
	depth: 545 m			2014)
				sedimentological and geochemical proxies
Prespa Co1204	1,050 cm	ca. 48,000 a	14 m	(Wagner et al., 2010), isotopes (Leng et al.,
				2010)
-				sedimentological and geochemical proxies,
				pollen (Aufgebauer et al., 2012;
Prespa Co1215	1,776 cm	ca. 92,000 a	14.5 m	Panagiotopoulos et al., 2013, 2014), isotopes
·				(Leng et al., 2013), diatoms (Cvetkoska et al.,
				2014a, 2015)

Table 1.2 Summary of existing sediment cores in Lakes Dojran, Ohrid and Prespa. * indicatescores analysed for diatoms in this study.

1.6 Structure of the thesis

The details of the study sites are presented in Chapter 2. Chapter 3 is the field and laboratory methodologies, including core recovery, diatom analysis, pigment analysis, and chronologies.

Chapter 4 is the Lateglacial and Holocene climate and environmental change in Lake Dojran, which is published in *Quaternary Science Reviews* (Zhang et al., 2014; see Appendix 1). This chapter also incorporates unpublished pigment-inferred recent change in Lake Dojran. Chapter 5 focuses on the high-resolution analysis of Lateglacial and Holocene climate and environmental change in Lake Ohrid, including comparisons with existing sediment cores in Lakes Ohrid and Prespa. This study is in preparation for submission to a special issue 'Integrated perspectives on biological and geological dynamics in ancient Lake Ohrid' of Biogeosciences. Chapter 6 is the study of recent anthropogenic impact on southeastern Lake Ohrid near Sveti Naum springs, which is published in Journal of Paleolimnology (Lorenschat et al., 2014; see Appendix 2). Chapter 7 presents the preliminary results of diatom response to glacial-interglacial cycles during the past more than one million years in the DEEP site Hole 1B of Lake Ohrid, and the parallel Hole 1C is published in *Scientific Drilling* (Wagner et al., 2014; see Appendix 3). Since most of the data are already published, the main interpretative discussions of each study are also incorporated in the relevant chapters (Chapter 4–7) rather than in the final discussion section. Chapter 8 is the final discussion linked to the aims of this study and the directions for future research. It includes a synthesis of the data from the two study sites, focusing on comparison and discussion of Holocene diatom response in the two contrasting types of lakes, on their recent conservation status and on discussion of directions for future research on the Quaternary Ohrid DEEP sequence. The conclusions are presented in Chapter 9.

Chapter 2 Study region and sites

2.1 The geological and climatological settings of the northeastern

Mediterranean region

The Mediterranean region has a long geological history with complex horizontal and vertical crustal movements since the Mesozoic (ca. 250 Ma). The Mediterranean Sea was generated from the former Tethys Ocean through the convergence and collision between the African and European tectonic plates. The leading edge of the African plate was subducted under the European plate and split the edge of the European plate into small islands and peninsulas (Reed et al., 2004). The current topography of the Mediterranean was formed by Tertiary Alpine orogenic activity, which, in the northeastern Mediterranean region, generated the mountain chain of the Dinarides in the western Balkans (along the coast of the Adriatic Sea), Pindus Mountains in western Greece (along the coast of the Ionian Sea), Mountains of Crete, and Taurus Mountains in southern Turkey (along the Mediterranean coast) during the Eocene (ca. 45 Ma) (Fig. 2.1; Reed et al., 2004; Mather, 2009). Later on during the Oligocene and Miocene (ca. 30–10 Ma), the ongoing motion of continental plates and microplates in this region generated the mountain chain of the Carpathians in Romania, Balkan Mountains in Bulgaria, and Pontic Mountains in northern Turkey (along the southern coast of Black Sea); the Apennines also developed at this time (Fig. 2.1; Reed et al., 2004; Mather, 2009). During the late Miocene (ca. 6.3–5.5 Ma), the closure of the Betic (southern Spain)–Rif (northern Morocco) Corridors and the opening of the Gibraltar Straits caused the isolation of the Mediterranean Sea from the Atlantic Ocean, resulting in the phase of strong evaporative concentration and desiccation termed the Messinian Salinity Crisis (Rouchy and Caruso, 2006), which had profound impacts on the climatology and ecology of the region (Reed et al., 2004; Mather, 2009). The Quaternary has been characterised by active seismic and volcanic activity, resulting in the formation of deep, volcanic crater lakes in Italy and Turkey in particular. Most lakes in this region are linked to tectonism in origin, and tectonic-karstic lakes are particularly common in the southern Balkan region (Roberts and Reed, 2009), including the study sites for this study, Lakes Ohrid and Dojran (Fig. 2.1).



Fig. 2.1 The northeastern Mediterranean region with main orogenic mountain chains and study sites Lakes Ohrid and Dojran.

The Mediterranean region is a primary global climate response hotspot (Giorgi, 2006) and a hotspot of biodiversity (Myers et al., 2000; Mittermeier et al., 2004). It is a transitional zone climatically influenced both by the mid-latitude westerlies and the Subtropical High pressure (anticyclone) belt, with the North Atlantic Oscillation (NAO) modulating winter precipitation and the migration of the Intertropical Convergence Zone (ITCZ) affecting summer drought (Lionello et al., 2006). It stretches longitudinally from the North Atlantic Ocean to continental Eurasia. It has a diversity of landscapes linked to spatial and altitudinal variation in climatic factors. Although winters are mild, wet and summers are hot, dry across the Mediterranean, the northeastern Mediterranean region is drier than the western Mediterranean region, and the southeastern Mediterranean region is arid. Precipitation decreases and temperatures become more extreme towards the south and east and from highlands to the coast (Harding et al., 2009). In the Balkan region, three main climate zones are defined (Furlan, 1977; Reed et al., 2004): the northern lowlands are open to central and eastern Europe under the influence of a continental climate with cold, dry winters and warm, wet summers; the mountainous regions have an alpine climate with altitudinal shifts in precipitation and temperature; and the southern lowlands, coastal regions and islands enjoy a typical Mediterranean climate, such as the basin of Lake Dojran. Lake Ohrid is influenced by both Mediterranean and continental climates (Watzin et al., 2002). Precipitation in the Balkans is

dictated largely by the presence of mountain chains, with major differences between western and eastern coasts and between lowlands and mountains (Furlan, 1977; Reed et al., 2004).

2.2 Lake Dojran

Lake Dojran (or Doirani) (41°12'N, 22°44'E, 144 m a.s.l.), a transboundary lake between Republic of Macedonia and Greece, sits within a karstic basin formed by a combination of Tertiary volcanic and tectonic activity, and the catchment sediments are largely composed of Quaternary alluvial and limnetic materials (Sotiria and Petkovski, 2004). In the catchment, the highland to the north is close to the Pirin and Rila Mountains in southwestern Bulgaria, and the lowland to the south is open to the Thessaloniki Plain and northern Aegean Sea (Fig. 2.2). The lake basin is surrounded by the Belasica (or Belles, Kerkini) Mountain (1847 m a.s.l.) to the north, the Kroussia (or Krusa, Dysoron) Mountain (766 m a.s.l.) to the east, the Boskija (or Boska) Mountain (714 m a.s.l.) to the northwest, and the Dab Mountain (689 m a.s.l.) to the southwest (Fig. 2.3; Sotiria and Petkovski, 2004). The lake is fed by small rivers, creeks and springs, with most of the runoff originating from the Belasica Mountain. Water loss is currently through evaporation and probably groundwater outflow, but during previous phases of high lake level, surface outflow was possible at the southern end of the lake through the Doiranity (or Ayiak) River, which drained into the Vardar (or Axios) River and then into the Aegean Sea (Sotiria and Petkovski, 2004). The lake water is essentially fresh (see below), suggesting groundwater throughflow in karstic aquifers. This is supported by hydrogeological investigations (Sotiria and Petkovski, 2004).



Fig. 2.2 The southern Balkan region of Macedonia, northern Greece and southwestern Bulgaria.



Fig. 2.3 The catchment of Lake Dojran and the coring sites Co1260 (this study; Francke et al., 2013) and Doirani-1/2 (Athanasiadis et al., 2000).

The local climate regime is a hot, dry summer (June–September) and mild, humid winter (November–February) (Table 2.1; Sotiria and Petkovski, 2004). In the lowlands of the catchment evergreen (*Quercus coccifera* L.) and deciduous oaks (*Q. pubescens* Willd., *Q. frainetto* Ten. and *Q. dalechampii* Ten.) are the dominant trees, and at higher altitudes

(>1000 m a.s.l.) beech forest (Fagus moesiaca Cz. and F. orientalis Lipsky) is dominant with a few scattered fir stands (Abies borisii-regis Mattf.) (Athanasiadis et al., 2000). The vegetation around the lake has been highly affected by human activity and agriculture is currently well developed. Reed beds occupy the fringe of the lake, and submerged plants are common in the littoral zone. Changes in the planktonic and periphytic microflora (including diatoms, chlorophytes, cyanobacteria, and dinoflagellates) indicate recent accelerated eutrophication and algal blooms (Griffiths et al., 2002; Levkov and Stojanovski, 2002; Sotiria and Petkovski, 2004). Recorded maximum lake level ranged from 7.9 to 10.0 m in 1951–1987, declined to 3.7 m in 2002 due to water abstraction practices and more intensive agriculture (Griffiths et al., 2002), and recovered to 6.7 m in 2010 due to an increase in rainfall, decrease in water use and additional water transfer from the Gjavato wells into the lake (Popovska and Bonacci, 2008; Stojov, 2012). Total phosphorus concentration ranged between 15–130 μ g l⁻¹ in 1953–1960 (Sotiria and Petkovski, 2004), with consistently higher minimum values of >50 µg I⁻¹ (eutrophic; Table 2.2; OECD, 1982) reported since 1996 and an occasional hypereutrophic state (Temponeras et al., 2000; Lokoska et al., 2006; Tasevska et al., 2010). Conductivity ranged from 0.4 to 0.6 mS cm⁻¹ in 1974–1988, increased to 1.5 mS cm⁻¹ in 2002 (Sotiria and Petkovski, 2004), and declined to 0.8 mS cm⁻¹ in 2010 (Lešoski et al., 2010). This is within the freshwater range of eutrophic lake water. Ionic concentration may be influenced slightly by mineral-rich spring input; some springs are of high conductivity (Levkov, unpublished data), but others are extremely fresh (33 μ S cm⁻¹; Griffiths et al., 2002). Dominance by fresh spring inflow is consistent with low δ^{13} C data of total dissolved inorganic carbon (-7.9 to -13.0 ‰ VPDB) in springs (Griffiths et al. 2002; Francke et al., 2013), suggesting that the effect of the karstic catchment is minor (Leng and Marshall, 2004) and the groundwater influence on lake-water conductivity and salinity is insignificant. Lake Dojran is shallow and monomictic, and has a very simple, flat-bottomed morphometry (Francke et al., 2013), suggesting that moisture balance and water chemistry are sensitive to and possibly respond linearly to climate and environmental change (Gasse et al., 1997; Fritz, 2008).

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Precipitation (mm)	44.1	53.0	52.5	53.5	58.1	44.1	35.7	34.5	32.0	54.6	85.5	64.5
Temperature (°C)	3.7	5.4	8.3	13.1	18.1	22.5	24.9	24.5	20.7	15.3	9.6	5.3

Table 2.1 Average monthly precipitation and mean air temperature at Nov Dojran station for the period between 1961–2000 (Sotiria and Petkovski, 2004).

Table 2.2 Trophic categories of lakes (OECD, 1982).

Trophic status	TP (μg l ⁻¹)
Hypereutrophic	>100
Eutrophic	35-100
Mesotrophic	10-35
Oligotrophic	4-10
Ultra-oligotrophic	<4

2.3 Lake Ohrid and its sister Lake Prespa

Lake Ohrid (693 m a.s.l., Macedonia/Albania) is an ancient graben lake with a long, continuous sediment record of more than 1.2 million years in age (Wagner et al., 2014). The lake basin has a relatively simple morphology with a deep flat central basin (maximum water depth 293 m, Wagner et al., 2012a), steep slopes along the western and eastern sides, and less inclined shelves in the northern and southern parts. Geological and topographical formations around the lake comprise Palaeozoic metamorphics to the northeast, karstified Triassic limestones of the Galicica Mountain (2256 m a.s.l.) and Mali i Thate Mountain (2276 m a.s.l.) to the east and southeast and of the Jablanica Mountain (2225 m a.s.l.) to the northwest, Jurassic ophiolites of the Mokra Mountain (1512 m a.s.l.) to the west (south of the Lini Peninsula), Tertiary molasse deposits to the southwest and south, and Quaternary fluvio-lacustrine deposits in the Struga, Ohrid and Starovo plains to the north, northeast and south, respectively (Stanković, 1960; Watzin et al., 2002; Hoffmann et al., 2010; Reicherter et al., 2011). The local climate belongs to the Mediterranean regime with minimum precipitation occurring in July and August (Table 2.3), and it is also influenced by the continental regime as it is surrounded by high mountains (Watzin et al., 2002). The vegetation in the catchment is distributed mainly in altitudinal belts as, in ascending order, mixed deciduous oak forest, beech forest, coniferous forest, and subalpine and alpine meadows (Lézine et al., 2010; Panagiotopoulos et al., 2013). Agricultural activities are widely

distributed in the Struga, Ohrid and Starovo plains around Lake Ohrid (Vogel et al., 2010).

Table 2.3 Average monthly precipitation and mean air temperature at Pogradec station for the period between 1961–1990 (Watzin et al., 2002).

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Precipitation (mm)	77.1	73.5	67.3	57.7	61.5	34.1	27.5	32.0	43.1	75.7	103.8	94.5
Temperature (°C)	2.1	3.2	6.0	10.3	14.8	18.4	20.8	20.6	17.4	12.6	9.7	3.9

Lake Ohrid has a very unusual hydrology in that it is fed mainly by karstic springs (53%, including 27% surface springs and 26% sublacustrine springs), with 23% of water input from direct precipitation on the lake surface and 24% from river inflow, mainly via the Sateska, Koselska, Velgoska, Cerava, Pogradec and Verdova Rivers. Direct outflow is via the Crni Drim River (66%), with 34% evaporative loss (Matzinger et al., 2006a). The largest surface springs are those of the Sveti Naum and Zagorican/Tushemisht springs at the southeastern edge of the lake, with two smaller ones comprising the Biljana and Bej Bunar springs in the northeastern region and the Dobra Voda and Sum springs in the northwest (Albrecht and Wilke, 2008). Sublacustrine springs are located mainly on the eastern shore of the lake (Fig. 2.4), and around five major zones of subaquatic inflows are known: Kaneo, Elešec, Velidab, Sveti Naum, and Kališta (Matter et al., 2010). The most important source of karstic springs is the Lake Prespa underground outflow, which provides 20% of the Lake Ohrid water inflow (Matzinger et al., 2006b). The karst aquifers are also charged by the infiltration of precipitation on the Galicica and Mali i Thate Mountains. The Sateska River was artificially diverted into the lake from the north in 1962, and it was a tributary of Lake Ohrid even before flowing directly into the Crni Drim River (Jordanoski et al., 2006). There is no water inflow close to the Lini Peninsula. The top 150 to 200 m of the water column is mixed every winter (a meromictic lake), and a complete circulation of the entire water column occurs roughly every seventh winter (an oligomictic lake; Stanković, 1960; Matzinger et al., 2006a). Northerly and southerly winds prevail, and an anticlockwise current down to the depth of 50 m due to the Ekman spiral effect brings the downwelling of warm surface waters near the shore and the upwelling in the center of the lake (Stanković, 1960; Matzinger et al., 2006a). Lake Ohrid is highly oligotrophic with an average pelagic total phosphorus (TP) concentration

of 4.6 μ g l⁻¹ in 2002–2004 (Matzinger et al., 2006a) and 6.0 μ g l⁻¹ in 2013–2014 (Veljanoska-Sarafiloska, 2014) and an average littoral TP concentration of 7.2 μ g l⁻¹ measured in 2009–2010 (Schneider et al., 2014), although average TP concentrations of surface springs in 2005–2008 (Jordanoska et al., 2012) and rivers in 1999–2000 (Patceva et al., 2004) and 2013–2014 (Veljanoska-Sarafiloska, 2014) were greater than 10.0 μ g l⁻¹.



Fig. 2.4 The catchment of Lake Ohrid and the coring sites Co1262 (this study; Wagner et al., 2012a; Lacey et al., 2014), Lz1120 (Wagner et al., 2009), Co1202 (Vogel et al., 2010; Reed et al., 2010), Co1204 (Wagner et al., 2010), Co1215 (Aufgebauer et al., 2012; Panagiotopoulos et al., 2012; Cvetkoska et al., 2014), Sv09 (this study; Lorenschat et al., 2014), St09 (Lorenschat et al., 2014), and DEEP site (this study; Wagner et al., 2014).

Since Lake Ohrid is hydraulically connected to Lake Prespa, it is appropriate to incorporate Lake Prespa's limnological characteristics. Lake Prespa (849 m a.s.l.,

Macedonia/Albania/Greece) is 156 m higher in altitude than Lake Ohrid and is located 10 km to the southeast, on the other side of the Galicica Mountain. Lake Prespa is also a tectonic basin, which may be of great age but is much shallower than Lake Ohrid. It is mostly
shallower than 30 m with a few local deeper holes (Matzinger et al., 2006b), and the maximum water depth is 58 m (Albrecht and Wilke, 2008). The lake basin is surrounded by Palaeozoic metamorphics of the Baba Mountain (2587 m a.s.l.) to the east, Triassic limestones of the Galicica and Mali i Thate Mountains to the west and northwest as well as limestones to the south, and Quaternary sediments to the north (Aufgebauer et al., 2012; Albrecht et al., 2012). Lake Prespa is fed by river inflow (56%, mainly comprising the Golema, Kranska, Brajcinska and Agios Germanos Rivers), direct precipitation (35%) and inflow from Lake Mikro Prespa (9%). Natural water loss is through evaporation (53%) and underground outflow (47%) that drains almost entirely through the karst aquifers into Lake Ohrid (Matzinger et al., 2006b). A drastic lake-level decline of 5–6 m occurred between 1987–1995 due to water abstraction and irrigation practices (Popovska and Bonacci, 2007). The water column is mixed completely from autumn to spring (a monomictic lake; Matzinger et al., 2006b), and an anticlockwise surface current exists in the northern part (Wagner et al., 2012b). The lake water average TP concentration was 18 μ g l⁻¹ in 1992, 34 μ g l⁻¹ in 2001–2003 (Patceva et al., 2006; Matzinger et al., 2006b), 58 μ g l⁻¹ in 2007–2008 (Jordanoski and Veljanoska-Sarafiloska, 2009), and 45 μ g Γ^1 in 2013–2014 (Veljanoska-Sarafiloska, 2014), indicating that Lake Prespa is currently in a meso-eutrophic state. The aquifer is a filter for phosphorus transport to Lake Ohrid and retains 65% of the TP from Lake Prespa, but there are still concerns that Lake Prespa may become a cause of accelerated eutrophication in Lake Ohrid (Matzinger et al., 2006b).

Chapter 3 Methodology

For clarity, a brief summary of the codes and characteristics of lake sediment cores analysed in this study is presented in Table 3.1.

Core code	Core length	Water depth
Dojran Co1260	717 cm	6.7 m
Ohrid Co1262	1006 cm	260 m
Ohrid Sv09	33 cm	50 m
Ohrid DEEP	569 m	243 m

Table 3.1 Summary of Lakes Dojran and Ohrid cores analysed for diatoms in this study.

3.1 Field methods

3.1.1 Lake Dojran core Co1260

In June 2011, following a detailed hydro-acoustic survey to assess lake bathymetry and sediment architecture, a 717 cm-long core Co1260 was recovered by B. Wagner and colleagues (Cologne) from the deepest (6.7 m water depth), south-central part of Lake Dojran using UWITEC gravity and piston coring equipments operated from a floating platform (www.uwitec.at). After recovery, the overlapping 300 cm-long sediment cores were cut into up to 100 cm-long sections, and core catcher samples were transferred at 2 cm resolution into plastic vials. They were stored in darkness at 4 °C.

3.1.2 Lake Ohrid 'Lini' core Co1262

Based on detailed hydro-acoustic surveys carried out between 2004 and 2009, a 1006 cm-long core Co1262 was recovered from 260 m water depth in front of the Lini Peninsula at the western margin of Lake Ohrid in June 2011, using UWITEC gravity and piston coring equipments from a floating platform (www.uwitec.at) by B. Wagner and colleagues (Cologne). After recovery, the individual 200 cm-long sediment cores were cut into ca. 100 cm-long sections and stored in the dark at 4 °C. Not taking into account a 200 cm-thick mass wasting deposit revealed by multichannel seismic data and parametric sediment echosounder data, and three small mass wasting deposits indicated by coarse grain size composition and low water content (Wagner et al., 2012a), the composite undisturbed sediment sequence is 785

cm long.

3.1.3 Lake Ohrid 'Sveti Naum' core Sv09

In September 2009, three parallel 33 cm-long cores Sv09 (36 cm apart) were collected from 50 m water depth near Sveti Naum springs in the southeastern tip of Lake Ohrid using a UWITEC gravity multicorer from a boat, by A. Schwalb and colleagues (Braunschweig). One core was subsampled for dating, one core was split into two halves for sediment description and photography, and the other core was extruded and subsampled at 1 cm intervals in the field for diatom, ostracod and geochemical analysis. Samples were stored at 4 °C.

3.1.4 Lake Ohrid DEEP site

The selection of the DEEP site to provide a high-resolution, continuous Quaternary sediment sequence from Lake Ohrid was based on a dense grid of multichannel seismic data and sediment echosounder data collected between 2004-2009 by B. Wagner and colleagues (Cologne). The DEEP Site is in a basement depression with maximum onlap fills and undisturbed sediments, located at 243 m water depth in the central basin of Lake Ohrid. Drilling was carried out in April and May 2013 by DOSECC (Drilling, Observation and Sampling of the Earths Continental Crust) using the Deep Lake Drilling System (DLDS; Fig. 3.1) with a hydraulic piston corer for upper sediments and rotation drill tools for deeper, harder sediments. Four parallel holes (1B, 1C, 1D and 1F) were drilled with a maximum drill depth of 569 m below the lake floor, and the composite field recovery is 545 m. After recovery, 300 cm-long cores were cut into ca. 100 cm-long sections on the barge (Fig. 3.2). Core catcher samples from the base of each core were collected in plastic bags, and stored in darkness at 4 °C. After drilling of each hole, borehole logging was carried out through the drill pipe at 10 cm vertical resolution.



Fig. 3.1 The barge of the Deep Lake Drilling System, DOSECC.



Fig. 3.2 The core cutting facilities on the barge.

3.2 Laboratory methods

3.2.1 Diatom analysis

For Lake Dojran core Co1260, the core sections were split into two halves in the laboratory in Cologne. One half was sealed airtight for archiving, and the other half was subsampled at 2 cm resolution and half of each sample was then freeze-dried. Sedimentological and geochemical analysis was carried out by A. Francke (Cologne; Francke et al., 2013), isotope

analysis was carried out by M.J. Leng (NIGL; Francke et al., 2013), and diatom analysis forms the focus for this study (Hull; Zhang et al., 2014). Techniques used to establish the chronology of this and other core sequences are explained below (Section 3.2.3). Diatom analysis was carried out on 107 subsamples, taken at 8 cm intervals but at a higher resolution of 4 cm for important phases comprising the bottom 30 cm, the 50 cm between ca. 11,800–11,400 cal yr BP, the 20 cm around ca. 8,200 cal yr BP, and the top 60 cm. The age resolution is ca. 70–150 years, except the top and bottom sections (ca. 30–40 years) and the middle section (ca. 200–500 years). The low age resolution between ca. 8,000–4,000 cal yr BP is correlated with low sediment accumulation rate indicated by the age model, and with a stable environment indicated by sedimentological and geochemical data (Francke et al., 2013).

For Lake Ohrid 'Lini' core Co1262, the core sections were split into two halves in the laboratory in Cologne, and one half was subsampled at 2 cm resolution and then freeze-dried. Sedimentological and geochemical analysis was carried out by A. Francke and B. Wagner (Cologne; Wagner et al., 2012a), isotope analysis was carried out by J.H. Lacey and M.J. Leng (NIGL and Nottingham; Lacey et al., 2014), and diatom analysis forms the focus for this study (Hull). Diatom analysis was carried out on 104 samples in the composite undisturbed sequence, taken every 8 cm but at a higher resolution of 4 cm around putative abrupt events at ca. 8,200 and 4,200 cal yr BP. The age resolution is ca. 80–110 years for the top 120 cm above the major mass wasting deposit, ca. 40–70 years between 120–240 cm (ca. 1,400–2,200 cal yr BP), ca. 100–200 years between 240–350 cm (ca. 2,200–4,400 cal yr BP), ca. 270–350 years for the middle section (350–435 cm, ca. 4,400–7,800 cal yr BP), and ca. 90–120 years for the lower part of the sequence. The low age resolution in the middle section is correlated with a stable environment indicated by sedimentological and geochemical data (Lacey et al., 2014). Two samples from the major mass wasting deposit were also analysed to examine the influence of mass movement on diatom preservation and composition.

For Lake Ohrid 'Sveti Naum' core Sv09, wet sediment subsamples were shipped to Hull for

laboratory preparation of diatom slides. Ostracod and geochemical analysis was carried out by J. Lorenschat (Braunschweig; Lorenschat et al., 2014), and diatom analysis forms the focus for this study (Hull; Lorenschat et al., 2014). Diatom analysis was based on 32 sediment samples taken at 1 cm resolution throughout.

In Lake Ohrid DEEP site Hole 1B, total organic carbon (TOC), total inorganic carbon (TIC), and carbonate stable isotopes ($\delta^{18}O_{carb}$ and $\delta^{13}C_{carb}$) were analysed on core catcher samples by J.H. Lacey and M.J. Leng (NIGL and Nottingham; Wagner et al., 2014). Magnetic susceptibility was measured on all cores by the SCOPSCO team members at 2 cm intervals on a multi-sensor core logger (MSCL) equipped with a whole core loop sensor (Wagner et al., 2014). Preliminary diatom screening on smear slides was made for two of the holes, which were analysed for diatom preservation and taxonomy while in the field in Ohrid. DEEP site Hole 1B forms the focus of this study, based on analysis of 177 core catcher samples (including the bottom 20 samples with no diatoms observed) at an approximate resolution of 3 m. Hole 1C was analysed separately by the Macedonian team, mainly comprising Z. Levkov and A. Cvetkoska (Skopje; Wagner et al., 2014), achieving strong taxonomic harmonization by working closely together. Smear slides were prepared by J. Diederich (Cologne), by adding a smear of wet sediment on a microscope slide and adding a cover slip. Around 100 valves were counted per slide in Hole 1B at ×1600 magnification using a Carl Zeiss Jena microscope from Z. Levkov's laboratory (Skopje).

For all other diatom laboratory analyses, standard techniques were adopted for preparation of microscope slides (Battarbee et al., 2001). Approximately 0.1 g samples of freeze-dried sediment in Lake Dojran core Co1260 and Lake Ohrid 'Lini' core Co1262 were used. For the short sediment core Sv09, approximately 0.1 g equivalent dry sediment weight was calculated from data on wet weight and water content. Samples were heated in 25-30 ml 30% H₂O₂ to oxidize organic materials, and then a few drops of concentrated HCI were added to remove carbonates and remaining H₂O₂. The residue was suspended in distilled water and centrifuged, decanted and rinsed 4-5 times to wash away clay and remaining HCI. The suspension was diluted to an appropriate concentration, and known quantities of plastic

microspheres were added to allow calculation of absolute diatom valve concentration. Well-mixed diatom suspension was pipetted onto a coverslip and allowed to evaporate. Dried coverslips were mounted on slides using Naphrax[™]. Diatom valves were counted along transects at ×1000 magnification under oil immersion on an OLYMPUS BX51 light microscope. More than 500 valves per slide (at least 300 valves in core Sv09) were counted, and around 100 valves for some slides where preservation was very poor. Diatom fragments were counted when the valve centre was included, or in the case of the valve end the count was divided by two (Battarbee et al., 2001).

Diatom identification was based on a range of published literature (Krammer and Lange-Bertalot, 1986, 1988, 1991a, 1991b; Lange-Bertalot, 2001; Krammer, 2002; Levkov et al., 2007; Levkov, 2009; Houk et al., 2010, 2014; Cvetkovska et al., 2012, 2014b) and diatoms of Lake Dojran (Levkov, unpublished data), adopting the nomenclature of the Catalogue of Diatom Names (on-line version) (Fourtanier and Kociolek, 2011) with the exception of the species Cyclotella radiosa (Grunow) Lemmermann, the genus name for which should revert to Cyclotella rather than Puncticulata (Houk et al., 2010). Following current taxonomic principles, Cyclotella ocellata Pantocsek consists of various forms differentiated by the number of ocelli in the valve centre, as Juggins (2001) pointed that heterovalvar cells exist and there is little difference in their environmental preferences. Small Stephanodiscus minutulus (Kützing) Cleve & Möller and S. parvus Stoermer & Håkansson are merged into S. minutulus/parvus in eutrophic Lake Dojran, because 1) they have similar morphological features and ecological preferences, and are difficult to split consistently under light microscope (Hobbs et al., 2011; Bennion et al., 2012), and 2) S. minutulus is a polymorphic taxon, and S. parvus is considered as a synonym of S. minutulus (Scheffler and Morabito, 2003; Cruces et al., 2010). Sometimes diatoms were described as 'spp.', where identification to species level was uncertain or combination of several species at the genus or genus sensu lato level existed. Diatom percentages and concentrations were calculated and displayed using Tilia version 1.7.16, and zone boundaries were defined based on diatom percentage data according to Constrained Incremental Sum of Squares (CONISS) cluster analysis (Grimm, 2011). To assess the quality of diatom preservation and the possibility of taphonomic bias,

Ryves' F index of the endemic species *Cyclotella fottii* Hustedt in Lake Ohrid was calculated as the ratio of pristine valves to all valves (sum of pristine and dissolved valves), where F=1 indicates perfect preservation while F=0 shows that all valves are visibly dissolved (Ryves et al., 2001). The taxonomy and nomenclature of Lake Ohrid diatoms in particular is under revision; where appropriate, the most recent nomenclature used here is also adopted for taxa whose species names have changed since publication of earlier studies (e.g. Wagner et al. 2009; Reed et al. 2010).

In Lake Dojran core Co1260 and Lake Ohrid 'Lini' core Co1262, unconstrained ordination techniques were used to explore the variance in the diatom data using Canoco for Windows 4.5 (Ter Braak and Šmilauer, 2002). The largest gradient length of initial detrended correspondence analysis (DCA) was considered when deciding whether to use the linear/monotonic or unimodal ordination method. If the longest gradient is shorter than about 2 SD (standard deviation units), principal components analysis (PCA) (a linear method) makes sense; if this value is larger than about 4 SD, DCA (a unimodal method) is appropriate; and if it is about 3 SD, DCA and PCA may result in similar configurations (Ter Braak, 1995; Lepš and Šmilauer, 2003). In core Co1260, DCA gave the largest gradient length of 3.91 SD, and thus it is better than PCA. In core Co1262, DCA gave the largest gradient length of 1.85 SD, and thus PCA is appropriate. Ordination was not performed for the Sveti Naum short core Sv09 or for the DEEP Site Hole 1B preliminary analysis.

In Lake Dojran core Co1260, quantitative diatom-inferred total phosphorus (DI-TP) and conductivity (DI-Cond) reconstructions were performed based on three TP training sets (Combined TP, Swiss and Central European) and the Combined Salinity training set available within the European Diatom Database (EDDI) (Juggins, 2001), using classic weighted averaging (WA) method in C2 version 1.7.3 (Juggins, 2007). Although some potential problems have been identified with the application of DI-TP transfer functions (Bennion et al., 2001, 2010; Sayer, 2001; Hall and Smol, 2010; Juggins et al., 2013; Reavie and Edlund, 2013) and the transfer function itself (Sayer et al., 2010; Juggins, 2013), the estimated species TP optimum and tolerance data, particularly of planktonic taxa, may still be useful for the

estimation of trophic status and the interpretation of diatom composition. Among the EDDI TP transfer functions, the Swiss training set is predominantly from mesotrophic and eutrophic lakes, the Central European training set is mainly from oligotrophic and mesotrophic lakes, and the Combined TP training set spans a long nutrient gradient from oligotrophic to hypereutrophic. The merging in the Combined TP training set improves the probability of finding modern analogues, but tends to extend the apparent distribution of species unevenly along the TP gradient, which not only affects species optimum estimates but also widens species tolerance ranges and makes them poor indicators of trophic status. The previous DI-TP reconstruction based on the Central European training set from a short core suggested that Lake Dojran maintained a mesotrophic state through its recent history (Griffiths et al., 2002). Lake Dojran is currently eutrophic to occasionally hypereutrophic (Lokoska et al., 2006). Thus the Swiss training set is the most relevant to core Co1260 in terms of the TP range, although the oligotrophic and hypereutrophic states are likely to be somewhat underestimated as they lie at the ends of the TP gradient in this training set. Importantly, the shifts between the dominance of centric (*C. ocellata* and *S.* minutulus/parvus) and fragilariod species in core Co1260 is well represented by their distributions along the TP gradient in the Swiss training set (Lotter et al., 1998). Additionally, the Swiss lakes share the characteristic of karstic bedrock with Lake Dojran. Because of the high proportion of the endemic taxon Cyclotella fottii Hustedt in Lake Ohrid and the lack of its modern analogues, DI-TP reconstruction is deemed inappropriate for cores Co1262 and Sv09. This is supported by the large discrepancy between the surface sediment DI-TP estimate (34.6 μ g l⁻¹) and lake water TP measurement (4.6 μ g l⁻¹) (Wagner et al., 2009).

3.2.2 Pigment analysis

Pigment analysis was carried out on the top 55 cm of Lake Dojran core Co1260 in S. McGowan's laboratory (Nottingham) to assess recent human impacts. Analysis of pigments (chlorophylls, carotenoids and their derivatives) involves extraction, separation, identification and quantification (Leavitt and Hodgson, 2001; McGowan, 2013). After core recovery, samples for pigment analysis were stored in darkness at 4 °C, and frozen at -18 °C. Samples were freeze-dried shortly before analysis and kept frozen until analysed. Fourteen samples

together with five dry sediment samples, which were freeze-dried immediately after core recovery in 2011 and stored in the vials in a dark box at room temperature, were analysed. These five dry sediment samples have corresponding wet sediments analysed, and the analysis of dry sediments is used to assess the degradation of pigments in referring to the results of wet sediments. For the extraction of pigments, approximately 0.2 g sediments were soaked in 5 ml extraction solvent (a mixture of 80% acetone, 15% methanol and 5% water) overnight in the freezer. Pigment extracts were filtered with a 0.22 μ m filter, dried under N₂ gas, dissolved in 500 μ l injection solvent (a 70: 25: 5 mixture of acetone, ion-pairing reagent (IPR, 0.75 g tetra butyl ammonium acetate and 7.7 g ammonium acetate in 100 ml water) and methanol), and placed in the autosampler tray in the high-performance liquid chromatography (HPLC) unit in an appropriate order.

The separation of pigments is based on polarity and mass. Pigment mixtures introduced to a column are separated based on their differential attraction to the packed small particles on the column (the stationary phase, non-polar) and the forcing solvents through the column (the mobile phase, polar). Polar pigments pass through the column rapidly and are the first to be detected due to their strong attractions to the polar solvents. Non-polar pigments attract strongly with the non-polar packing and will not be re-dissolved into the mobile phase until its polarity is decreased. Individual pigments are released from the stationary phase and flow to the detector in sequence of decreasing polarity, and the retention time is also influenced by the mass of each molecule. The separation was run using Chen100 method (Chen et al., 2001) in an Agilent 1200 series separation module consisting of quaternary pump, autosampler, ODS Hypersil column (205×4.6 mm; 5 µm particle size), and photo-diode array (PDA) detector. The mobile phase is solvent A (80:20 methanol: 0.5 M ammonium acetate), solvent B (90:10 acetonitrile: water), and solvent C (ethyl acetate). The separation conditions began with 100% solvent A, ramped to 100% solvent B in 4 min, then ramped to 25% solvent B and 75% solvent C over 34 min and held isocratically for 1 min, and returned to 100% solvent A in 4 min and finally remained isocratic for 9 min. Each run took 52 min, and the flow rate was 1 ml min⁻¹.

A chromatogram was produced when individual pigments were detected and retention times identified, which was achieved by the PDA detector scanning simultaneously at multiple wavelengths. Pigments were indentified according to spectral characteristics and retention times on the chromatogram in ChemStation Rev. B.03.01 software, referring to published key phytoplankton pigment data and graphics sheets (Jeffrey et al., 1997; Egeland et al., 2011). The typical sequence of pigments on the chromatogram is Chl c_3 , Chl c_2 , Peridinin, Phaeophorbide a, Fucoxanthin, Neoxanthin, Violaxanthin, Diadinoxanthin, Myxoxanthophyll, Alloxanthin, Diatoxanthin, Lutein, Zeaxanthin, Canthaxanthin, Chl *b*, Echinenone, Chl *a*, Chl *a*', Pheophytin *b*, Pheophytin *a*, Pyropheophytin *a*, and β -carotene. The quantification of pigments is based on the conversion of chromatogram peak areas to concentrations, and concentrations of pigments are expressed as nanomoles per g organic carbon (nmol gOC⁻¹).

3.3 Chronology

All core sequences analysed in this study have excellent chronological control. Since the analyses were carried out by teams other than the author, a brief summary is presented here.

3.3.1 Lake Dojran core Co1260

The age model of core Co1260 was established by Francke et al. (2013) by polynomial interpolation (a polynomial function of degree 3 in MATLAB) between the calibrated radiocarbon ages of six terrestrial plant macrofossils, one charcoal fragment, two bulk organic matter samples, and a regionally-correlated point of a CaCO₃ minimum (corresponding to 8.2 ka event). Three carbonate shell dates and one dislocated terrestrial plant date (Sample COL 1320.1.1: 460.9 cm, 10,820±420 cal yr BP) were not included into the calculations (Table 3.2; Francke et al., 2013). Sample COL 1320.1.1 was found on the surface of the core halves, and thus was probably dislocated during the opening of cores; while Sample COL 1321.1.1 (521.9 cm, 10,660±440 cal yr BP) was derived from the inner part of one core half and possibly provides the accurate age (Francke et al., 2013). The carbonate shell dates are more influenced by reservoir effects and probably redeposition. The age

model indicates that core Co1260 covers the last 12,500 years (Fig. 3.3). For the top 55 cm of the core selected for pigment analysis, the chronology was estimated through linear interpolation between two radiocarbon dates, of which one from terrestrial plant remains at 53.3 cm depth is 1544±87 cal AD and the other from bulk organic matter at 16.5 cm depth is 1809±131 cal AD. The separately-estimated chronology of the top 55 cm of core Co1260 reflects the sedimentation during the past ca. 480 years (since 1530 cal AD; Fig. 3.4).

Table 3.2 Ages from Lake Dojran core Co1260. The calibration of radiocarbon ages into calendar ages is based on Calib 7.0.2 (Stuiver and Reimer, 1993) and IntCal13 (Reimer et al., 2013) and on a 2σ uncertainty. * indicates the dates excluded into the calculations of the age model.

Core depth	Lab code	Material	Radiocarbon age	Calendar age
(cm)			(¹⁴ C yr BP)	(cal yr BP)
16.5	COL 1312.1.1	bulk organic matter	140±35	140±140
				(1809±131 AD)
53.3	COL 1324.1.1	terrestrial plant remains	360±70	410±110
				(1544±87 AD)
111.3	COL 1314.1.1	terrestrial plant remains	840±70	790±120
253.0	COL 1194.1.1	terrestrial plant remains	2,430±30	2,520±170
287.3	COL 1316.1.1	terrestrial plant remains	3,080±30	3,290±80
309.1	COL 1317.1.1	charcoal	3,560±40	3,850±130
404.9	ETH 44956.1.1	carbonate shell	6,410±40	7,350±80*
406.4	COL 1319.1.1	terrestrial plant remains	8,020±150	8,960±440
460.9	COL 1320.1.1	terrestrial plant remains	9,520±160	10,820±420*
502.9	ETH 44957.1.1	carbonate shell	9,840±40	11,250±60*
521.9	COL 1321.1.1	terrestrial plant remains	9,330±160	10,660±440
635.0	ETH 46615.1.1	bulk organic matter	10,220±70	11,920±310
682.0	ETH 44958.1.1	carbonate shell	28,570±170	32,830±650*



Fig. 3.3 Age-depth model of Lake Dojran core Co1260 (modified from Francke et al., 2013).



Fig. 3.4 A separate age-depth model for the top 55 cm of core Co1260.

3.3.2 Lake Ohrid 'Lini' core Co1262

Radiocarbon dating, tephrostratigraphy and cross correlation of carbonate and organic matter contents with other sediment cores from Lake Ohrid and hydraulically-linked Lake Prespa were used to provide chronological control for core Co1262. The age model was calculated using smoothing spline method (smoothing=0.1) in the software package Clam 2.2 (Blaauw, 2010), based on five calendar ages of terrestrial plant remains, three well-dated tephras (Somma-Vesuvius AD 472/512 tephra, Mount Etna FL tephra and Somma-Vesuvius Mercato tephra; Sulpizio et al., 2010; Damaschke et al., 2013) and five correlation points (Table 3.3; Wagner et al., 2012a; Lacey et al., 2014). One much older radiocarbon age of fish remains was excluded, in that the fish remains are influenced by a reservoir effect or they are redeposited (Wagner et al., 2012a). The age model shows that core Co1262 covers the past 12,300 years (Fig. 3.5).

Table 3.3 Ages from Lake Ohrid 'Lini' core Co1262. The calibration of radiocarbon ages into calendar ages is based on Calib 7.0.2 (Stuiver and Reimer, 1993) and IntCal13 (Reimer et al., 2013) and on a 2σ uncertainty. * indicates the dates excluded into the calculations of the age model.

Core depth	Lab code	Material	Radiocarbon age	Calendar age (cal
(cm)			(¹⁴ C yr BP)	yr BP)
17	COL 1251.1.1	terrestrial plant remains	164±20	140±145
122		the AD 472/512 tephra		1,478/1,438
240	COL 1735.1.1	terrestrial plant remains	2,176±46	2,190±140
315		the FL tephra		3,370±70
318	COL 1736.1.1	terrestrial plant remains	3,280±45	3,510±110
335	COL 1737.1.1	terrestrial plant remains	3,581±40	3,850±130
368	COL 1738.1.1	terrestrial plant remains	4,370±44	5,030±190
503		the Mercato tephra		8,540±50/8,890±90
548	COL 1243.1.1	fish remains	10,492±37	12,400±190*



Fig. 3.5 Age-depth model of Lake Ohrid 'Lini' core Co1262 (modified from Lacey et al., 2014).

3.3.3 Lake Ohrid ' Sveti Naum' core Sv09

The chronology was established using 210 Pb and 137 Cs dating, with the beginning of 137 Cs

production in 1955, the fallout bomb peak in 1963 and the Chernobyl peak in 1986 identified for ¹³⁷Cs dates and the Constant Flux and Constant Sedimentation rate (CFCS) model applied for ²¹⁰Pb dates (Lorenschat et al., 2014). This age model indicates that core Sv09 covers the last 60 years, dating back to ca. 1949 AD (Fig. 3.6).



Fig. 3.6 ¹³⁷Cs and unsupported ²¹⁰Pb concentrations on the log scale in cores Sv09 and St09 and the CFCS model with 1955, 1963, and 1986 fallout maxima determined by ¹³⁷Cs (from Lorenschat et al., 2014).

3.3.4 Lake Ohrid DEEP site

Initial data from borehole logging, on-site magnetic susceptibility measurements on all cores, and geochemical measurements on core catcher samples were generated (Wagner et al., 2014). Borehole logging data show a cyclic alternation of low and high spectral gamma ray values, magnetic susceptibility data show a pronounced cyclic pattern, and total inorganic carbon (TIC) content shows clear shifts, which are most likely related to glacial–interglacial cycles (Fig. 3.7; Wagner et al., 2014). The chronostratigraphical correlation with the global stacked marine isotope record indicates that the DEEP sequence in Lake Ohrid spans the last more than 1.2 million years (Wagner et al., 2014). The preliminary data are intended solely for the purpose of demonstrating the potential of Lake Ohrid to generate robust palaeoclimate data. While the final interpretation of the data awaits independent chronological control and analysis of the master sequence itself, it is appropriate in the thesis to present a preliminary speculative interpretation of the diatom data in terms of glacial–interglacial response.



Fig. 3.7 Core recovery of four parallel holes 1B, 1C, 1D, and 1F from the DEEP site [colours indicate coring tools. blue: hydraulic piston core (HPC); green: extended nose, non-rotating (XTN); red: extended core bit, rotating (Alien; ALN); white: core recovery gaps], composite recovery, magnetic susceptibility (MS), spectral gamma ray (GR) from borehole logging, and lithology, total organic carbon (TOC), total inorganic carbon (TIC) and carbonate stable isotopes from core catcher samples (from Wagner et al., 2014).

Chapter 4 Lake Dojran Holocene climate and environmental change and pigment recent change

This chapter uses diatoms as a strong proxy for lake levels and trophic status during the Lateglacial and Holocene in core Co1260, Lake Dojran, to strengthen previous interpretation based on sedimentological and geochemical data. In interpretation of Holocene limnological change in terms of regional climate effects *versus* the influence of local catchment processes, this chapter exploits extant regional palynological data for vegetation change in the highlands and lowlands. The importance of seasonality in driving Holocene climate change is assessed in this chapter by reference to the summer and winter latitudinal temperature gradient (LTG), which incorporates variation in the Subtropical High pressure and Arctic Oscillation (AO). This chapter also combines diatom and pigment data from the top 55 cm section of the Lake Dojran core to assess recent human impact (catchment deforestation and water abstraction) on the eutrophication of Lake Dojran.

4.1 Previous data on Holocene climate and environmental change in Lake

Dojran

Two previous studies have been made of Holocene climate and environmental change in Lake Dojran. One is based on sedimentological and geochemical data (Francke et al., 2013) from the same core as this study, and the other is based on pollen data from a separate littoral core Doirani-1/2 which covers the last 5,000 years (Athanasiadis et al., 2000). Francke et al. (2013) found that, during the Lateglacial period, high abundance of clay clasts, high mean grain size, an older shell fragment, and hydro-acoustic data indicated a low lake level and redeposition before ca. 12,100 cal yr BP. This was followed by a lake-level increase inferred from hydro-acoustic data, the absence of clay clasts, low mean grain size, and high potassium (K) concentration. During the earliest Holocene (ca. 11,500–10,700 cal yr BP), overall coarse sediment suggested high water inflow and high lake level, which led to high evaporation as indicated by high $\delta^{18}O_{carb}$ values; lower K concentration indicated lower erosion, and low organic matter content suggested low in-lake productivity. During the early

Holocene (ca. 10,700–8,300 cal yr BP), decreasing $\delta^{18}O_{carb}$ values suggested increasing humidity; lower K concentration implied less clastic input while increasing organic matter content was from more allochthonous supply. During the mid Holocene, relatively high lake level was inferred from hydro-acoustic data and finer grain-size distribution. After ca. 2,800 cal yr BP, hydro-acoustic data and fine grain-size distribution suggested a lake-level lowstand apart from around 1,000 cal yr BP (Francke et al., 2013), while pollen data indicated changes in the catchment from a natural landscape to one modified by intensified human impact (Athanasiadis et al., 2000).

4.2 Diatom results and interpretation

Six major diatom assemblage zones can be defined, which correlate clearly with lithostratigraphic boundaries from Francke et al. (2013) in Fig. 4.1. Diatom preservation quality is high with >500 valves counted and >10⁷ g⁻¹ concentration throughout until the late Holocene (Zone D-6). Diatom-inferred total phosphorus (DI-TP) log₁₀ values range from 1.02 to 2.18 (equivalent to 10.6–149.8 μ g l⁻¹), estimated standard error of prediction (eSEP) ranges from 0.26 to 0.29, and the error range (2×eSEP) varies from 0.51 to 0.58 (calculated as 13.7–210.8 μ g l⁻¹). Diatom-inferred conductivity (DI-Cond) log₁₀ values range from 2.39 to 3.62 (equivalent to 0.2–4.2 mS cm⁻¹), eSEP ranges from 0.47 to 0.67, and the error range varies from 0.93 to 1.34 (calculated as 0.8–13.4 mS cm⁻¹). The DI-TP and DI-Cond reconstructions are treated with caution, but provide corroboration for the interpretation, as explained below.

4.2.1 Zone D-1 (717-645 cm, ca. 12,500-12,000 cal yr BP)

In Subzone D-1a (717–696 cm, ca. 12,500–12,400 cal yr BP), the basal sample has relatively high abundance of benthic taxa (40%), possibly suggesting a lake-level lowstand at the base of the sequence, and this is followed at 713 cm depth by the dominance of planktonic taxa (50–70%), indicating relatively high lake level. Longer valves of *Fragilaria crotonensis* Kitton and *Asterionella formosa* Hassall have competitive advantages in deep waters for buoyancy and also prefer high nitrogen and silica concentrations (Bailey-Watts, 1986; Saros et al.,

2005), and *S. minutulus/parvus* prefers high phosphorus concentration (Bennion, 1995; Kilham et al., 1996). Together, this also indicates a eutrophic state, presumably from high catchment runoff and nutrient erosion processes. The subsequent dominance of mesotrophic *Stephanodiscus medius* Håkansson and oligotrophic-mesotrophic *C. ocellata* suggests ongoing water inflow but declining nutrient enrichment, supported by declining DI-TP values. In Subzone D-1b (696–645 cm, ca. 12,400–12,000 cal yr BP), the increase in the relative abundance of facultative planktonic taxa, mainly comprising *Pseudostaurosira brevistriata* (Grunow) Williams & Round and *Staurosira construens* var. *venter* (Ehrenberg) Hamilton, and the clear increasing trend in benthic taxa from 667 cm depth suggest shallowing, starting with the peak concentration in the entire sequence at the 696 cm depth.

4.2.2 Zone D-2 (645–591 cm, ca. 12,000–11,500 cal yr BP)

Planktonic C. ocellata is at low abundance, and together with high relative abundance of benthos, this indicates a very low lake level. Facultative planktonic Pseudostaurosira, Staurosira and Staurosirella species are also rare. However, planktonic Cyclotella meneghiniana Kützing, S. minutulus/parvus and Cyclostephanos dubius (Fricke) Round (diameter $< 5 \mu m$) are consistently present. C. meneghiniana lives in a wide range of habitats from shallow to deep waters (Gasse, 2002) and from fresh waters of high conductivity to saline conditions (Saros and Fritz, 2000). S. minutulus/parvus and C. dubius (small) are eutrophic freshwater taxa but tolerate oligosaline conditions (Fritz et al., 1993). Benthic taxa are remarkably diverse, most of which are eutrophic and halotolerant, such as Nitzschia frustulum (Kützing) Grunow, Tryblionella constricta (Kützing) Poulin, Ctenophora pulchella (Ralfs ex Kützing) Williams & Round, Tabularia fasciculata (Agardh) Williams & Round (Fritz et al., 1993; Reed, 1998a; Gasse, 2002; Reed et al., 2012). Importantly, the presence of rare obligate saline taxa such as Biremis circumtexta (Meister ex Hustedt) Lange-Bertalot & Witkowski and Campylodiscus clypeus (Ehrenberg) Kützing indicates aridity in a closed basin due to enhanced evaporative concentration, since the groundwater influence on lake-water conductivity and salinity is insignificant. Maximum DCA Axis 1 scores also make this zone distinctive. In Subzone D-2a (645–611 cm, ca. 12,000–11,700 cal yr BP), eutrophic, halotolerant benthic taxa are dominant, and the DI-Cond reconstruction indicates a peak

concentration of total dissolved solids (>3 mS cm⁻¹ conductivity). In Subzone D-2b (611–591 cm, ca. 11,700–11,500 cal yr BP), *S. minutulus/parvus* and *C. dubius* (small) increase distinctly. Since obligate saline taxa and eutrophic, halotolerant taxa indicate the maintenance of low lake level, enhanced nutrient input is inferred, supported by the peak in DI-TP.

4.2.3 Zone D-3 (591–525 cm, ca. 11,500–10,700 cal yr BP)

Zone D-3 exhibits a marked transition to the low-diversity dominance of planktonic oligotrophic-mesotrophic *C. ocellata* (70–90%), initially as a co-dominant with *P. brevistriata* (ca. 25%). The abundance of facultative planktonic taxa is <10% thereafter. Planktonic mesotrophic *S. medius* is consistently present at ca. 5% abundance. The abundance of benthic taxa is consistently <10%. A deep, oligotrophic to mesotrophic state can be inferred. A moderate, nearly stable nutrient level is shown by the DI-TP reconstruction. This zone is also clearly distinguished by stable, intermediate DCA Axis 1 scores.

4.2.4 Zone D-4 (525–407 cm, ca. 10,700–8,500 cal yr BP)

A shallow condition prevails in Zone D-4, clearly indicated by a transition to the co-dominance of *C. ocellata*, *S. medius* and *F. brevistriata* (ca. 20% each), to the dominance of *F. brevistriata* (up to 60%) and then to the relatively high abundance of *S. construens* var. *venter* (30–40%). Heavily-silicified facultative planktonic *Staurosirella martyi* (Héribaud) Morales & Manoylov and *S. lapponica* (Grunow) Williams & Round are consistently present. Benthic taxa are at higher abundance, including smaller *Amphora pediculus* (Kützing) Grunow and *Mayamaea atomus* (Kützing) Lange-Bertalot, and heavier *Diploneis mauleri* (Brun) Cleve and *Eolimna rotunda* (Hustedt) Lange-Bertalot, *Kulikovskiy* & Witkowski. *A. pediculus* is tolerant of oligotrophic to eutrophic conditions, *D. mauleri* and *E. rotunda* live mostly in mesotrophic waters, and *M. atomus* is a eutrophic species. A relatively high trophic level can also be inferred; this is not clear in the DI-TP reconstruction but is supported by high diatom concentration in this phase.



Fig. 4.1 Lithostratigraphy (modified from Francke et al., 2013) and summary diatom diagram of core Co1260, showing diatom-inferred total phosphorus (DI-TP) and conductivity (DI-Cond) reconstructions based on the Swiss TP and Combined Salinity training sets (EDDI; Juggins, 2001), respectively, and Axis 1 scores from detrended correspondence analysis (DCA). The calibrated radiocarbon chronology is marked at 1000-year intervals, with an estimated age of 12,500 cal yr BP at the base of the sequence.

4.2.5 Zone D-5 (407–277 cm, ca. 8,500–3,000 cal yr BP)

The relatively high abundance of planktonic eutrophic Aulacoseira granulata (Ehrenberg) Simonsen and mesotrophic S. medius, the consistent presence of eutrophic Stephanodiscus hantzschii Grunow, and the short-lived peak of eutrophic C. dubius around 353 cm depth (ca. 5,700 cal yr BP), indicate a relatively deep and turbid state. It is supported by relatively high DI-TP and diatom concentration, particularly between 377 and 329 cm depth (ca. 7,200–4,500 cal yr BP), where it correlates with a broad peak of plankton and high in-lake productivity. Low light availability in the deeper water would reduce the growth of benthic diatoms, while tychoplanktonic Pseudostaurosira, Staurosira and Staurosirella species (maintained at 40–60%) are commonly transported into the water column (Battarbee et al., 2001) and are tolerant of disturbed environments (Anderson, 2000). Larger and heavily-silicified planktonic diatoms sink rapidly in the absence of mixing, even in a deep lake with a long settling distance (Bennion et al., 2010; Wolin and Stone, 2010), and in a shallow lake there is insufficient mixing to suspend these taxa for long growth periods (Bennion, 1995). Thus it is relatively high lake level and mixing that make robust planktonic A. granulata, C. dubius, S. hantzschii and S. medius and tychoplanktonic S. martyi remain in the photic zone. This supports an interpretation of the planktonic abundance both in terms of productivity and increased lake level.

4.2.6 Zone D-6 (277–0 cm, ca. 3,000 cal yr BP–present)

Diatom concentration is low, with high dissolution, particularly between 209 and 177 cm depth (ca. 1,900–1,500 cal yr BP) and between 81 and 21 cm depth (ca. 600–100 cal yr BP), where the diatom count is <300 valves and assemblages are dominated by poorly-preserved valves of robust taxa. More fragile taxa such as *P. brevistriata* and *A. pediculus* are possibly dissolved. Despite the dissolution, the dominance of facultative planktonic taxa and low abundance of planktonic taxa indicate a shallow environment, possibly with the expansion of emergent vegetation, because the base of emergent macrophytes is a major habitat for small fragilaroid species (Sayer, 2001). After ca. 1,000 cal yr BP (in Subzone D-6b) there is a slight increase in *Amphora* species, but no major ecological shift occurs in the recent past. The topmost sample is distinguished by the relatively high abundance of *A. granulata*, which is

probably a reflection of the incorporation of living diatoms rather than an indication of recent accelerated eutrophication. In the light of the lake's modern eutrophic to hypereutrophic state, the ecologically-consistent diatom assemblages suggest that high trophic level possibly prevails in this zone, although nutrient reconstruction is not particularly sensitive here. There are several possible reasons for lack of diatom evidence for accelerated eutrophication in the recent past: 1) eurytopic diatoms with broad tolerance ranges tend to dominate at a high trophic state as an adaptation to wide fluctuations in water chemistry, compounding the aforementioned potential for poor reconstruction at the upper end of the nutrient gradient; 2) non-planktonic diatoms respond to water-column nutrient additions less directly than phytoplankton, and they are more sensitive to habitat availability as they can derive nutrients from sediments and macrophytes (Bennion et al., 2010; Hall and Smol, 2010); 3) other algae (chlorophytes, cyanobacteria and dinoflagellates) are the most important primary producers rather than diatoms in this lake at a high trophic level; and 4) a more turbid state due to increased phytoplankton growth in turn reduces diatom growth, while chlorophytes and cyanobacteria are better competitors for light (Tilman et al., 1986).

4.3 Multi-proxy, regional- and catchment-scale interpretation

The diatoms provide strong proxy data for Lateglacial and Holocene changes in lake levels and trophic status in Lake Dojran, and strengthen previous lake-level and palaeoclimate interpretation by comparison with extant sedimentological and geochemical data from the same core in Fig. 4.3. The diatom data are also important in disentangling regional climate effects from the influence of local catchment processes on Holocene hydrological variability, and we exploit extant regional pollen data with robust chronologies for vegetation change in the highlands and lowlands in Fig. 4.4. We compare with various proxy data from the northeastern Mediterranean, and assess the importance of seasonality in driving Holocene moisture availability by using the summer and winter latitudinal temperature gradient (LTG) to disentangle precipitation from temperature effects (Fig. 4.4).



Fig. 4.2 Northeastern Mediterranean palaeoenvironmental records referred to in this chapter. 1. Lake Dojran (this study; Athanasiadis et al., 2000; Francke et al., 2013), 2. Lake Trilistnika (Tonkov et al., 2008), 3. Lake Ribno (Tonkov et al., 2013), 4. SL152 (Kotthoff et al., 2008a, 2008b, 2011; Dormoy et al., 2009), 5. Tenaghi Philippon (Müller et al., 2011), 6. Lake Ohrid (Wagner et al., 2009; Leng et al., 2010), 7. Lake Prespa (Aufgebauer et al., 2012; Panagiotopoulos et al., 2013; Leng et al., 2013; Cvetkoska et al., 2014a), 8. Lake Maliq (Bordon et al., 2009), 9. Nisi Fen (Lawson et al., 2005), 10. Rezina Marsh (Willis, 1992a, 1992b), 11. Lake Gramousti (Willis, 1992a), 12. Lake Ioannina (Frogley et al., 2001; Lawson et al., 2004; Wilson et al., 2008; Jones et al., 2013), 13. Lake Xinias (Digerfeldt et al., 2007), 14. Lake Stymphalia (Heymann et al., 2013), 15. Lake Frassino (Baroni et al., 2006), 16. Lake Accesa (Drescher-Schneider et al., 2007; Peyron et al., 2011), 17. Valle di Castiglione (Di Rita et al., 2013), 18. Lake Albano (Guilizzoni et al., 2002), 19. Lago Grande di Monticchio (Allen et al., 2002), 20. MD90-917 (Combourieu-Nebout et al., 2013), 21. Lake Pergusa (Sadori and Narcisi, 2001; Sadori et al., 2008; Magny et al., 2012), 22. Lake Preola (Magny et al., 2011), 23. MD04-2797 (Desprat et al., 2013), 24. Lake Iznik (Roeser et al., 2012), 25. Lake Gölhisar (Eastwood et al., 2007), 26. Eski Acıgöl (Roberts et al., 2001; Turner et al., 2008), 27. Lake Van (Wick et al., 2003; Litt et al., 2009).

4.3.1 Younger Dryas (ca. 12,400–11,500 cal yr BP)

Francke et al. (2013) suggested that the presence of clay clasts, the occurrence of a 32,830 cal yr BP old shell fragment, and an undulated reflector in the hydro-acoustic data probably indicate a low lake level and redeposition between ca. 12,500–12,100 cal yr BP. This interpretation of a shallow state may be consistent with the relatively high abundance of benthic diatoms at the base of the sequence at ca. 12,500 cal yr BP. Subsequently in Subzone D-1a, even if the presence of eutrophic plankton may relate more to high productivity than lake level, the well-preserved diatom flora are important in indicating the presence of

permanent water. A viable interpretation is that redeposition may occur, but that diatoms indicate lake refilling after desiccation, from a shallow state with the relatively high abundance of benthos to a relatively high lake level and eutrophic state with the dominance of plankton just above the core base. In Subzone D-1b (ca. 12,400–12,000 cal yr BP), diatom-inferred shallowing appears inconsistent with redeposition, since diatoms are well preserved, with a clear shift from the dominance of facultative planktonic taxa (50–65%) to increasing abundance of benthos, and peak concentration at the base of this subzone. Diatoms can be preserved during redeposition, as in the mass wasting deposit from Lake Ohrid (see Chapter 5 below), but they would be present at extremely low concentration and with enhanced dissolution.

The diatom-inferred shallowing culminates in an extremely low lake level and eutrophic, oligosaline condition in the endorheic lake between ca. 12,000–11,500 cal yr BP (Zone D-2), indisputably interpreted as peak aridity of the Younger Dryas due to enhanced evaporative concentration. Based on strong evidence for the presence of permanent water derived from hydro-acoustic data, grain-size composition and the absence of clay clasts, Francke et al. (2013) interpreted this zone as one of higher lake level than the shallow or even desiccated state at the base of the sequence. Since extremely shallow or even ephemeral lakes may be characterised by 'lacustrine' sediment (Reed, 1998a, 1998b), the data in conjunction indicate that this later phase (Zone D-2) can be interpreted as a stable and lacustrine state, but with the classic enhanced aridity of the Younger Dryas.

In the northeastern Mediterranean, there is growing palynological evidence for aridity during the Younger Dryas, commonly marked by a peak in steppic pollen taxa *Artemisia* and Chenopodiaceae throughout the altitudinal range (e.g. Lake Ribno, 2184 m a.s.l., Tonkov et al., 2013; Lake Prespa, 849 m a.s.l., Panagiotopoulos et al., 2013; Valle di Castiglione, central Italy, 44 m a.s.l., Di Rita et al., 2013), and including a peak in *Ephedra* in marine records (e.g. Kotthoff et al., 2008a; Desprat et al., 2013). Pollen-based biome reconstructions (Allen et al., 2002; Bordon et al., 2009) and quantitative temperature and/or precipitation reconstructions (e.g. Bordon et al., 2009; Dormoy et al., 2009) also provide evidence of a cold, arid steppe

environment. Our results are important in strengthening the sparse regional palaeohydrological dataset, which to date only comprises a distinct decrease in planktonic diatoms (particularly *C. ocellata*) in Lake Ioannina (Wilson et al., 2008), a peak of the eutrophic diatom species *A. granulata* and facultative planktonic *Staurosirella pinnata* (Ehrenberg) Williams & Round in Lake Prespa, Macedonia/Albania/Greece (Cvetkoska et al., 2014a), a decrease in rubidium (Rb)/strontium (Sr) ratio in Lake Stymphalia, southern Greece (Heymann et al., 2013), and an increase in $\delta^{18}O_{carb}$ values and magnesium (Mg)/calcium (Ca) ratio in Lake Van, eastern Turkey (Wick et al., 2003; Litt et al., 2009).

4.3.2 The earliest Holocene (ca. 11,500–10,700 cal yr BP) (corresponding to the Preboreal period)

Diatom-inferred high lake level and relatively low trophic state during the earliest Holocene (Zone D-3) strengthens the previously tentative interpretation of high $\delta^{18}O_{carb}$ values. Francke et al. (2013) suggested that evaporation was promoted during this period by large lake surface area that was accompanied by lake-level increase in such a flat-bottomed basin. The high lake level in Lake Dojran is in accord with abrupt isotopic depletion at the Younger Dryas–Holocene transition in Lake Ioannina, Lake Van and Eski Acıgöl (central Turkey) (Roberts et al., 2008 and references therein). It is also in accord with the inference of high humidity from increased Rb/Sr ratio in Lake Stymphalia (Heymann et al., 2013). However, it is not in complete agreement with vegetation development in the northeastern Mediterranean during the earliest Holocene. Non-steppic herb pollen increased rather than Quercus pollen in SL152 in the northern Aegean region at this time (Kotthoff et al., 2008a). Non-steppic herb pollen were abundant during this period although Quercus pollen increased rapidly at the onset of the Holocene in Nisi Fen (Lawson et al., 2005) and Lake Accesa (central Italy) (Drescher-Schneider et al., 2007). Non-steppic herb and steppe pollen were replaced by Quercus pollen gradually until its maximum around 10,500 cal yr BP in Lake Prespa (Panagiotopoulos et al., 2013) and Tenaghi Philippon (northeastern Greece) (Müller et al., 2011). Non-steppic herb pollen was dominant, with a gradual increase of *Quercus* pollen until ca. 10,500 cal yr BP in Eski Acıgöl (Roberts et al., 2001; Turner et al., 2008) and MD04-2797 (Siculo-Tunisian Strait) (Desprat et al., 2013). Non-steppic herb pollen replaced

steppe pollen gradually during this period, along with a slightly increasing trend in *Quercus* pollen in Lake Van (Litt et al., 2009). Non-steppic herb taxa were more important in these records than the percentage data implied, because they are mostly lower pollen producers than *Quercus* (Broström et al., 2008).

The high lake level in Lake Dojran and isotopic depletion in the northeastern Mediterranean suggest that the increase in humidity during the earliest Holocene would be attributed to increased precipitation, since Younger Dryas mountain glaciations did not develop widely in this region (Hughes et al., 2006; Hughes, 2012) and meltwater input is an unlikely forcing function. However, the wide distribution of non-steppic herb taxa suggest that increased moisture availability was insufficient to support extensive forest development, since afforestation linked to soil development was asynchronous in this region. The limited increase in humidity is possibly the effect of high evaporation, corresponding to high pollen-inferred area-average summer and winter temperature in southeastern Europe (Davis et al., 2003) and high alkenone-inferred sea surface temperature (SST) at the beginning of the Holocene in the Mediterranean Sea (Abrantes et al., 2012). The comparison with the summer and winter LTG supports increased precipitation during the earliest Holocene. The negative (strong) winter LTG resulted in the negative phase of AO (Davis and Brewer, 2009), and promoted the penetration of more westerly moisture of North Atlantic origin in winter. The summer LTG suggests that the Subtropical High pressure was not strengthened and displaced northward (Davis and Brewer, 2009), and summer moisture was not scarce at this time. Thus the LTG and atmospheric moisture availability would contribute to the increase in precipitation during the earliest Holocene, modulated by high temperature-induced evaporation.

Changes in catchment vegetation and erosion can have a major influence on lake hydrology and nutrient input and hence diatom composition (Fritz and Anderson, 2013). At the catchment scale, the steppe vegetation was replaced by birch forest at high altitudes (Lakes Ribno and Trilistnika, the Rila Mountain, southwestern Bulgaria) (Tonkov et al., 2008, 2013) and by non-steppic herbs in the lowlands (SL152, northern Aegean Sea) (Kotthoff et al.,

2008a). Despite increased precipitation and water inflow, the vegetation development restrained catchment erosion and nutrient input, which is supported by lower clastic input indicated by decreased K concentration (Francke et al., 2013). Together with the dilution effect of increased freshwater input, lower nutrient input resulted in the relatively low trophic level and in-lake productivity, which is supported by low organic matter content (Francke et al., 2013). In the northeastern Mediterranean, low trophic levels during the earliest Holocene were also indicated by pigment and diatom data in Lake Albano, central Italy (Guilizzoni et al., 2002). In all, increased precipitation was a major contributor to the high lake level in Lake Dojran and increased humidity in the northeastern Mediterranean during the earliest Holocene, although high evaporation reduced the effect of increased precipitation.

4.3.3 The early Holocene (ca. 10,700–8,500 cal yr BP)

The diatom data show a low lake level and relatively high trophic state during the early Holocene (Zone D-4), which is not in accord with decreasing $\delta^{18}O_{carb}$ values in Lake Dojran. Francke et al. (2013) suggested that the littoral zone might extend during this phase. If valid, epiphytic and epipelic diatoms can be similarly facilitated, and they could reach the coring site through water mixing and/or sediment redistribution. However, water mixing would cause nutrients to become well distributed in the water column as well as in the pelagic zone, conflicting with the rather low relative abundance of planktonic taxa at the coring site; sediment disturbance would be unfavourable to the settlement and preservation of smaller, fragile valves, conflicting with the relatively high percentages of *A. pediculus* and *M. atomus*.



Fig. 4.3 Comparison of diatom data with selected sedimentological and geochemical data (Francke et al., 2013) in Lake Dojran. (a)-(d) the relative abundance of planktonic diatoms, *C. ocellata*, facultative planktonic diatoms and benthic diatoms; (e) absolute diatom concentration; (f) diatom DCA Axis 1 scores; (g) and (h) carbonate and organic matter contents; (i) mean grain size; (j) K concentration; (k) carbonate oxygen stable isotope data.



Fig. 4.4 Comparison of Lake Dojran diatom data with key palaeoclimate data. (a)-(d) the relative abundance of planktonic diatoms, *C. ocellata*, facultative planktonic diatoms and benthic diatoms; (e) K concentration (Francke et al., 2013); (f) carbonate oxygen stable isotope data (Francke et al., 2013); (g) percentage of *Quercus* pollen in SL152 (northern Aegean Sea) (Kotthoff et al., 2008a, 2008b); (h) palynostratigraphy with key pollen taxa and approximate average percentages from Lakes Trilistnika and Ribno (the Rila Mountain, southwestern Bulgaria) (Tonkov et al., 2008, 2013); (i) and (j) the Holocene winter and summer latitudinal temperature gradient (LTG) between northern and southern Europe (Davis and Brewer, 2009); (k) and (l) the Holocene winter and summer temperature anomalies in southeastern Europe (Davis et al., 2003).

The diatom-inferred low lake level is also inconsistent with low bulk carbonate δ^{18} O values in Lake Pergusa (Sicily) (Sadori et al., 2008), authigenic carbonate δ^{18} O values in Lake Gölhisar (southwestern Turkey) (Eastwood et al., 2007) and ostracod δ^{18} O values in Lake Ioannina (Frogley et al., 2001). Roberts et al. (2008) suggested that the freshening of surface water in the eastern Mediterranean Sea in parallel with sapropel formation would affect the isotopic composition of precipitation during the early Holocene. However, the low lake level in Lake Dojran is in line with relatively high δ^{18} O values of authigenic carbonates in Lake Ohrid (Macedonia/Albania) (Leng et al., 2010), Lake Prespa (Leng et al., 2013) and Lake Van (Litt et al., 2009), and mollusc δ^{18} O values in Lake Frassino (northern Italy) (Baroni et al., 2006). The apparent discrepancy in isotope proxy data is probably due to the control of different hydroclimatic parameters (Jones and Roberts, 2008) and the influence of catchment factors on the specific hydrology of each lake (Leng and Marshall, 2004). The diatom-based inferences in Lake Dojran are also in accord with the inference of low lake levels from low Rb/Sr ratio in Lake Stymphalia (Heymann et al., 2013) and high Ca/titanium (Ti) ratio in Lake Iznik, northwest Turkey (Roeser et al., 2012) at this time.

Palynological data are also complex, with the occurrence of different ecological pollen groups in this region (e.g. Sadori, 2013; Roberts et al., 2011b) and even in the same record (e.g. Peyron et al., 2011; Panagiotopoulos et al., 2013), which have been interpreted in different ways. The apparent discrepancy in the regional vegetation distribution was attributed to spatial and altitudinal variation in climatic factors (De Beaulieu et al., 2005; Sadori, 2013), and Roberts et al. (2011b) suggested that increased seasonality of climatic factors is an important factor. Willis (1992a) invoked the distance from mountain refugia of different taxa, and Sadori et al. (2011) linked this to edaphic conditions and water retention capacity suitable for different plant growth. With respect to the combination of ecologically-incompatible pollen groups in the same record, Panagiotopoulos et al. (2013) attributed this to a more even distribution of annual precipitation, while Magny et al. (2013) invoked high seasonality of precipitation. Roberts et al. (2011b) cautioned against interpreting this pollen flora too closely in terms of modern climate analogues. Despite this complexity, the Lake Dojran diatom data are supported by pollen-based quantitative

reconstructions of higher winter precipitation and lower or consistently low summer precipitation in SL152 (Dormoy et al., 2009), Lake Accesa (Peyron et al., 2011), Lake Pergusa (Magny et al., 2012; Peyron et al., 2013) and MD04-2797 (Desprat et al., 2013). The low lake level and relatively high trophic state in Lake Dojran are probably driven by strong seasonal hydrological contrasts, and extreme summer aridity offset the effect of winter precipitation recharge. This is consistent with the wide distribution of *Quercus ilex* in the northern Aegean region rather than *Quercus* deciduous type (Kotthoff et al., 2008b), although moisture availability was sufficient to support tree growth.

The comparison with the summer and winter LTG supports this climatic interpretation as high seasonality. The negative (strong) winter LTG suggests that AO was in the negative phase (Davis and Brewer, 2009), the storm track was in a southerly path and moisture availability in winter was high during the early Holocene. The positive (weak) and increasing summer LTG suggests that the Subtropical High pressure was migrating northward (Davis and Brewer, 2009), blocking westerly moisture penetration in summer and leading to much drier summers than today. It is associated with the intensified African monsoon and the large number of lake records in the Sahara and Sahel (Lézine et al., 2011), and with sapropel formation in the eastern Mediterranean Sea since 10,800 cal yr BP (De Lange et al., 2008). Thus the LTG and high seasonality of moisture availability would contribute to the reduced lake level and increased nutrient level in Lake Dojran during the early Holocene.

At the catchment scale, the Lake Dojran diatom data coincide with extensive forest development, mainly comprising deciduous oak forest (*Quercus robur* and *Quercus cerris*) at high altitudes (Lakes Ribno and Trilistnika, southwestern Bulgaria) (Tonkov et al., 2008, 2013) and evergreen oak forest (*Quercus ilex*) in the lowlands (SL152, northern Aegean Sea) (Kotthoff et al., 2008a, 2008b). According to the contrasting growth requirements of deciduous and evergreen oaks (Roberts et al., 2011b), it can be posited that the dense, thick vegetation would reduce runoff and erosion in the catchment throughout the year through soil absorption and retention, which may contribute to the low lake level, high shell abundance and lower K concentration during this phase (Francke et al., 2013). However,

forest vegetation would enhance chemical weathering and nutrient supply through soil development, which may contribute to the relatively high trophic level in spite of the limited water inflow. This is supported by high diatom concentration, as well as higher organic matter and carbonate content (Francke et al., 2013), indicating high in-lake productivity. In all, the low lake level and relatively high trophic state in Lake Dojran may result climatically from high seasonality of precipitation and locally from dense forest development and limited, nutrient-rich catchment runoff.

4.3.4 The mid Holocene (ca. 8,500–3,000 cal yr BP)

A relatively high lake level and maximum Holocene trophic level are inferred during the mid Holocene (Zone D-5). This is supported by decreased $\delta^{18}O_{carb}$ values. Francke et al. (2013) also discussed a relatively high lake level during this phase based on sedimentological data. The relatively high lake level in Lake Dojran is consistent with low $\delta^{18}O_{carb}$ values in Lake Prespa (Leng et al., 2013) and Lake Van (Litt et al., 2009), low mollusc δ^{18} O values in Lake Frassino (Baroni et al., 2006), and high lake levels in Lake Xinias, central Greece (Digerfeldt et al., 2007). However, in the northeastern Mediterranean, an aridification trend was shown by isotopic enrichment in Eski Acıgöl (Roberts and Jones, 2002), diatom succession in Lake Ioannina (Wilson et al., 2008; Jones et al., 2013), and lithological changes in Lake Pergusa (Sadori and Narcisi, 2001). Sadori et al. (2011) and Roberts et al. (2011b) improved understanding of this aridification process after ca. 8,000 cal yr BP based on a regional synthesis of pollen and isotope data, respectively. The comparison with the summer and winter LTG does not give support to increased humidity during the mid Holocene. Both the summer and winter LTG were more positive (weaker) during this period (Davis and Brewer, 2009), and the positive phase of AO and the northern position of the Subtropical High pressure suggest that winter was not influenced by the northward-shifted storm track and summer was controlled mostly by the downdraught of dry air, respectively. This would lead to low winter precipitation and much drier summers than today, although several regional syntheses of temperature (Davis et al., 2003; Finné et al., 2011; Abrantes et al., 2012) suggested cooling and decreased evaporation during the mid Holocene.

At the catchment scale, the relatively high lake level and high trophic state in Lake Dojran coincide with the dominance of coniferous forest (mainly firs) at high altitudes at ca. 8,500–7,800 cal yr BP (Lakes Ribno and Trilistnika, southwestern Bulgaria) (Tonkov et al., 2008, 2013) and the opening of the oak forest with an increase in non-steppic herbs in the lowlands (SL152, northern Aegean Sea) (Kotthoff et al., 2008a, 2008b). The reduction of forest density in the lowlands, most probably corresponding to the aridification process discussed above, was also clearly indicated by a distinct decrease in *Quercus* pollen concentration at ca. 8,400 cal yr BP (Kotthoff et al., 2008a), which would cause an increase in nutrient mobility. The expansion of firs at high altitudes is a regional signal across the southern Balkans, including Rezina Marsh (1800 m a.s.l., northwestern Greece) at ca. 8,600 cal yr BP (Willis, 1992b). Fir trees developed in more humid and organic soils (Sadori et al., 2011), and the wetting of the highlands and forest development enhanced runoff and nutrient supply. In all, the wetting of the highlands and the drying of the lowlands and associated local vegetation succession enhanced catchment runoff and nutrient erosion, and resulted in the relatively high lake level and eutrophic state in Lake Dojran.

4.3.5 The late Holocene (ca. 3,000–0 cal yr BP)

Despite low diatom concentration and high dissolution, a low lake level and high trophic state can be inferred during the late Holocene (Zone D-6). Late-Holocene aridity prevailed in the northeastern Mediterranean, indicated by isotope data (e.g. Roberts et al., 2008, 2011b; Leng et al., 2013) and lake-level reconstructions (e.g. Harrison and Digerfeldt, 1993; Digerfeldt et al., 2007; Magny et al., 2011). The comparison with the summer and winter LTG suggests that atmospheric moisture availability is not a determining factor, because the Subtropical High pressure regressed and AO index was slightly negative, which would not result in the obvious moisture deficit in this region. In contrast, the increase in regional temperature (Davis et al., 2003; Finné et al., 2011) and high evaporation may contribute to the aridity during the late Holocene, although one model simulation suggests that anthropogenic deforestation may itself have caused a decrease in summer and winter temperature in southern Europe due to increased albedo effect (Strandberg et al., 2014).

A previous late-Holocene palynological study in the littoral zone of Lake Dojran revealed that the oak forest in the lowlands and the conifer and beech forests in the mountain region were replaced by herb vegetation and secondary trees at ca. 2,800 cal yr BP as a result of intensified human impact (Athanasiadis et al., 2000). At the catchment scale, beech and spruce forests expanded widely at high altitudes, and beech trees were favoured by human agricultural and stock-breeding activities and resultant soil deterioration (Tonkov et al., 2013; Marinova et al., 2012). Non-steppic herbs expanded in the lowlands along with the further decline of the oak forest, and human disturbance was an important factor (Kotthoff et al., 2008a). Deforestation at mid-low altitudes during the late Holocene was also a regional event, for example, in Nisi Fen (475 m a.s.l.) the temperate forest declined at ca. 3,500 cal yr BP (Lawson et al., 2005; Kotthoff et al., 2008a), and in Lake Ohrid (693 m a.s.l.) it was reflected by the reduction of the coniferous forest at ca. 2,500 cal yr BP (Wagner et al., 2009). Thus human impact is possibly an important factor not only leading to the high trophic state during the late Holocene by deforestation and enhanced nutrient erosion, but also contributing to the low lake level through agriculture and irrigation.

4.4 Pigment recent change

4.4.1 Pigment degradation/preservation

Phaeophorbide *a*, fucoxanthin, alloxanthin, diatoxanthin, lutein, canthaxanthin, chlorophyll *a*, Chl *a'*, pheophytin *b*, and pheophytin *a* are identified successively in the chromatograms, and quantified as nanomoles per g organic carbon (nmol gOC⁻¹). The comparison of pigment concentrations in dry sediment samples, freeze-dried immediately after core recovery and stored at room temperature, with their corresponding wet sediments, stored at 4 °C until the analysis, reveals the degradation of pigments and supports the influence of sediment storage conditions on the accuracy of pigment analysis (Reuss and Conley, 2005). Exposure to oxygen, light and heat (for example, room temperature) promotes pigment degradation, and dry samples have a powdery texture which maximizes exposure to oxygen (Leavitt and Hodgson, 2001). Reuss and Conley (2005) suggested that freeze-dried sediment should be always stored frozen. Taking surface sediment samples (DOJ1-1 and DOJ1-2; Fig. 4.5) for example,

apart from Chl *a*', no new degradation product occurred, while fucoxanthin and diatoxanthin degraded and lowered below the limit of detection. Fucoxanthin contains an epoxy group that makes pigments more susceptible to degradation (Reuss and Conley, 2005). Among the xanthophylls, lutein, alloxanthin, canthaxanthin and diatoxanthin contain no epoxy group and show relatively high stability, although their concentrations decreased as well. Because of the long chain of alternating double bonds, carotenoids are susceptible to degradation and converted to undetectable colourless compounds (McGowan, 2013). Chls consist mainly of a tetrapyrrole ring, and their breakdown products of different types (oxidation, loss of Mg, and loss of phytol chain) are still coloured and detectable (McGowan, 2013). Chl *a* is very labile and its derivative pheophytin *a* is very stable (Reuss and Conley, 2005), and this study supports the high stability of pheophytin *a*. This study also indicates that, due to the high stability of the tetrapyrrole ring, phaeophorbide *a* is one other stable Chl *a* derivative, which is supported by the findings in an incubation experiment (Veuger and van Oevelen, 2011). Pheophytin *b* is the derivative of Chl *b*, and shows high stability in this study, while Chl *b* is not detected and shows very high instability.



Fig. 4.5 Comparison of pigment concentrations between wet sediments stored at 4 °C until pigment analysis (DOJ*-1) and dry sediment samples freeze-dried immediately after core recovery (DOJ*-2).


Fig. 4.6 Pigment concentrations in the top-55 cm Co1260 section and comparison with diatoms, carbonate and organic matter content.

4.4.2 Pigment-inferred recent eutrophication

Chl a is a broadly-distributed pigment that derives from all algae and aquatic higher plants as well as detrital material of terrestrial origin (Leavitt and Hodgson, 2001), but it is poorly preserved in the terrestrial detritus owing to its long exposure to oxygen at the soil surface (Lami et al., 2000), particularly under the condition of accelerated human deforestation in the catchment of Lake Dojran (Athanasiadis et al., 2000). Thus the concentration of Chl a and its derivatives is usually used to provide information on total productivity (Leavitt and Hodgson, 2001; McGowan, 2013). The (phaeophorbide a+pheophytin a)/(Chl a+Chl a') ratio is tentatively used as an indicator of pigment preservation (Veuger and van Oevelen, 2011). In the top-55 cm Co1260 section (Fig. 4.6), a decreasing trend of the (phaeophorbide a+pheophytin a)/(Chl a+Chl a') ratio suggests higher degradation of pigments in Zone P-1 (55–19 cm, ca. 1530–1790 cal AD). Lower concentration of Chl a and its derivatives in Zone P-1 results from lower productivity and/or higher degradation. Increased concentration of Chl a and its derivatives in Zone P-2, particularly increased phaeophorbide a concentration that is from planktonic algae as a result of zooplankton grazing (Guilizzoni and Lami, 2002), indicates higher productivity. This is consistent with lake-level decline due to human activity. The maximum water level in Lake Dojran was about 15 m at the beginning of the 19th century, and in 1808 a 1.3 km-long channel was dug from the lake to connect the Gjolaja River; the channel was gradually deepened since then until 2002 (maximum lake level was less than 4 m) to reduce the lake area for larger agricultural land and to take more water for irrigation downstream along the Gjolaja River (Stojov, 2012). This resulted in the reduction of littoral zone and its macrophytic vegetation (Griffiths et al., 2002; Sotiria and Petkovski, 2004), and thus higher concentration of Chl a and its derivatives in Zone P-2 indicates algal blooms and lake eutrophication.

Most xanthophylls are used as indicators for specific algal classes or functional groups (Leavitt and Hodgson, 2001). Despite lower pigment degradation, higher lutein concentration in Zone P-2 (19–0 cm, ca. 1790–2010 cal AD), in accord with higher pheophytin *b* concentration, possibly indicates increased abundance of chlorophytes (McGowan et al., 2012). Slightly higher canthaxanthin concentration in Zone P-2 possibly indicates increased abundance of filamentous cyanobacteria (McGowan, 2013). High alloxanthin concentration in Zone P-2 indicates high abundance of cryptophytes that is exclusively planktonic (Leavitt and Hodgson, 2001; Guilizzoni and Lami, 2002). Distinctly increased concentrations of labile fucoxanthin and relatively stable diatoxanthin in Zone P-2 possibly indicate increased

abundance of siliceous algae (diatoms, chrysophytes and dinoflagellates) (McGowan, 2013) rather than reduced degradation. This is consistent with increasing diatom concentration in Zone P-2, although there is no response of the relative abundance of planktonic diatom taxa, such as eutrophic *Aulacoseira granulata* and mesotrophic *Stephanodiscus medius*. This also suggests that low diatom concentration in Zone P-1 is probably due primarily to low productivity rather than high diatom dissolution. In all, despite reduced degradation after ca. 1790 cal AD, the pigment data show an increase in the abundance of green algae, blue-green algae, diatoms, dinoflagellates and planktonic cryptophytes, indicating algal blooms and nutrient enrichment, and are consistent with increased diatom concentration in this core section as well as in a short core DOJ97B from the central basin of Lake Dojran (Griffiths et al., 2002), other algae could respond or new toxic taxa of other algae could appear in such a changed circumstance, such as found during the floral investigations in the 1990s (Sotiria and Petkovski, 2004). Lake eutrophication and increased algal biomass since the 1790s and 1800s decades is largely due to water abstraction practices and more intensive agriculture.

4.5 Summary

The Lake Dojran diatom data, supported by extant sedimentological and geochemical data from the same core and late-Holocene palynological data from a separate littoral core, give a new insight into Younger Dryas and Holocene changes in lake levels and trophic status in the northeastern Mediterranean. The Lake Dojran diatom data provide more robust evidence and strengthen previous lake-level interpretation based on sedimentological and geochemical data during the earliest, mid and late Holocene, and also clarify previous uncertainty in interpretation of Younger Dryas and early-Holocene lake-level change. Following a very shallow or even desiccated state at the core base at ca. 12,500 cal yr BP, indicated by sedimentological and hydro-acoustic data, diatoms indicate lake infilling, from a shallow state with abundant benthos to a plankton-dominated relatively high lake level and eutrophic state thereafter. Diatom-inferred shallowing between ca. 12,400-12,000 cal yr BP and a very low lake level and eutrophic, oligosaline state between ca. 12,000–11,500 cal yr BP provide clear evidence for aridity during the Younger Dryas. Although a slightly higher lake level was previously inferred during the second part of this period, the lacustrine state with permanent water does not conflict with the diatom-inferred salinity shift. Lake Dojran's water level increased markedly during the earliest Holocene (ca. 11,500-10,700 cal yr BP). A low lake level and relatively high trophic state are inferred during the early Holocene (ca.

10,700–8,500 cal yr BP), conflicting with the previous inference of increased humidity from decreasing $\delta^{18}O_{carb}$ values and sedimentological data. Lake Dojran was relatively deep and exhibited the maximum Holocene trophic level during the mid Holocene (ca. 8,500–3,000 cal yr BP), and it became shallow during the late Holocene (ca. 3,000–0 cal yr BP). These results indicate that, being located at the juncture of the proposed boundaries between the west–east and north–south contrasting Holocene climatic domains, Lake Dojran cannot be classified simply into the western or eastern sector, or the northern or southern sector in the Mediterranean. The pigment data, supported by diatom concentration and carbonate content, provide evidence for algal blooms and lake eutrophication since the 1790s and 1800s decades, primarily due to human-induced lake-level decline and more intensive agriculture.

These results are also important in disentangling regional climate effects from local catchment dynamics during the Holocene, and to this end we exploit extant regional palynological data for vegetation change in the highlands and lowlands. The importance of seasonality in driving Holocene climate change is assessed by reference to the summer and winter LTG model, linked to the Subtropical High pressure and AO, respectively. We suggest that diatom-inferred high lake level during the earliest Holocene was attributed to the increase in precipitation, in spite of high pollen-inferred, temperature-induced evaporation, and is coherent with high winter and summer atmospheric moisture availability inferred from the LTG. The relatively low trophic state at this time was possibly driven in part by vegetation development and reduced catchment erosion. The diatom-inferred early-Holocene lake-level reduction and increased trophic level may result climatically from high seasonality of precipitation, coherent with the contrasting summer and winter LTG, and locally from limited, nutrient-rich runoff in a densely-forested catchment. The relatively deep, eutrophic state in Lake Dojran during the mid Holocene shows strong affinity with palaeolimnological data from central Greece, northern Italy and eastern Turkey, but not with other records in the northeastern Mediterranean, where aridification is recognised. It is also not coherent with the LTG-inferred low atmospheric moisture availability. This may reflect local complexity of climate variability, but may also indicate that changes were driven more by local vegetation succession and associated changes in catchment processes than by climate change. During the late Holocene, diatom-inferred shallow and high trophic state is consistent with strong regional evidence for temperature-induced aridity, coupled with the influence of intensified human land use.

Overall, this study is important in strengthening existing multi-proxy interpretation of Lateglacial and Holocene palaeohydrology and associated shifts in nutrient status. This study improves understanding of Younger Dryas and Holocene climate change in the northeastern Mediterranean, providing a coherent interpretation which suggests the important role of the LTG on moisture availability during the Holocene and clarifies the influence of catchment processes on Holocene hydrological variability and, in the more recent past, water quality status.

Chapter 5 Lake Ohrid 'Lini' Holocene change and comparison with other sediment cores in Lakes Ohrid and Prespa

This chapter uses the high-resolution relative abundance and absolute concentration data of planktonic diatom taxa from core Co1262, western Lake Ohrid, to test diatom response to Lateglacial and Holocene climate, environmental and limnological change in this deep, ancient lake, and compares with sedimentological, geochemical and isotope data from the same core. This chapter compares the diatom data from core Co1262 with extant low-resolution diatom data from cores Lz1120 (southeastern Lake Ohrid) and Co1202 (northeastern Lake Ohrid) to test whether Holocene environmental change within the lake basin is consistent, and also compares with palynological data for catchment vegetation change from core Lz1120 and the hydraulically-linked Lake Prespa core Co1215 to disentangle the influence of catchment processes on nutrient supply from mixing-induced nutrient upward supply in the water column.

5.1 Diatom results

Nine major diatom assemblage zones can be defined according to CONISS (Fig. 5.1), which match well with changes in absolute diatom concentration (Fig. 5.2). Relative abundance data (abbr. abundance) are effective in summarising changes in diatom composition at the coring site, and absolute concentration data (abbr. concentration) would inform on independent shifts of diatom taxa at the coring site. Diatom preservation quality is high, allowing a count of >500 valves per sample; F dissolution index values for the endemic taxon *Cyclotella fottii* Hustedt are >0.75 throughout, reflecting a high proportion of intact valves.

In Zone D-1 (785–743 cm, ca. 12,300–11,800 cal yr BP), endemic, hypolimnetic planktonic *C. fottii* (see Fig. 5.3) predominates (ca. 90% abundance), and facultative planktonic taxa, mainly comprising *Staurosirella pinnata* (Ehrenberg) Williams & Round and *Pseudostaurosira brevistriata* (Grunow) Williams & Round, are present at ca. 8% abundance. Diatom concentration is extremely low throughout, and diatom PCA Axis 1 scores are low, tracking the *C. fottii* domination.

In Zone D-2 (743–639 cm, ca. 11,800–10,600 cal yr BP), hypolimnetic *C. fottii* is still dominant (ca. 80–90% abundance), and the transition is marked by a distinct increase in the abundance (ca. 5–15%) of small (3-5 μ m), epilimnetic planktonic *Cyclotella minuscula* (Jurilj) Cvetkoska (see Fig. 5.3). The abundance of facultative planktonic taxa decreases slightly to

<5%. Diatom PCA Axis 1 scores exhibit a slight increase. Diatom concentration is still very low, starting to rise only at the upper zone boundary.

In Zone D-3 (639–551 cm, ca. 10,600–9,500 cal yr BP), epilimnetic planktonic taxa are at high abundance (ca. 20–40%), matching with relatively high diatom PCA Axis 1 scores. The concentration of small, epilimnetic *C. minuscula* is high throughout. The relative abundance of hypolimnetic *C. fottii* decreases (ca. 50–70%), particularly for the large forms of >20 μm in diameter. In Subzone D-3a (639–607 cm, ca. 10,600–10,200 cal yr BP), epilimnetic *Cyclotella ocellata* Pantocsek (see Fig. 5.3) is at relatively high abundance (ca. 10–30%), hypolimnetic *Stephanodiscus transylvanicus* Pantocsek (see Fig. 5.3) occurs, and diatom concentration, comprising both epilimnetic and hypolimnetic taxa, is relatively high. In Subzone D-3b (607–551 cm, ca. 10,200–9,500 cal yr BP), *C. minuscula* is at high abundance (ca. 20–40%) at the expense of *C. ocellata* and *S. transylvanicus*, *C. minuscula* attains high concentration, while the concentration of all other taxa decreases distinctly.

In Zone D-4 (551–463 cm, ca. 9,500–8,500 cal yr BP), the concentration of epilimnetic *C. ocellata* and hypolimnetic *C. fottii* is high throughout. *C. ocellata* is at high abundance (ca. 20–60%), matching with high diatom PCA Axis 1 scores. In Subzone D-4a (551–511 cm, ca. 9,500–9,000 cal yr BP), the abundance of *C. ocellata* (>3 ocelli) is relatively high (ca. 10–20%). Subzone D-4b (511–463 cm, ca. 9,000–8,500 cal yr BP) is marked by a distinct increase in the abundance (ca. 5–10%) and concentration of hypolimnetic *S. transylvanicus*.

In Zone D-5 (463–449 cm, ca. 8,500–8,200 cal yr BP), the concentration of hypolimnetic *C*. *fottii* and *S. transylvanicus* is low, along with a decrease in the abundance of hypolimnetic planktonic taxa. The abundance (ca. 10–15%) and concentration of small, epilimnetic *C. minuscula* is relatively high. There is a distinctive sample with peak abundance (ca. 60%) and peak concentration of epilimnetic *C. ocellata* and maximum diatom PCA Axis 1 scores at 459 cm depth (ca. 8,400 cal yr BP).

In Zone D-6 (449–269 cm, ca. 8,200–2,600 cal yr BP), the concentration of hypolimnetic *C. fottii* and *S. transylvanicus* is high. *C. fottii* is at high abundance (ca. 60–85%), and *S. transylvanicus* is consistently present at ca. 5–10% abundance. The concentration of epilimnetic *C. ocellata* is low, and *C. ocellata* is at relatively low abundance (ca. 10–20%), matching with relatively low diatom PCA Axis 1 scores.



Fig. 5.1 Lithostratigraphy (modified from Wagner et al., 2012a) and summary diagram of diatom relative abundance data from core Co1262, showing F dissolution index values of endemic *C. fottii*, and Axis 1 scores from principal component analysis (PCA).



Fig. 5.2 Summary diagram of absolute diatom concentration from core Co1262.

hypolimnetic: Cyclotella fottii



Fig. 5.3 Main epilimnetic and hypolimnetic diatom taxa in Lake Ohrid.

In Zone D-7 (269–214 cm, ca. 2,600–2,000 cal yr BP), epilimnetic *C. ocellata* shows renewed high abundance (ca. 50-60%), and diatom PCA Axis 1 scores are high. The concentration of *C. ocellata* is high, and the concentration of *C. fottii* (<20 μm) and *S. transylvanicus* is also

relatively high, although less so than the previous zone. The concentration of *C. fottii* (>20 μ m) decreases distinctly.

In Zone D-8 (214–118 cm, ca. 2,000–1,400 cal yr BP), diatom concentration is low. In Zone D-8a (214–199 cm, ca. 2,000–1,900 cal yr BP), the abundance of small, epilimnetic *C. minuscula* is high (ca. 35%), and diatom PCA Axis 1 scores are high. In Zone D-8b (199–118 cm, ca. 1,900–1,400 cal yr BP), the abundance of hypolimnetic *C. fottii* (ca. 50–60%) increases at the expense of epilimnetic *C. ocellata* (ca. 20–30%) and *C. minuscula* (ca. 5–15%), matching with decreased diatom PCA Axis 1 scores.

In Zone D-9 (118–0 cm, ca. 1,400 cal yr BP–present), the concentration of epilimnetic taxa increases. The abundance of epilimnetic *C. ocellata* (ca. 30–50%) and *C. minuscula* (ca. 15–30%) increase at the expense of hypolimnetic *C. fottii* (ca. 20–40%), matching with increased diatom PCA Axis 1 scores.

5.2 Diatom interpretation and comparison with other cores in Lakes Ohrid and Prespa

In deep, ancient Lake Ohrid, preliminary analysis of diatoms in the DEEP site Hole 1C (Wagner et al., 2014) and Hole 1B (see Chapter 7 below) shows the consistent domination of plankton during ~MIS 31–1 and the frequent occurrence of non-planktonic taxa during > MIS 31, which suggests that no major lake-level change occurs during the past about 1 million years or, unlike shallower Mediterranean lakes, lake-level change is not a major driver of shifts in diatom composition. In the Lateglacial-Holocene sequence Co1262, changes in the relative abundance of epilimnetic and hypolimnetic planktonic diatom taxa can be interpreted in terms of lake productivity, and this is supported by results of diatom analysis during the last glacial-interglacial cycle in core Co1202 (ca. 136 ka to present; Reed et al., 2010) and also over the last half century in a short core Sv09 (ca. 1949–2009 AD; Lorenschat et al., 2014). Diatom PCA Axis 1 scores in core Co1262 vary clearly according to the relative abundance of epilimnetic taxa, with high positive scores with the dominance of epilimnetic taxa and high negative scores in zones of low-diversity hypolimnetic C. fottii dominance. Variation in the absolute concentration of total diatoms and main epilimnetic and hypolimnetic taxa can also be interpreted coherently in terms of productivity in this deep lake, and this is supported by results of diatom analysis in core 9 (ca. MIS 3–1; Roelofs and Kilham, 1983). Fig. 5.3 shows comparison of diatoms with sedimentological, geochemical

and isotopic data from the same core, and Fig. 5.4 shows comparison with diatoms in core Lz1120 and catchment pollen signal from cores Lz1120 and Co1215.

5.2.1 The Lateglacial period (ca. 12,300–11,800 cal yr BP)

During the Lateglacial period (ca. 12,300–11,800 cal yr BP), extremely low diatom concentration and the low-diversity domination of endemic, hypolimnetic, oligothermic and oligophotic C. fottii (Stanković, 1960), along with low diatom PCA Axis 1 scores, correlate with low organic matter and carbonate content, and indicate low productivity as a consequence of low temperature. This interpretation is supported by the low-diversity C. fottii domination during MIS 2 in core Co1202 (Reed et al., 2010) and core 9 (Roelofs and Kilham, 1983). The regular distribution (ca. 8% abundance) of pioneering, facultative planktonic fragilaroid taxa (S. pinnata and P. brevistriata) probably corresponds to cold waters with the occurrence of ice cover (Schmidt et al., 2004), which is in accord with the deposition of ice-rafted debris and the inference of low winter temperature (Wagner et al., 2012a). Low winter temperature would result in the high frequency and long duration of complete lake circulation usually occurring in severe winters (Stanković, 1960; Matzinger et al., 2006a), or Lake Ohrid was probably a dimictic lake during this period rather than oligomictic from the onset of the Holocene to the present (Roelofs and Kilham, 1983). This is consistent with a well-oxygenated water column inferred from high oxygen (O) index (Lacey et al., 2014). High $\delta^{13}C_{org}$ values indicate low soil-derived CO₂ input (Lacey et al., 2014), which is in accord with the wide distribution of steppic herb vegetation during the Younger Dryas in the northeastern Mediterranean region (Zhang et al., 2014; and references therein). However, high potassium (K) concentration suggests high clastic input (Wagner et al., 2012a), which is related to high erosion. In this phase of low temperature and lake ice cover, high external nutrient input and high mixing-induced nutrient supply are insufficient to stimulate the growth of epilimnetic taxa. The diatom-inferred low temperature during this period in Lake Ohrid is coherent with pollen-based quantitative temperature reconstruction during the Younger Dryas in Lake Maliq, Albania (Bordon et al., 2009) and SL152, northern Aegean Sea (Kotthoff et al., 2011).



same core.



Fig. 5.5 Comparison of diatoms in core Co1262 with diatom data from core Lz1120 (Wagner et al., 2009) and pollen data from Ohrid core Lz1120 (Wagner et al., 2009) and Prespa core Co1215 (Aufgebauer et al., 2012; Panagiotopoulos et al., 2012).

5.2.2 Early Holocene I (ca. 11,800–10,600 cal yr BP)

Between ca. 11,800–10,600 cal yr BP, despite low diatom concentration, a distinct increase in the abundance of small ($3-5 \mu m$), epilimnetic *C. minuscula*, along with slightly increased diatom PCA Axis 1 scores, is consistent with increasing organic matter content, and suggests a slight increase in lake productivity possibly due to increasing temperature. Despite the continuous dominance of hypolimnetic C. fottii in the diatom composition, facultative planktonic taxa become rare (<5% abundance), probably corresponding to a prolonged ice-free period, which is consistent with the disappearance of ice-rafted debris deposition since ca. 11,300 cal yr BP (Wagner et al., 2012a). There was a distinctly expanding trend of temperate forest in the catchment during this period at the expense of herb vegetation in core Co1215, Lake Prespa (Aufgebauer et al., 2012); however, along with increased water inflow due to a distinct increase in precipitation and effective moisture during the earliest Holocene in the northeastern Mediterranean region (Zhang et al., 2014; and references therein), high K concentration in core Co1262 (Wagner et al., 2012a) implies high erosion and external nutrient input. This is also consistent with low $\delta^{13}C_{org}$ values which suggest high soil-derived CO_2 input (Lacey et al., 2014). Increased TS content and low TOC/TS ratio, along with decreasing O index values (Lacey et al., 2014), indicate an oxygen-depleted, stratified water column during this period. Climate warming and increasing lake surface temperature would result in thermal stratification, less frequent complete circulation (Matzinger et al., 2006a) and even decreased maximum mixing depth (Matzinger et al., 2007). Thermal stratification then results in increased sinking velocities and thus actuates small-sized planktonic taxa with low sinking rates (Winder et al., 2009; Catalan et al., 2013), which provides a viable interpretation for the increase in the abundance of small, epilimnetic C. *minuscula*. In the light of high external nutrient input, reduced nutrient redistribution into the epilimnion may not serve as a factor of increased small C. minuscula abundance during this phase. In Lake Ohrid, the diatom-inferred Lateglacial–Holocene transition in core Co1262 is stronger than core Co1202 (Reed et al., 2010); however, this transition is muted compared to the marked diatom shifts observed in shallower southern Balkan lakes such as Lake Ioannina (Wilson et al., 2008; Jones et al., 2013), Lake Prespa (Cvetkoska et al., 2014a) and Lake Dojran (Zhang et al., 2014), driven by a distinct increase in lake level and moisture availability. Diatom concentration, indicative of temperature-induced productivity, is also low during the earliest Holocene in Lake Baikal (a deep, ancient, oligotrophic, and meromictic lake; Shimaraev et al., 1994), with an increase starting at ca. 10,500 cal yr BP (core CON01-605-3: 675 m water depth, data from Morley et al., 2005, age model revised by

Mackay et al., 2011; core VER92-2 GC-24: 355 m water depth, data from Karabanov et al., 2004, age model revised by Prokopenko et al., 2007; core 305-A5: 290 m water depth, data from Bradbury et al., 1994, age model revised by Prokopenko et al., 2007). Bradbury et al. (1994) suggested that this may be related to reduced lake transparency caused by high river runoff bringing in more clastic material in Lake Baikal, which is consistent with high K concentration and low $\delta^{13}C_{org}$ values at this time in Lake Ohrid and also with the growth of small-sized diatoms (i.e. *C. minuscula*) that possess high light absorption efficiency (Finkel et al., 2009). However, this interpretation is not likely to be fit for Lake Ohrid, because diatom composition and concentration at this time are similar to the Lateglacial period in Lake Ohrid.

5.2.3 Early Holocene II (ca. 10,600–9,500 cal yr BP)

Between ca. 10,600–9,500 cal yr BP, high abundance of epilimnetic taxa, comprising C. ocellata between ca. 10,600–10,200 cal yr BP and C. minuscula between ca. 10,200–9,500 cal yr BP, along with relatively high diatom PCA Axis 1 scores, indicates relatively high productivity. This is also indicated by consistently high C. minuscula concentration during this period. This is coincident with the establishment of maximum temperate forest vegetation (mainly oaks) in the catchment, which is indicated by distinctly increased percentage and accumulation rate of *Quercus* pollen in core Co1215, Lake Prespa (Aufgebauer et al., 2012; Panagiotopoulos et al., 2012). Catchment erosion and external nutrient input are thus possibly low, probably due also to high seasonality and lower moisture during the early Holocene in the northeastern Mediterranean region (Zhang et al., 2014; and references therein). High TS content and low TOC/TS ratio possibly indicate strong thermal stratification, and thus mixing-induced nutrient supply is low as well. Thus consistently high C. minuscula concentration during this period is possibly due to high stratification and/or low nutrient availability, as small-sized planktonic taxa have low sinking rates but also have high efficiency of nutrient uptake (Winder et al., 2009). This may result from climate warming and increasing lake surface temperature, which leads to enhanced thermal stratification, less frequent complete circulation and even weaker partial circulation in cold winters (Matzinger et al., 2006a, 2007). Relatively high abundance of epilimnetic, mesotrophic C. ocellata (Lorenschat et al., 2014) between ca. 10,600–10,200 cal yr BP is consistent with relatively high diatom concentration (comprising both epilimnetic and hypolimnetic taxa) and distinctly increased organic matter content, as a result of increased temperature. High abundance of small, epilimnetic C. minuscula between ca. 10,200–9,500 cal yr BP is consistent with high C.

minuscula concentration and increased carbonate content, as a result of increased temperature. Relatively low organic matter content between ca. 10,200–9,500 cal yr BP is possibly due to the dilution from carbonates. Low concentration of *C. ocellata* and *C. fottii* might result from the sedimentation of phosphorus that is absorbed onto the surface of precipitating carbonate particles (Allen and Ocevski, 1976), which aggravates the deficiency of nutrients and leads to the high abundance of small *C. minuscula* at the expense of *C. ocellata*.

5.2.4 Early Holocene III (ca. 9,500–8,500 cal yr BP)

Between ca. 9,500–8,500 cal yr BP, high concentration of epilimnetic C. ocellata and hypolimnetic C. fottii, together with high mesotrophic C. ocellata abundance, is consistent with high organic matter content, and indicates high productivity. This is coincident with decreased K concentration in the same core (Wagner et al., 2012a) and the establishment of maximum forest vegetation in the catchment in core Co1215, Lake Prespa (Aufgebauer et al., 2012; Panagiotopoulos et al., 2012), which indicate low erosion and low nutrient input (see details below). Decreasing TS content and distinctly increased TOC/TS ratio possibly indicate enhanced lake circulation, and thus pulsed nutrient supply may contribute to the high abundance and concentration of epilimnetic, mesotrophic C. ocellata. This may be attributed to an increase in total lake temperature rather than a decrease in winter surface temperature. The lake-water equilibrium at high temperature would result in frequent complete circulation due to increased thermal expansivity (Matzinger et al., 2006a). High hypolimnetic C. fottii concentration may result from high spring temperature, high light availability and/or high nutrient upward transport (see details below). An increase in the abundance and concentration of hypolimnetic, mesotrophic S. transylvanicus (previously designated as S. astraea var. intermedia Fricke, Roelofs and Kilham, 1983; S. neoastraea Håkansson & Hickel, Wagner et al., 2009; and S. galileensis Håkansson & Ehrlich, Reed et al., 2010) between ca. 9,000–8,500 cal yr BP coincides with increased carbonate content. This probably indicates increased summer productivity, as carbonate precipitation in Lake Ohrid occurs mainly in summer (Matzinger et al., 2007). The increase in the abundance and concentration of S. transylvanicus also corresponds with the Mercato tephra layer at around 9,000 cal yr BP, but the tephra effect is negligible as it may be important only for a very short time period (Lotter et al., 1995), and there is no evidence for the influence of the Mercato eruption on diatom composition in core Co1202, Lake Ohrid (Cvetkoska et al., 2012).

5.2.5 The 8.2 ka event (ca. 8,500–8,200 cal yr BP)

Between ca. 8,500–8,200 cal yr BP, low hypolimnetic C. fottii and S. transylvanicus concentration, which corresponds with low abundance of hypolimnetic taxa, is consistent with low organic matter and carbonate content. Low organic matter and/or carbonate content is also shown in other cores of Lakes Ohrid and Prespa (Lz1120, Co1204 and Co1215) (Wagner et al., 2009, 2010; Aufgebauer et al., 2012), and this may result from low productivity, high organic matter degradation/carbonate dissolution and/or dilution from high clastic input. Low concentration of endemic C. fottii indicates low productivity, which results probably from low temperature and/or low light availability rather than low nutrient supply (see below). Higher O index values indicate a more oxygenated water column (Lacey et al., 2014), which, despite low productivity and low dissolved oxygen consumption in the deep water, is possibly due to frequent complete circulation due to low winter temperature (Stanković, 1960; Matzinger et al., 2006a). Nutrient redistribution into the epilimnion due to intense mixing results in the peak abundance and concentration of epilimnetic, mesotrophic C. ocellata and peak diatom PCA Axis 1 scores at ca. 8,400 cal yr BP, and this is consistent with high C. ocellata abundance at ca. 8,400 cal yr BP in core Lz1120, Lake Ohrid (Wagner et al., 2009). High $\delta^{13}C_{org}$ values suggest low soil-derived CO₂ input (Lacey et al., 2014), which is consistent with a small peak of herbs in cores Lz1120 and Co1215 (Wagner et al., 2009, 2010; Aufgebauer et al., 2012; Panagiotopoulos et al., 2012). High K concentration suggests high clastic input (Wagner et al., 2012a), which is also shown in core Co1215 (Aufgebauer et al., 2012) and is consistent with high magnetic susceptibility in core Lz1120 (Wagner et al., 2009). Thus, high clastic input and decreased lake transparency possibly result in the relatively high abundance and concentration of small, epilimnetic C. minuscula at this time, as small-sized planktonic taxa have high light absorption efficiency (Finkel et al., 2009; Winder et al., 2009). This is consistent with the peak of *C. minuscula* abundance in core Co1215, Lake Prespa (Cvetkoska et al., 2014a). This interpretation of light limitation is supported by the finding of increased C. minuscula abundance in the mass wasting deposit (see below). The diatom-inferred low winter temperature in Lake Ohrid is coherent with pollen-based quantitative temperature reconstruction in Lake Maliq, Albania (Bordon et al., 2009) and Tenaghi Philippon, northeastern Greece (Pross et al., 2009) as well as larger temperature anomaly in winter than in summer in SL152, northern Aegean Sea (Dormoy et al., 2009).

5.2.6 The mid Holocene (ca. 8,200–2,700 cal yr BP)

During the mid Holocene (ca. 8,200–2,700 cal yr BP), high hypolimnetic C. fottii and S.

transylvanicus concentration, which is in line with high abundance of hypolimnetic taxa, is consistent with high carbonate content and relatively high organic matter content. High abundance of hypolimnetic C. fottii and S. transylvanicus is also shown during this period in core Lz1120, Lake Ohrid (Wagner et al., 2009). Coeval high carbonate and organic matter content during the mid Holocene is shown in cores Co1202, Lake Ohrid (Vogel et al., 2010) and Co1215, Lake Prespa (Aufgebauer et al., 2012). TIC (total inorganic carbon) content is ca. 2.5–4.5 times higher than TOC (total organic carbon) content during the mid Holocene in the three cores (Lz1120, Co1202 and Co1262) of Lake Ohrid (Wagner et al., 2010, 2012a). Carbonate precipitation in the water column in Lake Ohrid occurs mainly in summer (Matzinger et al., 2007), and thus, given the dominance of authigenic carbonates (Wagner et al., 2008), high carbonate content during this period indicates high summer temperature and high summer productivity. Given the dominant algal source of organic matter (Lacey et al., 2014) and the similar summer and winter sedimentation of organic matter (Matzinger et al., 2007), organic matter content during this period in core Co1262 is largely regulated by degradation and/or dilution from carbonates, although organic degradation is not clearly indicated in cores Lz1120 and Co1202 from less than 150 m water depth. Endemic C. fottii in Lake Ohrid thrives and dominates the phytoplankton in the water column in spring (Stanković, 1960; Ocevski and Allen, 1977; Petrova et al., 2008), and thus high C. fottii concentration during this period indicates high spring productivity possibly due to high spring temperature, high light availability and/or high nutrient supply that follows enhanced winter circulation and/or more external nutrient input. Although low $\delta^{13}C_{org}$ values suggest high soil-derived CO₂ input (Lacey et al., 2014), low K concentration suggests low clastic input (Wagner et al., 2012a), which is also shown in core Co1215 (Aufgebauer et al., 2012) and is consistent with low minerogenic input indicated by low magnetic susceptibility in core Lz1120 (Wagner et al., 2009). This is consistent with a densely-vegetated catchment indicated by pollen data in cores Lz1120 and Co1215 (Wagner et al., 2009; Panagiotopoulos et al., 2012). Thus, external nutrient input is low, which is consistent with diatom-inferred low trophic state during the mid Holocene in shallow, monomictic Lake Prespa (Cvetkoska et al., 2014a). In deep, oligomictic Lake Ohrid, relatively low concentration and abundance of epilimnetic, mesotrophic C. ocellata, occurring in spring and summer (Stanković, 1960), may result from less frequent complete circulation and weaker circulation due to high winter temperature (Matzinger et al., 2006a, 2007), which reduce nutrient availability in the epilimnion. Thermal stratification is supported by oxygen depletion indicated by low O index values (Lacey et al., 2014). Moreover, in line with high carbonate precipitation, more nutrients such as

phosphorus are lost from the epilimnion through the carbonate scavenging effect (Allen and Ocevski, 1976; Roelofs and Kilham, 1983).

5.2.7 Late Holocene I (ca. 2,700–2,000 cal yr BP)

During the first part of late Holocene (ca. 2,700–2,000 cal yr BP), high concentration (and abundance) of epilimnetic, mesotrophic C. ocellata and relatively high concentration of hypolimnetic taxa comprising C. fottii (<20 µm) and S. transylvanicus are consistent with high carbonate content and relatively high organic matter content. Relatively high *C. ocellata* abundance is also shown during this period in core Lz1120, Lake Ohrid (Wagner et al., 2009). This is probably due to climate change rather than human impact, as anthropogenic deforestation shown by pollen data in cores Lz1120 and Co1215 is coincident with a distinct decrease in carbonate and organic matter content (Wagner et al., 2009; Aufgebauer et al., 2012), while changes in diatom composition and concentration during this period occur before the distinct decline of carbonate and organic matter content. As discussed above, high carbonate precipitation indicates high summer temperature and high summer productivity, and meanwhile stimulates high phosphorus sedimentation in summer. Low K concentration indicates low clastic input (Wagner et al., 2012a), which also suggests low nutrient input, as clastic input (K concentration) is correlated with minerogenic input (magnetic susceptibility in core Lz1120; Wagner et al., 2009) and allochthonous phosphorus input is mainly of inorganic, apatite-bound form (Matzinger et al., 2007). Thus, epilimnetic, mesotrophic C. ocellata may occur mainly in spring during this period. High C. ocellata concentration (and abundance) along with relatively high C. fottii (<20 µm) and S. transylvanicus concentration indicates high spring productivity, which results largely from enhanced winter complete circulation and nutrient upward transport into the epilimnion due to decreased winter temperature, as high spring temperature and/or high light availability actuate C. fottii rather than C. ocellata during the mid Holocene (see above). It can be deduced that, decreased C. fottii (>20 µm) concentration (and abundance) suggest that larger C. fottii form might always exist in the hypolimnion and rarely occur in the surface layer.

5.2.8 Late Holocene II (ca. 2,000–1,400 cal yr BP)

Between ca. 2,000–1,900 cal yr BP, extremely low diatom concentration is consistent with drastically decreased carbonate and organic matter content, which coincides with high K concentration (Wagner et al., 2012a) and the onset of deforestation in the catchment from pollen data in cores Lz1120 and Co1215 (Wagner et al., 2009; Panagiotopoulos et al., 2012).

Low carbonate and organic matter content may result from low productivity, high organic matter degradation/carbonate dissolution and/or dilution from high clastic input. High O index indicates a well oxygenated condition (Lacey et al., 2014), which may result from low productivity and low dissolved oxygen consumption in the deep layer and/or frequent winter complete circulation (Matzinger et al., 2006a, 2007). Low concentration of both epilimnetic and hypolimnetic planktonic taxa indicates low productivity, and this is not in accord with human-induced deforestation and high nutrient input and/or probably temperature-induced frequent complete circulation and nutrient upward transport. However, high clastic input may restrain diatom growth through reducing light availability, and decreased water clarity advocates the high relative abundance of small, epilimnetic C. minuscula, as small-sized planktonic taxa have high efficiency of light absorption (Finkel et al., 2009; Winder et al., 2009). This is consistent with extremely low diatom concentration and increased C. minuscula relative abundance in the mass wasting deposit (see below). This human-induced short-term event may be due to the construction of an ancient Roman road Via Egnatia between 146–120 BC, which ran through many nations and important cities in modern Albania, Macedonia, Greece and European Turkey (Lolos, 2007), and could feasibly have caused ca. 100 years' impact on water clarity and nutrient status. This event is not shown in core Co1202 near the city of Ohrid that is one of the key sites along the Via Egnatia, and thus the influence of this event might also be related with a distinctive local geomorphology of fault-controlled staircase-like landscapes and steep subaquatic slopes close to the Lini Peninsula, described in Hoffmann et al. (2010), Reicherter et al. (2011) and Wagner et al. (2012a).

Between ca. 1,900–1,400 cal yr BP, low diatom concentration, along with relatively low abundance of epilimnetic taxa (*C. ocellata* and *C. minuscula*), is consistent with relatively low carbonate and organic matter content. Low diatom concentration and low abundance of epilimnetic *C. ocellata* and *C. minuscula* (previously designated as *Discostella stelligera* (Cleve & Grunow) Houk & Klee, Wagner et al., 2009) are also shown between ca. 1,900-1,200 cal yr BP in core Lz1120, Lake Ohrid (Wagner et al., 2009). This is coincident with relatively high K concentration in core Co1262 (Wagner et al., 2012a) and low abundance of arboreal pollen in core Lz1120 (Wagner et al., 2009). Relatively low carbonate and organic matter content results probably from relatively low productivity and/or anthropogenic deforestation and associated relatively high clastic input. Relatively high nutrient input is possibly a concomitant circumstance, but low diatom concentration and relatively low abundance of

epilimnetic taxa indicate low productivity particularly in the epilimnion. This is probably attributed to high sediment accumulation rate and reduced nutrient recycling due to enhanced stratification that is clearly indicated by high TS content as well as generally low O index (Lacey et al., 2014). The AD 472/512 tephra deposition and an earthquake-induced mass wasting deposit overlie this zone (Wagner et al., 2012a). Diatoms are also found in this mass wasting deposit, but diatom concentration is very low, and common facultative planktonic and benthic taxa (ca. 15% abundance) may have been transferred from the littoral zone. The abundance of epilimnetic *C. ocellata* in the mass wasting event is lower than its underlying and overlying zones, increased abundance of small, epilimnetic *C. minuscula* is comparable with the overlying zone, and hypolimnetic *C. fottii* is at a decreasing abundance between the underlying and overlying zones. Increased *C. minuscula* abundance, along with lower *C. ocellata* abundance, is possibly due to light limitation that is related to massive clastic input at the time of earthquake(s) in the early 6th century.

5.2.9 Late Holocene III (ca. 1,400–0 cal yr BP)

Following the AD 472/512 tephra and earthquake-induced mass wasting deposit (after ca. 1,400 cal yr BP), increased abundance of epilimnetic C. ocellata and C. minuscula at the expense of hypolimnetic C. fottii, in accord with increased C. ocellata and C. minuscula concentration, indicates high productivity in the epilimnion. The influence of volcanic eruption on diatom composition is very short in duration (Lotter et al., 1995), and no significant change in diatom morphology corresponding to the AD 472/512 tephra layer is shown in core Co1202 (Cvetkoska et al., 2012); the occurrence of decreased C. ocellata abundance in the mass wasting deposit, in reference to the increase in C. minuscula abundance, is not an artefact of the intrusion of littoral non-planktonic taxa. Thus changes in diatom composition during this period are not possibly driven by the AD 472/512 volcanic eruption and earthquake-induced mass movement. Moreover, this is possibly consistent with increasing diatom concentration and increased abundance of epilimnetic C. ocellata and C. minuscula after ca. 1,200 cal yr BP in core Lz1120 (Wagner et al., 2009), which is not affected by mass movement. In the light of marked fluctuations of carbonate content during this period, it is decomposition that plays a major role in the consistently relatively low organic matter content. The increase in the abundance and concentration of epilimnetic taxa in core Co1262 also coincides with decreased K concentration in the same core (Wagner et al., 2012a) and increased catchment forest vegetation in core Lz1120 (Wagner et al., 2009), and thus erosion is reduced along with relatively low clastic and soil-derived nutrient input.

Increasing O index suggests a more oxygenating condition (Lacey et al., 2014), which is in line with low TS content and high TOC/TS ratio and may result from accelerating lake circulation, and thus nutrient redistribution into the epilimnion may contribute to the increase in the abundance and concentration of epilimnetic taxa. Meanwhile, diatom data in core Co1215 show that the trophic and water level in Lake Prespa was unstable during this period (Cvetkoska et al., 2014a) and peak carbonate oxygen isotope values around 1,000 cal yr BP, along with the location of historical settlements, indicate very low Prespa lake level (Leng et al., 2013). The lake-level decline and eutrophication in Lake Prespa may result in increased phosphorus delivery to Lake Ohrid through karstic channels (Matzinger et al., 2006b) and have a profound effect on diatom composition as revealed in a short core Sv09 near Sveti Naum springs (Lorenschat et al., 2014). Nutrient transport from Lake Prespa and mixing-induced nutrient upward transport in Lake Ohrid thus advocate the growth of mesotrophic epilimnetic *C. ocellata*, and small *C. minuscula* benefits from reduced light availability possibly due to eutrophication in Lake Ohrid.

5.3 Summary

The diatom relative abundance and concentration data from core Co1262, Lake Ohrid, supported by extant sedimentological and geochemical data from the same core and sedimentological, geochemical, pollen and diatom data from other cores in Lake Ohrid and hydraulically-linked Lake Prespa, provide a clear, thorough picture of Lateglacial and Holocene changes in lake productivity and temperature. During the Lateglacial period (ca. 12,300–11,800 cal yr BP), extremely low diatom concentration and hypolimnetic C. fottii domination in the diatom composition indicate low productivity as a consequence of low temperature. During the earliest Holocene (ca. 11,800–10,600 cal yr BP), a distinct increase in the abundance of small, epilimnetic *C. minuscula* suggests slightly increased productivity due to climate warming. Between ca. 10,600–9,500 cal yr BP, high C. minuscula concentration and high abundance of epilimnetic taxa indicate relatively high productivity as a result of increased temperature. Between ca. 9,500–8,500 cal yr BP, high concentration of epilimnetic C. ocellata and hypolimnetic C. fottii, together with high C. ocellata abundance, indicates high temperature and high productivity. The diatom data reveal a gradual warming process during the early Holocene. The 8.2 ka cold event is clearly indicated by low hypolimnetic C. fottii and S. transylvanicus concentration, and epilimnetic C. ocellata and C. minuscula are probably promoted by high nutrient supply and low light availability, respectively. High hypolimnetic C. fottii and S. transylvanicus concentration indicates high

temperature and high productivity during the mid Holocene (ca. 8,200–2,700 cal yr BP), and low *C. ocellata* concentration and abundance result possibly from high thermal stratification and low erosion. Whereas, high *C. ocellata* concentration and abundance between ca. 2,700–2,000 cal yr BP are probably due to decreased winter temperature and increased lake circulation. This is followed by a human-induced event between ca. 2,000–1,900 cal yr BP, characterised by extremely low diatom concentration and high *C. minuscula* abundance. Low diatom concentration and relatively low abundance of epilimnetic taxa between ca. 1,900–1,400 cal yr BP are related to anthropogenic deforestation and high sediment accumulation rate. After the earthquake-induced mass movement, increased abundance and concentration of epilimnetic *C. ocellata* and *C. minuscula* indicate eutrophication in Lake Ohrid, possibly due to mixing-induced nutrient upward transport and nutrient transport from Lake Prespa.

Chapter 6 Recent anthropogenic impact on Lake Ohrid

This chapter uses diatoms from a short sediment core Sv09 near Sveti Naum springs in southeastern Lake Ohrid and compares with ostracod data from the same core to assess the influence of nutrient supply through springs from Lake Prespa on changes of productivity in the southeastern part of Lake Ohrid. This chapter also compares with monitoring data for water-level change in Lake Prespa and its eutrophication due to human activity, to assess whether Lake Prespa drive changes in Lake Ohrid in the recent past.

6.1 Diatom results

A total of 274 diatom taxa was identified from the short core Sv09 near Sveti Naum springs in the southeastern part of Lake Ohrid. The majority are endemic to Lake Ohrid, Little Lake Sveti Naum (700 m long, 250 m wide, and 3.5 m deep; Fig. 6.1 and 6.2) and Lake Prespa (Levkov et al., 2007), underlining the high biodiversity value of this ancient lake system. Since benthic taxa were very diverse but only present at low abundance, 24 groups and complexes (Fig. 6.3) were established by combining species with similar morphological features and apparent ecological preferences. For example, although *Gomphonema olivaceum* (Hornemann) Kützing complex lacks stigmata in the central area and a stigma is present in the central area of *Gomphonema minutum* (Agardh) Agardh, *Gomphonema pumilum* (Grunow) Reichardt & Lange-Bertalot, *Gomphonema parvulum* (Kützing) Kützing and *Gomphonema angustum* Agardh complexes, they are combined into a 'Gomphonema spp.' group. *Navicula*, *Placoneis*, *Sellaphora*, *Fallacia*, *Luticola*, *Cavinula*, *Eolimna*, *Craticula*, *Aneumastus*, *Hippodonta*, *Geissleria* and *Prestauroneis* genera are combined into a 'Navicula sensu lato' group.

Four main diatom assemblage zones (Fig. 6.3) can be defined using CONISS. The quality of preservation is high, as indicated by the F index values for *Cyclotella fottii*. In Zone D-I (33–24 cm, ca. 1949–1965 AD), endemic, planktonic *Cyclotella fottii* Hustedt is dominant (20–40%), while planktonic, mesotrophic *Cyclotella ocellata* Pantocsek is at relatively low abundance (5–10%). Benthic *Amphora pediculus* (Kützing) Grunow is present consistently at low abundance (5%). Zone D-II (24–18 cm, ca. 1965–1976 AD) exhibits very low diatom concentrations. A peak in the abundance of planktonic *Cyclotella radiosa* (Grunow) Lemmermann at the expense of benthic taxa occurs at 24–22 cm depth, and is followed by an increase in the relative abundance of *A. pediculus*, *Staurosirella pinnata* (Ehrenberg) Williams & Round and *Navicula* sensu lato taxa with an associated reduction in the

abundance of *C. fottii*. Zone D-III (18–7 cm, ca. 1976–1996 AD) exhibits a gradually increasing diatom concentration, and an increase to 10-20% abundance throughout in *C. ocellata*. Zone D-IV (7–0 cm, ca. 1996–2009 AD) is marked by a trend towards the increasing abundance of *C. ocellata* at the expense of *C. fottii*, and there is an abrupt increase in diatom concentration towards the surface. The higher relative abundance of *A. pediculus* and *S. pinnata* is maintained throughout the depth of 22–0 cm.



Fig. 6.1 Sveti Naum surface spring water inflow in the southeastern tip of Lake Ohrid.



Fig. 6.2 Sveti Naum springs (Little Lake Sveti Naum).



Fig. 6.3 Summary diatom diagram of 'Sveti Naum' short core Sv09, showing diatom concentration and F index values for endemic Cyclotella fottii.



Fig. 6.4 Summary ostracod diagram of 'Sveti Naum' short core Sv09 (modified from Lorenschat et al., 2014).



Fig. 6.5 Comparison of shifts in diatom composition, diatom and ostracod concentrations in core Sv09 with lake-level monitoring data for Lake Prespa (Popovska and Bonacci, 2007; Popovska, 2011), with solid-line boundaries defined by diatoms and dashed lines defined mainly by ostracod concentration.

6.2 Diatom interpretation and comparison with ostracod data from the same core and lake-level monitoring data for Lake Prespa

Relatively low diatom concentration in Zone D-I along with relatively low abundance of mesotrophic *C. ocellata* indicates relatively low productivity in the southeastern part of Lake Ohrid, with little nutrient input from Lake Prespa in the 1950s and early 1960s. Lake Prespa underwent a relatively high water-level phase between 1950 and 1962 (Popovska and Bonacci, 2007; Popovska, 2011), which reduced nutrient enrichment in Lake Prespa. This effect on less nutrient input to Lake Ohrid would 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 Galicica and Mali i Thate mountain range precipitation (Popovska and Bonacci, 2007). Juvenile valves of the ostracod *Prionocypris zenkeri* Chyzer & Toth are found only in this zone (Lorenschat et al., 2014). This species prefers waters connected to springs (Meisch, 2000) and was probably imported from the springs of Sveti Naum into the lake (Lorenschat et al., 2014).

The peak in the abundance of C. radiosa in the lower part of Zone D-II corresponds with an abrupt lake-level increase in Lake Prespa in 1963 (Popovska and Bonacci, 2007; Popovska, 2011), which increased the subterranean water flow into Lake Ohrid but largely decreased nutrient concentration (Matzinger et al., 2006a). The higher-energy flow may cause decreased productivity, decreased sediment accumulation rate and decreased diatom preservation in this part of Lake Ohrid. The age model shows no clear change of sediment accumulation rate (Lorenschat et al., 2014), and the F index of endemic C. fottii does not show evidence of increased diatom dissolution. Thus the very low diatom concentration does support a decline in productivity. Increased subterranean inflow may have resulted in small-sized diatoms such as A. pediculus and S. pinnata being less likely to settle out of the water column, and small forms of diatoms are also known to be vulnerable to sediment focusing (Biskaborn et al., 2013); this would explain their decrease in relative abundance, with a concomitant increase in large forms of C. radiosa and C. fottii in the sediment. In the late 1960s and early 1970s, there was a slowly decreasing trend in the Prespa lake level, and decreasing subterranean water flow and increasing nutrient concentration possibly triggered the production and deposition of small A. pediculus and S. pinnata in this part of Lake Ohrid, as shown in the upper part of Zone D-II.

Since the mid 1970s, there has been an accelerated, fluctuating lake-level decline in Lake

Prespa, and the most dramatic decrease of 5–6 m occurred between 1987 and 1995 (Popovska, 2011). Models suggest that lake-level lowering of Lake Prespa by less than 20 m can increase the nutrient concentration of this lake and lead to increased nutrient input via springs to Lake Ohrid, in spite of a decrease in underground flow (Matzinger et al., 2006a). Lake Prespa itself was undergoing eutrophication at the time, amplifing the effects of the lake-level decrease (Matzinger et al., 2006a). The lake-level drop and nutrient increase in Lake Prespa were mainly attributed to intensified agriculture and associated water abstraction, fertilizer utilisation and enhanced soil erosion (Matzinger et al., 2006a). The increase in the abundance of mesotrophic C. ocellata, along with increasing diatom concentration, is consistent with the effects of accelerated nutrient input to Lake Ohrid. However, it seems that, in the highly oligotrophic condition of Lake Ohrid, the subtle changes of nutrients have no clear effect on the endemic hypolimnetic species C. fottii. The diatom data do not show an oscillation of nutrient input linked to the renewed water-level rise in Lake Prespa between 1979–1986 and the dramatic decline between 1987–1995. However, a distinct increase in ostracod concentration shows a response to this lake-level decline in Lake Prespa.

From ca. 1996 AD on, the further increase in the abundance of epilimnetic *C. ocellata* is mainly the result of the overall decreasing trend of the Prespa lake level (Popovska, 2011) and the further increasing trend of the Ohrid nutrient input (Matzinger et al., 2006a). The decrease in the relative abundance of hypolimnetic *C. fottii* is possibly an artifact of increased *C. ocellata* abundance, and is also possibly due to increased production of green and/or blue-green algae in the surface layer (the top 20 m) and reduced light availability at great depths (Allen and Ocevski, 1976; Matzinger et al., 2006b). High *C. ocellata* abundance and low *C. fottii* abundance since ca. 2000 AD is correlated with very low Prespa lake level. Meanwhile, the ostracod concentration has a distinct increase, and the diversity of ostracod species reaches a maximum.

The diatom record in core Sv09 does not show clear changes for the major eutrophication, but there has been an increasing trend in nutrient concentration and productivity in southeastern 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 the estimates from a simple linear model give an increase in TP concentration from ca. 3.7 g l⁻¹ in the mid 1960s to ca. 4.8 g l⁻¹ in the late 2000s decade (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 core Sv09 occur ca. 1–2 years later than the changes of water level in Lake Prespa, probably because the average drainage time from Lake Prespa to the springs of Sveti Naum 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 Lake Prespa has an impact on diatom ecology across the lake as a whole.

6.3 Summary

The diatom and ostracod data from core Sv09 indicate an increasing trend in nutrient concentration and productivity in the southeastern part of Lake Ohrid, linked to the subterranean flow and associated nutrient supply from Lake Prespa. In the early 1970s, the increase in the abundance of small-sized benthic and facultative planktonic diatom taxa is correlated with slightly decreasing Prespa lake level and associated decreasing subterranean flow. Since the mid 1970s, the increase in the abundance of mesotrophic C. ocellata along with increasing diatom concentration indicates increased nutrient input, resulting largely from the gradual lake-level decline in Lake Prespa and the eutrophication. Increased ostracod concentration in the late 1980s shows a response to the dramatic decline of the Prespa lake level. High C. ocellata abundance and low C. fottii abundance in the first decade of the 21st century indicate high productivity, corresponding with low Prespa lake level; this is supported by increased ostracod concentration and maximum ostracod diversity. This study supports that, although Lake Ohrid is consistently in a highly oligotrophic state, human-induced lake-level decline in Lake Prespa and eutrophication of Lake Prespa have potential to exert a major influence on the productivity in the southeastern part of Lake Ohrid through springs and associated nutrient supply.

Chapter 7 Preliminary analysis of diatom response to glacial–interglacial cycles during the past more than 1.2 Ma in Lake Ohrid DEEP site Hole 1B

This chapter uses the preliminary diatom data from core catcher samples in the DEEP site Hole 1B and compares with shifts of total inorganic matter (TIC) content and particularly borehole logging spectral gamma ray data to generate a preliminary interpretation of diatom response to glacial–interglacial cycles during the past more than 1.2 Ma. This chapter is also important to assess the response of diatoms to temperature-induced productivity that is clearly indicated over the last glacial–interglacial cycle.

Preliminary diatom data were generated from core catcher samples at ca. 3 m resolution from two holes (1B and 1C) at the DEEP site. Four holes (1B, 1C, 1D and 1F) were drilled at the DEEP site, the maximum drilling depth is 569 m in Hole 1D, Hole 1F is 550 m, and Holes 1B (this study) and 1C (Skopje diatom laboratory; Wagner et al., 2014) are both 480 m long. With ongoing taxonomic revision by Z. Levkov (Skopje) of highly diverse *Cyclotella* species in the DEEP sequence, there are minor differences in nomenclature between the two holes but they show very strong correlation. Results of Hole 1B are shown here (Fig. 7.1). Diatoms are preserved throughout apart from at the base of the hole (480–426 m). Five major diatom assemblage zones can be defined using CONISS, and marine isotope stages (MIS) are identified tentatively based on shifts in diatom composition and TIC (total inorganic carbon) and by comparison with the borehole logging spectral gamma ray data (Wagner et al., 2014) and the global stacked marine isotope record 'LR04' (Lisiecki and Raymo, 2005). Although tentative, the clear fluctuations in proxy data between glacial and interglacial stages allows a convincing estimate to be made of the definition of MIS throughout the record.

In Zone D-1 (480–426 m), no diatoms are observed in Hole 1B, and this is consistent with very rare diatoms present during this phase in Hole 1C (Wagner et al., 2014). Poor diatom preservation during this phase is correlated with the coarse grain-size distribution (Unit A in Fig. 7.1) and low TIC content, indicating a very shallow, lacustrine or fluvial state (Wagner et al., 2014). Diatoms are preserved above 426 m depth, and this corresponds to lithological Unit B of silty clay or clayey silt (Wagner et al., 2014). Planktonic taxa are consistently dominant throughout the uppermost 365 m (MIS 31–1), reflecting a stable, deep lake state. The section between 426 and 365 m depth is characterised by high abundance of facultative planktonic taxa and their domination at intervals of probably MIS 42, MIS 40–38 and MIS

34–32. High abundance of facultative planktonic taxa between 426 and 365 m depth and the plankton dominance starting approximately at MIS 43, MIS 37 and MIS 31, respectively, probably reflect fluctuating initial lake infilling, incorporating a long-term trend towards increased abundance of plankton. It seems that diatom response to glacial-interglacial cycles during the initial lake infilling stage (426–365 m) may overlie the signature of the infilling and is largely reflected in the changing ratio between planktonic and facultative planktonic taxa. The planktonic diatom flora in Zone D-2 (426–320 m) is characterised by transitions between cosmopolitan, probably epilimnetic Cyclotella species, comprising Cyclotella ocellata Pantocsek, Cyclotella cyclopuncta Håkansson & Carter, Cyclotella radiosa (Grunow) Lemmermann, Cyclotella distinguenda Hustedt and Cyclotella cf. kuetzingiana Thwaites (maybe small forms of Cyclotella prespanensis Cvetkoska). The peak of C. ocellata at 425 m depth, along with high TIC content, is correlated with MIS 43, and the peaks of C. cyclopuncta at 415 m and 400 m depth are correlated with MIS 41 and MIS 37, respectively. MIS 39 is not indicated by preliminary diatom and TIC data, but it is clearly shown in the spectral gamma ray data. The peak of C. radiosa at 385 m depth is correlated with MIS 35, the peak of C. distinguenda at 375 m depth is probably correlated with MIS 33, and the peak of C. cf. kuetzingiana at around 360 m depth, along with the highest TIC content, is correlated with MIS 31. Cyclotella cf. schumannii (Grunow) Håkansson is dominant at the upper boundary of Zone D-2, and along with a small peak of C. cf. kuetzingiana (20% abundance), is probably correlated with MIS 25. Cyclotella schumannii is a fossil to recent species found in oligotrophic lakes (Houk et al., 2010), and is possibly a hypolimnetic species in Lake Ohrid (see below). Cyclotella ocellata is dominant between MIS 31 and MIS 25, and peak abundances at 345 m and 330 m depth are probably correlated with MIS 29 and MIS 27, respectively. In summary, the response of planktonic diatoms to the interglacial climate in Zone D-2 is mainly indicated by the peaks of epilimnetic taxa. It should be noted that, high-frequency TIC fluctuations in Zone D-2 are probably attributed to the 41 ka obliquity cycle (Wagner et al., 2014).



glacial-interglacial cycles. Unit A: sand, silt, clay; Unit B: silty clay or clayey silt (Wagner et al., 2014).

Zone D-3 (320–240 m) is characterised by the domination of Cyclotella iris Brun & Héribaud. C. iris is mainly a fossil species found in oligotrophic waters (Krammer and Lange-Bertalot, 1991a), and it has similar morphological characteristics to C. schumannii, C. fottii Hustedt and C. hustedtii Jurilj. Thus, C. fottii, C. hustedtii, C. iris and C. schumannii are likely to have similar ecological niches. In common with the Lake Ohrid endemic taxon C. fottii (Simonsen, 1987a, 1987b, 1987c), C. iris and C. schumannii are likely to function as hypolimnetic species in Lake Ohrid. Zone D-3 is one of the least diverse period of the sequence, being dominated to >70% by C. iris between 320 and 260 m depth. This makes the definition of MIS difficult. MIS 21, MIS 19 and MIS 17 may be indicated by slightly higher *C. iris* abundance, but there is no apparent evidence in the preliminary diatom data for MIS 23. Epilimnetic Cyclotella species are at low abundance in this zone, and C. ocellata becomes dominant at the upper zone boundary. This zone exhibits a decrease in the TIC frequency, probably corresponding to the middle Pleistocene transition (MPT) with the dominant driver of the 41 ka obliquity cycle replaced by the 100 ka eccentricity cycle (Wagner et al., 2014). In Zone D-4 (240–160 m), C. cf. schumannii is renewed, and very small Cyclotella minuscula (Jurilj) Cvetkoska is frequent and even dominates at intervals inferred to represent the glacial stages of MIS 14 and MIS 12. High abundance of C. cf. kuetzingiana and C. prespanensis between 240 and 220 m depth is correlated with MIS 15. MIS 13 is correlated with the peak of C. iris at 205 m depth and subsequent peak C. cf. schumannii abundance between 200 and 190 m depth, and MIS 11 is correlated with high C. cf. schumannii abundance between 175 and 160 m depth. Zone D-5 (160–85 m) is characterised by high C. ocellata abundance, along with a generally decreasing trend of C. cf. schumannii abundance. The peak of Stephanodiscus parvus Stoermer & Håkansson at 150 m depth is correlated with the onset of MIS 9, and distinct peaks of C. cf. schumannii at 145 m and 130 m depth may be correlated with MIS 9e and MIS 9a, respectively. Peak C. ocellata abundance is correlated with MIS 8. MIS 7 is correlated with high C. iris abundance between 110 and 85 m depth, and MIS 7e and MIS 7a might be also identified. In summary, in Zones D-3, D-4 and D-5, diatom response to the interglacial climate is mainly indicated by the peaks of hypolimnetic taxa, while the peaks of epilimnetic C. ocellata and C. minuscula correspond with glacial stages. Zone D-6 (85–0 m) is characterised by the domination of *C. fottii* and *C. hustedtii*. Epilimnetic *C. ocellata* provides clear evidence for interglacial stages (MIS 5, MIS 3 and MIS 1) and high abundance of hypolimnetic taxa corresponds with glacial stages (MIS 6, MIS 4 and MIS 2), which are supported by the results of diatom response to the last glacial-interglacial cycle in core Co1202 spanning the last 136 ka (Reed et al., 2010). High C. ocellata abundance between 55 and 30 m depth is correlated

with MIS 5, and the peaks of *C. ocellata* at 20 m and 5 m depth are correlated with MIS 3 and MIS 1, respectively. Diatom response to MIS 3 is much more sensitive than TIC, and the spectral gamma ray data corresponding to MIS 3 are not easily interpreted.

In summary, initial infilling of Lake Ohrid is clearly revealed by preliminary diatom data from core catcher samples in the DEEP sequence spanning the last >1.36 Ma (the lower boundary age of MIS 43). The identification of marine isotope stages through TIC and diatoms is strongly supported by the borehole logging spectral gamma ray data. Diatom response to the glacial-interglacial cycles is complex, and this is associated with the evolution of diatoms, such as major shifts of C. iris at 320 m depth, C. cf. schumannii at 240 m depth, and C. fottii and C. hustedtii at 85 m depth probably representing key boundaries of evolution. During the initial lake infilling stage (426–365 m), diatom response to glacial-interglacial cycles is largely indicated by the ratio between planktonic and facultative planktonic taxa. In Zone D-2 (426–320 m, including the natural lake infilling stage), the response of planktonic diatoms to interglacials is mainly indicated by the peaks of epilimnetic taxa, and hypolimnetic species occur from nearly the upper zone boundary on. In Zones D-3, D-4 and D-5 (320–85 m), diatom response to interglacial stages appears to be indicated by the peaks of hypolimnetic species (C. iris or C. cf. schumannii), while the peaks of epilimnetic C. ocellata and C. minuscula during this interval correspond with glaciations. In Zone D-6 (85–0 m), epilimnetic C. ocellata provides clear evidence for interglacials, and high abundance of hypolimnetic taxa (C. fottii and C. hustedtii) corresponds with glacial stages. Diatom taxonomy and high-resolution diatom analysis in the next steps will assess the preliminary findings and explore the mechanisms of responses.

Chapter 8 Discussion

8.1 Comparison and integration of diatom responses to Younger Dryas and Holocene climate change in the contrasting types of lakes (Lakes Dojran and Ohrid)

Although Lakes Dojran and Ohrid (around $41^{\circ}10'$ N) are both ancient lakes in karstic basins and only 160 km apart, their limnological characteristics differ markedly. Lake Dojran is shallow (current maximum water depth 7 m) and currently eutrophic to hypereutrophic (minimum total phosphorus >50 µg l⁻¹), and Lake Ohrid is deep (maximum water depth 293 m) and highly oligotrophic (average total phosphorus 4.5 µg l⁻¹). Apart from direct precipitation and evaporation on lake surface, Lake Dojran receives water from small tributaries, and there is no surface outflow today, but it was possible through the Gjolaja River during previous phases of high lake level; Lake Ohrid is fed mainly by spring water inflow that is not affected by seasonality (Matzinger et al., 2006a), and surface outflow through the Crni Drim River is a primary component of the water balance. A comparison of inferred limnological change during the Lateglacial and Holocene affords the opportunity to assess the degree to which their response to environmental forcing differs according to differences in response thresholds, or may be the result of local rather than regional factors.

Shifts in diatom species assemblage composition in both the lakes exhibit a strong response to Younger Dryas and Holocene climate change, but clearly differ in their response thresholds. The clear shifts between planktonic and non-planktonic diatom taxa in Lake Dojran, which may be interpreted as indicative of lake-level change, demonstrate that the primary driver of limnological change in shallow Lake Dojran is that of shifts in moisture availability. In contrast, planktonic diatom taxa predominate throughout in Lake Ohrid, and shifts in diatom species assemblage composition appear to represent an indirect response to temperature change, which is more complex than temperature-induced productivity.

During the Lateglacial, in Lake Dojran, a plankton-dominated flora is replaced by facultative planktonic fragilaroid species at ca. 12,400 cal yr BP, and fragilaroid species are replaced by benthic taxa (mainly *Nitzschia* species) at ca. 12,000 cal yr BP. Macrophytes, the habitat of fragilaroid species, are possibly covered by organic sediment that inhibits the development of this species (Levkov and Stojanovski, 2002), linked to early nutrient enrichment in the shallow lake which favours eutrophic *Nitzschia* species (Levkov and Stojanovski, 2002). The dominance of eutrophic, halotolerant taxa and the sporadic occurrence of obligate saline
taxa between 12,000–11,500 cal yr BP indicate low lake level and increased evaporative concentration in a closed basin, clearly demonstrating Younger Drays aridity. Lake Dojran's high sensitivity to shifts in moisture availability is presumably due to a combination of its shallow, plate-shaped lake morphometry and the susceptibility of small inflow rivers to aridity. In the southern Balkans, diatom-inferred shallowing during the Younger Dryas is also indicated in shallow Lake Ioannina (Wilson et al., 2008) and Lake Prespa (Cvetkoska et al., 2014a). In contrast, in Lake Ohrid, despite the regular occurrence of facultative planktonic fragilaroid species between 12,300–11,800 cal yr BP, the low-diversity domination of planktonic Cyclotella fottii indicates high lake level and more importantly low temperature. Cyclotella fottii is a hypolimnetic, oligothermic and oligophotic species that is an opportunistic species that can extend its growth into the epilimnion when temperature is low, while thermophilic epilimnetic planktonic taxa do not survive extremely low temperature. The lack of diatom response to moisture change is presumably due to its extremely deep, tub-shaped lake morphometry, significant water storage capacity within the karstic Galicica and Mali i Thate Mountains to the east of the lake and naturally-adjustable surface outflow through the Crni Drim River in the north. Low diatom concentration in Lake Ohrid, indicative of low productivity, is consistent with low temperature during the Lateglacial. In Lake Dojran, diatom-inferred eutrophic state between ca. 12,000–11,500 cal yr BP, due to nutrient enrichment, is not consistent with low temperature-induced productivity; low diatom concentration between ca. 12,200–11,500 cal yr BP, compared to the peak between ca. 12,400–12,200 cal yr BP, is possibly related to low habitat availability in a turbid state. In summary, diatoms in the two contrasting types of lakes provide strong limnological evidence for coldness and aridity during the Younger Dryas in the southern Balkans, which is consistent with pollen-inferred low temperature and precipitation in Lake Malig (Bordon et al., 2009) and SL152 (Kotthoff et al., 2011), and also in accord with alkenone- and foram-inferred low sea surface temperature (SST) in MNB3, northern Aegean Sea (Gogou et al., 2007; Geraga et al., 2010). Meanwhile, this comparison highlights the importance of absolute concentration of planktonic diatom species in demonstrating in-lake productivity and the important role of habitat availability for the growth of benthic diatom taxa.

During the earliest Holocene, in Lake Dojran, the low-diversity domination of planktonic *Cyclotella ocellata* indicates high lake level between ca. 11,500–10,700 cal yr BP. Although climate warming and reduced ice cover drive the increase of *Cyclotella* species (Smol et al., 2005; Rühland et al., 2008), the low-diversity *C. ocellata* dominance is clearly an indication of

high lake level, and the transformation from a eutrophic, oligosaline state during the late Younger Dryas to a freshwater, oligotrophic-mesotrophic state needs an increase in precipitation rather than temperature. In Lake Ohrid, between ca. 11,800–10,600 cal yr BP, despite the C. fottii dominance, the increase in the abundance of small epilimnetic C. minuscula is attributed to climate warming and enhanced thermal stratification, favouring small-sized planktonic taxa with low sinking rates (Winder et al., 2009; Catalan et al., 2013). Diatom concentration remains low in both the lakes during this period. In Lake Ohrid, low diatom concentration is unlikely to relate to high runoff and clast-induced light restriction. It is possible that the warming is subtle, probably corresponding to foram-inferred slightly increased sea surface temperature (SST) between ca. 11,600–10,500 cal yr BP in MNB3, northern Aegean Sea (Geraga et al., 2010), and that low diatom concentration reflects relatively low temperature-induced productivity. In Lake Dojran, low diatom concentration results possibly from nutrient dilution rather than low temperature. In summary, climate warming and wetting are inferred from diatoms in the two contrasting lakes, and more importantly, this comparison clearly demonstrates that this period is hydrothermally distinct from the subsequent early Holocene (see below). Although the earliest Holocene is also distinct in the pollen record of SL152 (Kotthoff et al., 2008a), pollen assemblage composition is more likely the combined result of temperature and humidity. This comparison also confirms the importance of both relative abundance and absolute concentration data in diatom-based reconstruction.

During the early Holocene, in Lake Dojran, decreased *C. ocellata* abundance and high abundance of benthic taxa, along with increased abundance of fragilaroid species, indicate low lake level and moisture availability between ca. 10,700–8,500 cal yr BP, which is possibly due to high seasonality of precipitation (Zhang et al., 2014). In Lake Ohrid, high abundance of epilimnetic taxa between ca. 10,600–8,500 cal yr BP responds indirectly to the increase in temperature. Shifts of epilimnetic *C. minuscula* and *C. ocellata* abundance and concentration during this period are mainly related to temperature-induced mixing and nutrient availability in the epilimnion. Increasing lake surface temperature leads to enhanced thermal stratifcation, while high total lake temperature results in more frequent complete circulation (Matzinger et al., 2006a). High diatom concentration of both epilimnetic *C. ocellata* and hypolimnetic *C. fottii* between ca. 9,500–8,500 cal yr BP is an indication of high temperature and temperature-induced productivity, and this is in accord with high *C. ocellata* abundance. Despite the low trophic preference of *C. ocellata* and the highly oligotrophic state of Lake

Ohrid, compared to C. fottii, C. ocellata is an indicator of high nutrient concentration, which is supported by the increase in *C. ocellata* associated with eutrophication in the recent decades (Lorenschat et al., 2014). In Lake Dojran, along with lake-level reduction and nutrient enrichment, high diatom concentration indicates high productivity. High temperature could contribute to the lake-level reduction through increased evaporation, and could also contribute to the high abundance of small benthic taxa (Amphora pediculus and Mayamaea atomus) through enhanced thermal stratification and reduced mixing-induced disturbance, but the possible contributions of high temperature do not shake the inference of low water level and moisture deficit in Lake Dojran. In summary, diatoms in the two lakes reveal high temperature and low humidity during the early Holocene in this region, which is in accord with pollen-inferred high temperature and high seasonality of precipitation (high winter precipitation and low summer precipitation) in SL152 (Dormoy et al., 2009), and is also consistent with foram-inferred high sea surface temperature (SST) in MNB3, northern Aegean Sea (Geraga et al., 2010). Meanwhile, this comparison is important in improving understanding of the ecological behaviours of planktonic C. ocellata in the contrasting types of lakes, which is a cosmopolitan species and probable species complex with ambiguous ecological preferences (Wunsam et al., 1995; Rioual et al., 2007).

It is surprising that the 8.2 ka event is not indicated by diatoms in shallow Lake Dojran, suggesting either that its regional expression remains unclear, or that the event is mainly expressed as a shift in temperature rather than moisture availability. This abrupt climate event is clearly indicated by low concentration of hypolimnetic taxa (C. fottii and S. transylvanicus) between ca. 8,500–8,200 cal yr BP in Lake Ohrid. High abundance of epilimnetic taxa during this period would at face value be taken as indicative of high rather than low temperature. Instead, the apparently anomalous abundance of C. ocellata is attributed to mixing-induced nutrient replenishment as a result of the decrease in temperature, and relatively high C. minuscula abundance results from high clastic input and the decrease in lake transparency, as small-sized planktonic taxa have high light absorption efficiency (Finkel et al., 2009; Winder et al., 2009). Thus, the 8.2 ka event is probably more a cooling event than one of aridity at least in the southern Balkans. This is consistent with pollen-inferred low winter temperature in Lake Maliq (Bordon et al., 2009), Tenaghi Philippon (Peyron et al., 2011) and SL152 (Dormoy et al., 2009), consistent with dinocyst-inferred low winter sea surface temperature (SST) in SL21 (Marino et al., 2009), and also consistent with alkenone- and foram-inferred low SST in MNB3, northern Aegean Sea (Gogou et al., 2007;

Geraga et al., 2010). This cooling event results in an interruption of the sapropel formation in the eastern Mediterranean Sea (Abrantes et al., 2012). This event is driven by cold northerly polar/continental air outbreaks (Rohling et al., 2002). Low winter precipitation is also inferred from these pollen-based quantitative reconstructions (Bordon et al., 2009; Dormoy et al., 2009; Peyron et al., 2011), but, if the model output is reliable, the aridity of the 8.2 ka event probably does not exert significant influence on diatom growth and limnological properties in their growing season, and thus an 8.2 ka event is perhaps unlikely to be shown by aquatic bioindicators as a drying event in this region. It may also explain why diatom studies of other shallow lakes in the southern Balkans (Lake Ioannina: Wilson et al., 2008; Jones et al., 2013; Lake Prespa: Cvetkoska et al., 2014a) can provide only tentative evidence for the impact of an 8.2 ka event.

During the mid Holocene, in Lake Dojran, high abundance of planktonic taxa, comprising Aulacoseira granulata, Cyclostephanos dubius, Stephanodiscus hantzschii and S. medius, indicates a relatively deep and turbid state between ca. 8,500–3,000 cal yr BP. In Lake Ohrid, the mid Holocene (ca. 8,200–2,600 cal yr BP) is a stable phase with low epilimnetic C. ocellata abundance and high abundance of hypolimnetic taxa, unlike the Lateglacial C. fottii domination and C. ocellata absence; Cyclotella fottii is in high concentration during the mid Holocene, unlike its extremely low concentration during the Lateglacial. High concentration of hypolimnetic taxa (C. fottii and S. transylvanicus) possibly indicates high spring temperature, as the bloom of C. fottii occurs in spring at all depths (Stanković, 1960); low C. ocellata abundance and concentration are possibly attributed to increased winter temperature (compared to the 8.2 ka reversal) and reduced mixing, restraining nutrient availability for the growth of C. ocellata in the epilimnion in spring and summer. High temperature could directly contribute to the development of large planktonic species in Lake Dojran, as A. granulata and large Stephanodiscus species are dominant diatom forms in summer (Temponeras et al., 2000); however, water depth and mixing are essential prerequisites for them to remain in the water column (Bennion, 1995; Bennion et al., 2010; Wolin and Stone, 2010). Relatively high diatom concentration in Lake Dojran, indicating high productivity, is consistent with the eutrophic preference of these species. In summary, a warm and wet mid Holocene is indicated by diatoms from the two lakes, which is consistent with mid-Holocene high lake level in Lake Xinias (using the lake centre-to-shore core correlation method; Digerfeldt et al., 2007) and pollen-inferred increased summer precipitation in SL152 (Dormoy et al., 2009). Diatoms in the contrasting lakes respond to high

temperature in different pathways (directly in Lake Dojran and indirectly in Lake Ohrid) and diatom response is also related to the trophic state and mixing regime of lakes (Lake Dojran: eutrophic, mixing; Lake Ohrid: stratified, nutrient-depleted), which is in accord with studies of diatom response to recent climate warming in contrasting lake types (Berthon et al., 2014).

During the late Holocene, the signal of natural climate change, particularly nutrient availability, is obscured by local anthropogenic impacts from activities including forest clearance and agriculture in the catchments of both the lakes. However, in Lake Dojran, the dominance of facultative planktonic fragilaroid species after ca. 3,000 cal yr BP possibly indicates a shallow environment and low humidity, which is consistent with lake-level reconstructions in the Balkans (Harrison and Digerfeldt, 1993); in Lake Ohrid, high *C. ocellata* abundance between ca. 2,600–2,000 cal yr BP (a period before clear human impact) is possibly attributed to decreased winter temperature and increased nutrient supply in spring, which might correspond with a gradual decrease in alkenone-inferred sea surface temperature (SST) from ca. 2,000 cal yr BP onwards in AD91-17, Otranto Strait that connects Adriatic Sea and Ionian Sea (Sangiorgi et al., 2003). Global mean temperature from proxies decreases to the 1961–1990 AD average value at ca. 3,000 cal yr BP (Marcott et al., 2013), in spite of a data-model inconsistency in global mean temperature during the Holocene that is not apparent for the Lateglacial (Marcott and Shakun, 2015). The late Holocene is thus probably cool and dry in this region.

Overall, comparison and combination of diatoms in the contrasting types of lakes (Lakes Dojran and Ohrid) clearly reveal temperature and hydroclimatic changes in the southern Balkans, that is, cold and arid Younger Dryas, warming and wetting earliest Holocene, warm and arid early Holocene, cooling 8.2 ka event, warm and wet mid Holocene, and cool and dry late Holocene, and thus improve understanding of Lateglacial and Holocene climate and environmental change in the northeastern Mediterranean. Meanwhile, this comparison sheds some light on the importance of both relative abundance and absolute concentration data in diatom-based reconstruction, the importance of habitat availability for benthic diatoms, different ecological dynamics of cosmopolitan planktonic *C. ocellata* in contrasting types of lakes, and different responses of planktonic diatoms to high temperature in contrasting lake types.

8.2 Conservation status of southern Balkan Lakes Dojran and Ohrid

In Lakes Dojran and Ohrid, human impact exerts significant influence on lake status during the late Holocene. In Lake Dojran, human impact is an important factor not only leading to high trophic state during the late Holocene by deforestation in the catchment and enhanced nutrient erosion, but also possibly contributing to low lake level through intensified agriculture and irrigation. In Lake Ohrid, anthropogenic deforestation and intensified agriculture enhance nutrient erosion, but more importantly reduce light availability through high clastic input. Lake-level reduction and eutrophication in Lake Prespa, which is partly the result of artificial management practices, possibly exert influence on the trophic status in Lake Ohrid through spring water inflow in spite of the buffering effect of aquifers. The studies on recent diatoms in both the lakes, supported by pigment analysis in Lake Dojran, clarify the impact of human activities on lake conservation status. The diatom and pigment analysis in the top-55 cm section (spanning the past ca. 480 years) of the Dojran core Co1260 reveals that increased algal biomass and lake eutrophication occurring around ca. 1800 cal AD is attributed to human water abstraction and intensified agriculture, which is in accord with a channel dug in 1808 to reduce the lake area for larger agricultural land and to take more water for irrigation downstream along the Gjolaja River (Stojov, 2012). This channel was gradually deepened and water abstraction practices continued until 2002, when the maximum lake level was only 3.7 m, and a 4.5 m lake-level decline occurred in the period of 1989–2002. The investigation on diatom composition in Lake Dojran between 1988–2001 reveals that, along with the dramatic decrease in lake level and water quality, eutrophic and halotolerant diatom species appeared in 1996–1998 (Levkov and Stojanovski, 2002). Apart from diatoms, other new algal species also occurred in response to the changes in water quality, and toxic species of cyanobacteria became a serious threat to the food webs (Sotiria and Petkovski, 2004). Despite an increase in lake level to 7.0 m in 2011 due to decreased water use and additional water transfer from the Gjavato wells into the lake (Popovska and Bonacci, 2008), the lake is still in an urgent state of conservation, as to some extent indicated by high TP concentration (323 μ g l⁻¹) of lake water in the littoral zone measured in August/September 2012 and nutrient-rich water inflow, of which the entrances into the lake are surrounded visibly by algal bloom. Griffiths et al. (2002) and Levkov and Stojanovski (2002) have proposed restoration measures, comprising the cessation of water abstraction from the lake and underground aquifers, the treatment of communal and industrial waste waters, the development of sustainable agriculture, the balance of fishery, the injection of additional fresh water from some other sources, and the formulation of management

strategies between Macedonia and Greece. Compared to the previous short-core study of Griffiths et al. (2002), the longer, Holocene study provides a deeper insight into the lake's natural baseline state. The diatom data in core Co1260 show that Lake Dojran is a eutrophic lake through most of the Holocene, and thus the reference condition and recovery target for the lake may be difficult to define. The outcome of restoration measures is possibly limited due to internal phosphorus recycling and/or climate warming, and thus it may not necessarily return to its pre-eutrophication reference status (Batterbee et al., 2012).

In Lake Ohrid, the late-Holocene diatom study on core Co1262 near the Lini Peninsula in the western part of Lake Ohrid shows that, high clastic input, due to human deforestation, restrains light availability and diatom growth, while at the same time human-induced external nutrient input does not show positive effects on diatom growth, suggesting that light availability is probably a more important limiting factor than nutrient availability since in deep lakes mixing-induced internal nutrient redistribution is an alternative for external nutrient supply. However, when the lake-level decline in Lake Prespa occurs, it is possible that more nutrient transfer from Lake Prespa through spring water inflow exerts influence on the productivity in the epilimnion, possibly suggesting that nutrient availability is an important stimulating factor when light availability is not limited. The study on a short core Sv09 (spanning the last ca. 60 years) near Sveti Naum springs in the southeastern part of Lake Ohrid reveals that the shifts in diatom composition and ostracod concentration are correlated with the Prespa lake-level changes, although ca. 1–2 year delay of diatom response could be interpreted as the drainage time from Lake Prespa to the Sveti Naum spring area while it is surprising that nearly no such delay occurs in ostracod response. The increase in the abundance of epilimnetic, mesotrophic Cyclotella ocellata at the expense of hypolimnetic Cyclotella fottii in ca. 1976 AD and 1996 AD, and the increase in ostracod concentration in ca. 1988 AD and 2001 AD, are possibly driven by increased nutrient transfer from Lake Prespa, which is related to human-induced lake-level decrease and eutrophication in Lake Prespa. Cyclotella ocellata may represent shallow mixing depth and strong thermal stratification in some lakes (Whitlock et al., 2012), but in Lake Ohrid, the Holocene study shows that *C. ocellata* is at high abundance under the condition of strong lake circulation, confirming the broad ecological preferences of C. ocellata (Rioual et al., 2007), and much smaller Cyclotella minuscula prefers to the stratification in Lake Ohrid. Thus, the increase in the abundance of C. ocellata in core Sv09 is possibly attributed to eutrophication in Lake Ohrid rather than global warming and associated enhanced stratification. Although Lake

Ohrid is still an oligotrophic lake, it is in an urgent state of conservation, as a 3.5 fold increase in phosphorus concentration over the past century is detected in a couple of sediment cores and it is clearly in the process of eutrophication (Matzinger et al., 2007). The short core Sv09 has demonstrated that the recent eutrophication trend in the southeastern part of Lake Ohrid is mainly driven by the lake-level decline and eutrophication in Lake Prespa through the underground hydraulic connection, although the aquifer is a natural filter that retains 65% of the transported phosphorus (Matzinger et al., 2006b). The Sveti Naum spring area is a relatively pristine site in Lake Ohrid, but it is currently under the threat of eutrophication. What about the conservation status in severely polluted sites, such as the area near the City of Struga? What about the response of diatoms to urban pollution in these sites? In order to fully understand the state of conservation in Lake Ohrid and to test whether the influence of Lake Prespa has an impact on diatom ecology across the lake as a whole, another short core St09 (spanning the last ca. 90 years) near the City of Struga will be analysed in the future.

8.3 Diatom response to orbital climate in the DEEP sequence and directions for future research

The DEEP sequence provides a rare opportunity to examine the response of diatoms to glacial-interglacial cycles during the past more than 1.36 Ma in ancient, deep Lake Ohrid. The preliminary results show that diatom response to orbitally-induced climate change is more complex than predicted. Reed et al. (2010) found that, in core Co1202, northeastern Lake Ohrid, during the last glacial-interglacial cycle, epilimnetic Cyclotella ocellata is dominant during interglacial periods, and hypolimnetic Cyclotella fottii is dominant during glacial periods, indicating diatom response to temperature-induced productivity in Lake Ohrid. This hypothesis is confirmed by the preliminary diatom results in the DEEP sequence, central Lake Ohrid. During MIS 6–1, endemic C. fottii (including its small form C. hustedtii) is the hypolimnetic species, and C. ocellata is at high abundance during MIS 5, 3 and 1 and at low abundance during MIS 6, 4 and 2. However, this hypothesis is not fit for the Holocene, and a detailed Holocene study in core Co1262, western Lake Ohrid, and a previous low-resolution study in core Lz1120, southeastern Lake Ohrid, show that C. fottii is dominant during the mid Holocene and it is distinguished from the Lateglacial period by high concentration of C. fottii. In the DEEP sequence, during MIS 25–7, fossil Cyclotella iris (including its similar form Cyclotella cf. schumannii) is possibly a hypolimnetic species. The high abundance of epilimnetic species is not always correlated with interglacials or interstadials, for example, high abundance of epilimnetic Cyclotella prespanensis and its similar small form Cyclotella cf.

kuetzingiana corresponds with MIS 15, while peak C. ocellata abundance correlates with MIS 8 and peak epilimnetic Cyclotella minuscula abundance occurs during MIS 14 and 12. In contrast, the high abundance of hypolimnetic species, C. iris or C. cf. schumannii, is correlated with interglacials rather than glaciations. During MIS 31–26, epilimnetic species is dominant, and no particular hypolimnetic species occurs. During MIS 43–32, the shifts between epilimnetic species and facultative planktonic species possibly suggest that this is an initial lake infilling stage, interglacials and interstadials are dominated by epilimnetic planktonic species, and high abundance of facultative planktonic species is correlated with glaciations or stadials. Thus, there is not a simple pattern of diatom response to orbital climate change in Lake Ohrid. This is possibly modulated by the evolution of diatoms, for example, the originations of hypolimnetic C. iris and C. fottii at the depth of 320 m (MIS 25/24) and 80 m (MIS 7/6), respectively, are possibly accompanied by the key stages of evolution (Wagner et al., 2014). Diatom analysis in Lake Baikal reveals an evolutionary pattern that glaciations bring about species extinctions and interglacials result in the originations or recolonisations of new endemic species (Mackay et al., 2010). Apart from the evolutionary processes, the complex diatom responses in Lake Ohrid possibly represent climate change, for example, C. ocellata is dominant during the 8.2 ka cooling event and C. fottii is dominant during the Lateglacial, so it is possible that the temperature during the 8.2 ka cooling event is still higher than that of the Lateglacial period when the temperature was very low to restrain the growth of epilimnetic species. In the future research, 1) diatom taxonomy will be harmonised between labs, which is important for the comparison of diatom results between different marine isotope stages allocated to three labs (Hull, Utrecht and Skopje); 2) a detailed, standard diatom analysis will be carried out, so as to assess the existing hypotheses and preliminary results from smear slides of core catcher samples and more importantly to generate a long diatom record during the past >1.36 Ma in Lake Ohrid; 3) since the preliminary diatom results do not exhibit a simple, linear response to temperature in the DEEP sequence, a multi-proxy approach will be adopted in the future diatom analysis, so as to understand limnological characteristics and ecological preferences of diatom species; 4) following understanding the mechanisms of diatom response to glacial-interglacial cycles, the pattern of diatom evolution over the past >1.36 Ma in Lake Ohrid will be discovered; and 5) because of the influence of both natural lake infilling and orbitally-induced climate change on diatoms, the initial lake infilling stage in the earlier part of the sequence will be focused on in attempting palaeoclimate reconstruction.

Chapter 9 Conclusions

The southern Balkans is located at the juncture between the west-east and north-south contrasting Holocene climate and hydrological domains across the Mediterranean, and Lake Dojran (Macedonia/Greece) is a shallow and currently hypereutrophic lake controlled by a classic Mediterranean climate. The Lake Dojran diatom data provide a new insight into changes in lake level and trophic status during the Younger Dryas and Holocene in the northeastern Mediterranean region, and are also important in disentangling regional climate effects from local catchment dynamics during the Holocene. The pigment data from the upper part of the sequence provide clear evidence for accelerated eutrophication of Lake Dojran due to water abstraction and intensified agriculture during the recent several centuries. Ancient lakes in Europe are restricted to the southern Balkan region, and Lake Ohrid (Macedonia/Albania), under the influence of Mediterranean and somewhat continental climates, is a rare example with a high degree of biodiversity and endemism. In deep and highly oligotrophic Lake Ohrid, the diatom data provide a clear picture of Lateglacial and Holocene changes in temperature and lake productivity which is primarily modulated through stratification or mixing regime and associated nutrient redistribution in the water column, and comparison with the data from Lake Dojran reveals different responses of diatoms to climate in the contrasting types of lakes. Diatom analysis of a short core in the southeastern part of Lake Ohrid reveals human-induced eutrophication of Lake Ohrid in the recent several decades influenced by nutrient transfer through springs from hydraulically-linked Lake Prespa. Preliminary diatom analysis of the ICDP deep core in Lake Ohrid generates a preliminary interpretation of the response of diatoms to glacial-interglacial cycles and the evolution of endemic diatom species during the past more than one million years.

The diatom-based Lateglacial and Holocene climate and environmental reconstructions in these two lakes are: in Lake Dojran, diatom-inferred shallowing between ca. 12,400–12,000 cal yr BP and a very low lake level and eutrophic, oligosaline state between ca. 12,000–11,500 cal yr BP provide strong evidence for aridity during the Younger Dryas; the plankton domination indicates a high lake level during the earliest Holocene (ca. 11,500–10,700 cal yr BP) as a result of an increase in precipitation; a lake-level reduction and increased trophic level occurred during the early Holocene (ca. 10,700–8,500 cal yr BP), which may result climatically from high seasonality of precipitation and locally from limited, nutrient-rich catchment runoff; the lake was relatively deep and exhibited the maximum

Holocene trophic level during the mid Holocene (ca. 8,500–3,000 cal yr BP), which is possibly driven by local vegetation succession and associated changes in catchment processes, rather than showing a close relationship to climate change; the lake became shallow during the late Holocene. In Lake Ohrid, extremely low diatom concentration and the domination of hypolimnetic species indicate low temperature and productivity during the Lateglacial period (ca. 12,300–11,800 cal yr BP); a distinct increase in smaller epilimnetic species indicates climate warming and enhanced thermal stratification during the earliest Holocene (ca. 11,800–10,600 cal yr BP); high abundance of epilimnetic taxa and an increase in diatom concentration indicate high temperature and productivity during the early Holocene (ca. 10,600–8,500 cal yr BP); the 8.2 ka cooling event is clearly indicated by low concentration of hypolimnetic taxa, while high abundance of epilimnetic taxa is probably due to mixing-induced high nutrient supply; high concentration of hypolimnetic taxa indicates high temperature and productivity during the mid Holocene (ca. 8,200–2,600 cal yr BP), and low abundance of eplilimnetic taxa results possibly from low nutrient supply due to high thermal stratification and low cathcment erosion; during the late Holocene, a decrease in winter temperature possibly occurred between ca. 2,600–2,000 cal yr BP, and this is followed by enhanced human impact between ca. 2,000–1,400 cal yr BP; the influence of nutrient transfer from Lake Prespa may be important in driving the increase in epilimnetic taxa and lake productivity during the recent one millennium. In summary, this study improves understanding of Lateglacial and Holocene temperature and hydroclimatic changes in the northeastern Mediterranean region, and meanwhile reveals different responses of diatoms to climate in the two contrasting types of lakes.

From the thesis, although equifinality may occur in some cases, diatoms can be a strong proxy for lake level and moisture change in shallow lakes, and improve sedimentological, geochemical and isotopic interpretation. In deep lakes, diatom response to temperature change is complex, and multi-proxy analysis can be used to understand the mechanisms of diatom response. Diatom composition is directly determined by limnological change, such as lake level, water temperature, nutrient availability, water conductivity, light availability, water-column stratification or mixing regime, and habitat availability. Diatom concentration is largely related to lake productivity. The limnological change can be affected by regional climate change (precipitation and/or temperature) but also local catchment processes (catchment vegetation, runoff and erosion). The multi-proxy approach can thus be used to assess the factors that may exert influence on limnological change and then to understand

which factors control diatom composition. Thus, in palaeolimnological research, diatoms can be regarded as a strong biological indicator of lake level and nutrient concentration, and menawhile multi-proxy analysis is important in understanding the relationships between diatom composition and limnological characteristics at the coring site (usually in the deepest lake centre). The multi-proxy approach can also provide the potential to strengthen climate and environmental interpretation, although the indications of abiotic proxies are not very clear in most cases and even conflict. Thus, all techniques have strengths and weaknesses, which underlines the value of the multi-proxy approach in palaeoenvironmental research. In the future, diatom analysis, together with the analysis of multiple proxies related to regional climate effects and the influence of local catchment processes, will be helpful for understanding limnological and ecological change. In terms of diatom analysis, diatom composition, diatom concentration, ordination, transfer function and diatom dissolution are usually taken into consideration. Diatom preservation and dissolution is a key problem for diatom-based reconstruction of various environmental variables. F index, a simple dissolution index, can sometimes function, for example, in a lake with diatoms consistently dominated by low-diversity centric species; while in most cases, this index seems not to be effective due to the clear shifts between dominant species. Thus, diatom dissolution should be evaluated using a comprehensive approach in the future. Diatom-based quantitative reconstruction is commonly used in palaeolimnological research, and the transfer function method is recently found to be inappropriate in long-term climate and environmental reconstruction in particular; however, the diatom training sets established by a lot of diatomists around the world are still useful for understanding the ecologies of different diatom species. Diatom concentration is to some extent affected by some factors such as sediment accummulation rate and the size of different diatom species, and thus diatom accummulation rate, or diatom biovolume accummulation rate, is better than diatom concentration. The volume of diatom species is difficult to estimate, partly because the size of one species may vary, and diatom accummulation rate should at least be estimated in the future if possible. As pointed out above, there are still some needs to improve diatom analysis and the analysis of multiple proxies in the future.

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Appendices

Appendix 1:

Lateglacial and Holocene climate and environmental change in the northeastern Mediterranean region: diatom evidence from Lake Dojran (Republic of Macedonia/Greece). *Quaternary Science Reviews*, 2014, 103, 51–66.

Appendix 2:

Recent anthropogenic impact in ancient Lake Ohrid (Macedonia/Albania): a palaeolimnological approach. Journal of Paleolimnology, 2014, 52, 139–154.

Appendix 3:

The SCOPSCO drilling project recovers more than 1.2 million years of history from Lake Ohrid. *Scientific Drilling*, 2014, 17, 19–29.



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Lateglacial and Holocene climate and environmental change in the northeastern Mediterranean region: diatom evidence from Lake Dojran (Republic of Macedonia/Greece)



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ABSTRACT

The juncture between the west-east and north-south contrasting Holocene climatic domains across the Mediterranean is complex and poorly understood. Diatom analysis of Lake Dojran (Republic of Macedonia/Greece) provides a new insight into lake levels and trophic status during the Lateglacial and Holocene periods in the northeastern Mediterranean. Following a very shallow or even desiccated state at the core base at ca. 12,500 cal yr BP, indicated by sedimentological and hydro-acoustic data, diatoms indicate lake infilling, from a shallow state with abundant benthos to a plankton-dominated relatively high lake level and eutrophic state thereafter. Diatom-inferred shallowing between ca. 12,400 -12,000 cal yr BP and a very low lake level and eutrophic, oligosaline state between ca. 12,000 -11,500 cal yr BP provide strong evidence for Younger Dryas aridity. The earliest Holocene (ca. 11,500 -10,700 cal yr BP) was characterised by a high lake level, followed by a lake-level reduction and increased trophic level between ca. 10,700-8,500 cal yr BP. The lake was relatively deep and exhibited peak Holocene trophic level between ca. 8,500–3,000 cal yr BP, becoming shallow thereafter. The diatom data provide more robust evidence and strengthen previous lake-level interpretation based on sedimentological and geochemical data during the earliest, mid and late Holocene, and also clarify previous uncertainty in interpretation of Lateglacial and early-Holocene lake-level change. Our results are also important in disentangling regional climate effects from local catchment dynamics during the Holocene, and to this end we exploit extant regional palynological evidence for vegetation change in the highlands and lowlands. The importance of seasonality in driving Holocene climate change is assessed by reference to the summer and winter latitudinal temperature gradient (LTG) model of Davis and Brewer (2009). We suggest that increased precipitation drove the high lake level during the earliest Holocene. The early-Holocene low lake level and relatively high trophic state may result climatically from high seasonality of precipitation and locally from limited, nutrient-rich catchment runoff. We argue that the mid-Holocene relatively deep and eutrophic state was driven mainly by local vegetation succession and associated changes in catchment processes, rather than showing a close relationship to climate change. The late-Holocene shallow state may have been influenced by a temperature-induced increase in evaporative concentration, but was coupled with clear evidence for intensified human impact. This study improves understanding of Lateglacial and Holocene climate change in the northeastern Mediterranean, suggests the important role of the LTG on moisture availability during the Holocene, and clarifies the influence of catchment processes on palaeohydrology.

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1. Introduction

The Mediterranean region is a primary global climate response hotspot (Giorgi, 2006) and a hotspot of biodiversity (Myers et al., 2000; Mittermeier et al., 2004). It is a transitional zone climatically influenced both by the mid-latitude westerlies and the Subtropical High pressure (anticyclone) belt, with the North Atlantic

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Oscillation (NAO) modulating winter precipitation and the migration of the Intertropical Convergence Zone (ITCZ) affecting summer drought (Lionello et al., 2006). It stretches longitudinally from the North Atlantic Ocean to continental Eurasia. It has a diversity of landscapes linked to spatial and altitudinal variation in climatic factors.

Palaeoenvironmental analysis offers potential to improve understanding of Mediterranean climate change, but the clear definition of regional contrasts is still elusive. An early review of lakelevel reconstruction proposed an east-west contrast during the Holocene (Harrison and Digerfeldt, 1993). More recently, Roberts et al. (2008, 2011a) confirmed this, defining a marked contrast during the Holocene to the east and west of a line running through the Balkans, southern Italy and Tunisia, based on stable isotope data and model output; on a centennial-decadal timescale, the complexity of regional patterns was also demonstrated in an east-west contrast between the northern Iberian Peninsula and central Turkey (Roberts et al., 2012). In contrast, Magny et al. (2013) proposed a north-south divide around ca. 40°N during the Holocene in the central Mediterranean from carbonate-based lake-level reconstruction. Peyron et al. (2013) supported this from pollenbased quantitative reconstruction of summer precipitation, and also proposed a similar pattern in the Aegean Sea. This is coherent with a north-south contrast in fire activity in the western Mediterranean (Vannière et al., 2011).

From the foregoing, the southern Balkans is a key location for understanding Mediterranean climate change, being located at the juncture of the proposed boundaries between west—east and north—south contrasting climate and hydrological domains. The southern Balkans is particularly complex, and patterns and mechanisms of climate and environmental change are still poorly understood. The complexity of palaeoenvironments is indicated, for example, by discrepancies in vegetation reconstruction between adjacent sites such as Lake Ioannina (northwestern Greece) and Nisi Fen (northern Greece) (Lawson et al., 2004, 2005), and between Lake Gramousti at low altitude and Rezina Marsh at high altitude in northwestern Greece (Willis, 1992a).

Here, we build on previous multi-proxy palaeoclimate research in investigating the Lateglacial and Holocene record of Lake Dojran (Macedonia/Greece), by using diatom analysis as a strong proxy for lake levels and trophic status to strengthen interpretation based on sedimentological and geochemical data from the same core (Francke et al., 2013). In interpretation of Holocene limnological change in terms of palaeoclimate shifts versus the influence of local catchment dynamics, we exploit extant regional palynological data for vegetation change, comprising late-Holocene pollen data from a separate littoral Dojran sequence (Athanasiadis et al., 2000) and chronologically-robust Holocene pollen data from the highlands and lowlands in the southern Balkans (Kotthoff et al., 2008a; Tonkov et al., 2008, 2013). Adopting a novel approach, the importance of seasonality in driving Holocene climate change is assessed by reference to the summer and winter latitudinal temperature gradient (LTG) model (Davis and Brewer, 2009), which incorporates variation in the Subtropical High pressure and Arctic Oscillation (AO). For clarity, this is expanded upon in Section 2. We also compare with proxy data from the northeastern Mediterranean (the Balkans, Italy and Anatolia) (Fig. 1).

2. Review of Holocene climatic forcing

2.1. Summer climate mode and the Subtropical High pressure

The character and influence of the Holocene summer insolation maximum across the Mediterranean is a topic for vigorous ongoing debate (Tzedakis, 2007). In a major review, Tzedakis (2007) argued that the enhanced African monsoon did not extend to the



Fig. 1. Map of the northeastern Mediterranean showing the locations of the study site (*red*), relevant palynological records with robust chronologies (*purple*) and other palaeoenvironmental records (*black*) referred to in this paper. 1. Lake Dojran (this paper; Athanasiadis et al., 2000; Francke et al., 2013), 2. Lake Trilistnika (Tonkov et al., 2008), 3. Lake Ribno (Tonkov et al., 2013), 4. SL152 (Kotthoff et al., 2008a, 2008b, 2011; Dormoy et al., 2009), 5. Tenaghi Philippon (Müller et al., 2011), 6. Lake Ohrid (Wagner et al., 2009; Leng et al., 2010), 7. Lake Prespa (Aufgebauer et al., 2012; Panagiotopoulos et al., 2013; Leng et al., 2013; Cvetkoska et al., 2014), 8. Lake Maliq (Bordon et al., 2009), 9. Nisi Fen (Lawson et al., 2005), 10. Rezina Marsh (Willis, 1992a, 1992b), 11. Lake Gramousti (Willis, 1992a), 12. Lake Ioannina (Frogley et al., 2001; Lawson et al., 2004; Wilson et al., 2007), 14. Lake Stymphalia (Heymann et al., 2013), 15. Lake Frassino (Baroni et al., 2006), 16. Lake Accesa (Drescher-Schneider et al., 2007; Peyron et al., 2011), 17. Valle di Castiglione (Di Rita et al., 2013), 18. Lake Albano (Guilizzoni et al., 2002), 19. Lago Grande di Monticchio (Allen et al., 2002), 20. MD90-917 (Combourieu-Nebout et al., 2013), 21. Lake Pergusa (Sadori and Narcisi, 2001; Sadori et al., 2008; Magny et al., 2012), 22. Lake Preola (Magny et al., 2011), 23. MD04-2797 (Despat et al., 2007), 24. Lake Lanik (Roeser et al., 2012), 25. Lake Gölhisar (Eastwood et al., 2007), 26. Eski Acigôl (Roberts et al., 2017); Turner et al., 2008), 27. Lake Van (Wick et al., 2003), Litt et al., 2007), 209. Stereet et al., 2007), 209. Stereet et al., 2009). The dashed-line rectangle shows the range of Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Mediterranean, and the monsoonal effect has been mainly indirect in terms of Nile discharge and runoff along the North African coast. On the other hand, the northward-migrated, strengthened North Atlantic Subtropical High pressure in response to high summer insolation blocked westerly moisture penetration into the Mediterranean (Desprat et al., 2013; Magny et al., 2013). Tzedakis (2007) also suggested that the enhanced Indian monsoon may have accentuated summer aridity in the eastern Mediterranean. Modelling experiments show little sign of summer precipitation in spite of high summer insolation (Brayshaw et al., 2011). Magny et al. (2013) discussed the influence of ice sheets in the Northern Hemisphere on humidity in the Mediterranean, and suggested that the rapid melting of ice sheets and associated fresh water forcing in the North Atlantic Ocean contribute to summer aridity during the earliest Holocene in the south-central Mediterranean.

Davis and Brewer (2009) reconstructed Holocene changes in the latitudinal temperature gradient (LTG) based on differences in pollen-based area-average temperatures between northern (55-70°N) and southern Europe (35-45°N). The LTG reflects combined effects of the differential heating of insolation (the latitudinal insolation gradient, LIG) and the high-latitude cooling influence of remnant ice sheets (Davis and Brewer, 2009). The Subtropical High pressure is located at ca. 36°N when the summer LTG is zero (Davis and Brewer, 2009). A weaker (more positive) summer LTG drives a northern position of the Subtropical High pressure (Davis and Brewer, 2009), and the tendency would be towards much drier summers than today. The quantitative reconstruction of the Subtropical High pressure may be relevant to moisture change in the northeastern Mediterranean. The additional, area-average temperature reconstruction for southeastern Europe (Davis et al., 2003), supported by other regional syntheses (Finné et al., 2011; Abrantes et al., 2012), may be relevant in terms of evaporation and its effect on moisture balance.

2.2. Winter climate mode and the Arctic Oscillation (AO)

Modelling experiments show high winter precipitation during the early Holocene (Brayshaw et al., 2011), which is coherent with a southward-shifted storm track and responds to weak winter insolation (Desprat et al., 2013). Desprat et al. (2013) also suggested that the rapid melting of ice sheets in the Northern Hemisphere and associated reorganisation of atmospheric circulation contribute to high winter precipitation during the early Holocene in the southcentral Mediterranean. Roberts et al. (2008, 2011a) and Magny et al. (2013) suggested that this is probably attributed to winter cyclogenesis and local precipitation. However, it is inconsistent with the positive AO/NAO and resultant aridity in the north-central Mediterranean (Magny et al., 2013). Data-model comparison shows that models underestimate the role of AO/NAO (Gladstone et al., 2005; Brewer et al., 2007; Mauri et al., 2013), and Davis and Brewer (2009) proposed that models overestimate low-latitude warming in summer and high-latitude warming in winter.

The Mediterranean exhibits a dry climate during the positive phase of AO/NAO and more precipitation during their negative phase (Martinson et al., 2000; Wanner et al., 2001). However, AO has a larger horizontal scale (Thompson and Wallace, 1998), and NAO alone cannot account for changes in winter precipitation in Turkey (Jones et al., 2006). In terms of precipitation, the northeastern Mediterranean is distinguished from the Levant and southeastern Mediterranean (Felis and Rimbu, 2010), and from the NAO-highly related Iberia and western Mediterranean (Roberts et al., 2012). The prominent role of AO/NAO in influencing Holocene hydroclimatic change across the Mediterranean is revealed not only at the centennial scale (e.g. Lamy et al., 2006) but also at the millennial scale (e.g. Davis and Stevenson, 2007; Fletcher et al., 2013). The AO index is zero when the winter LTG is zero (Davis and Brewer, 2009). A weaker (more positive) winter LTG drives a more positive AO, and the tendency would be towards dry winters. The AO quantitative reconstruction (Davis and Brewer, 2009) may be more relevant than the NAO in interpretation of northeastern Mediterranean climatic records.

3. Site description

Lake Dojran (41°12'N, 22°44'E, 144 m a.s.l.), a transboundary lake between Macedonia and Greece, sits within a karstic basin formed initially by a combination of Tertiary volcanic and tectonic activities, and the catchment sediments are largely composed of Quaternary alluvial and limnetic materials (Sotiria and Petkovski, 2004). In the catchment, the highland to the north is close to the Pirin and Rila Mountains in southwestern Bulgaria, and the lowland to the south is open to the Thessaloniki Plain and northern Aegean Sea (Fig. 2). The lake basin is surrounded by the Belasica (or Belles, Kerkini) Mountain (1847 m a.s.l.) to the north, the Kroussia (or Krusa, Dysoron) Mountain (766 m a.s.l.) to the east, the Boskija (or Boska) Mountain (714 m a.s.l.) to the northwest, and the Dab Mountain (689 m a.s.l.) to the southwest (Fig. 3; Sotiria and Petkovski, 2004). The lake is fed by small rivers, creeks and springs, with most of the runoff originating from the Belasica Mountain. Water loss is currently through evaporation and probably groundwater outflow, but during previous phases of high lake level, surface outflow was possible at the southern end of the lake through the Doiranity (or Ayiak) River, which drained into the Vardar (or Axios) River and then into the Aegean Sea (Sotiria and Petkovski, 2004). The lake water is essentially fresh (see below), suggesting groundwater throughflow in karstic aquifers. This is supported by hydrogeological investigations (Sotiria and Petkovski, 2004).

The local climate regime is a hot and dry summer (June-September) and mild and humid winter (November-February) (Sotiria and Petkovski, 2004). In the lowlands of the catchment evergreen (Quercus coccifera L.) and deciduous oaks (Quercus pubescens Willd., Quercus frainetto Ten. and Quercus dalechampii Ten.) are the dominant trees, and at higher altitudes (>1000 m a.s.l.) beech forest (Fagus moesiaca Cz. and Fagus orientalis Lipsky) is dominant with a few scattered fir stands (Abies borisii-regis Mattf.) (Athanasiadis et al., 2000). Reed beds occupy the fringe of the lake, and submerged plants are common in the littoral zone. Recorded maximum lake level ranged from 7.9 to 10.0 m in 1951-1987, declined to 3.7 m in 2002 due to water abstraction practices and more intensive agriculture (Griffiths et al., 2002), and recovered to 6.7 m in 2010 due to an increase in rainfall, decrease in water use and additional water transfer from the Gjavato wells into the lake (Popovska and Bonacci, 2008; Stojov, 2012). Total phosphorus ranged from 15 to 130 µg l⁻¹ in 1953–1960 (Sotiria and Petkovski, 2004), with consistently higher minimum values of >50 μ g l⁻¹ reported since 1996 and an occasional hypereutrophic state (Temponeras et al., 2000; Lokoska et al., 2006; Tasevska et al., 2010). Conductivity ranged from 0.4 to 0.6 mS cm^{-1} in 1974–1988, increased to 1.5 mS cm^{-1} in 2002 (Sotiria and Petkovski, 2004), and declined to 0.8 mS cm⁻¹ in 2010 (Lešoski et al., 2010). This is within the freshwater range of eutrophic lake water. Ionic concentration may be influenced slightly by mineralrich spring input; some springs are of high conductivity (Levkov, unpublished data), but others are extremely fresh (33 μ S cm⁻¹; Griffiths et al., 2002). Dominance by fresh spring inflow is consistent with low $\delta^{13}C$ data of total dissolved inorganic carbon (-7.9 to -13.0% VPDB) in springs (Griffiths et al., 2002; Francke et al., 2013), suggesting that the effect of the karstic catchment is minor (Leng and Marshall, 2004) and the groundwater influence on


Fig. 2. Map of the adjacent region of Lake Dojran (Macedonia, northern Greece and southwestern Bulgaria) with the sites 1–13 in Fig. 1. The dashed-line rectangle shows the range of Fig. 3.

lake-water conductivity and salinity is insignificant. Lake Dojran is shallow and monomictic, and has a very simple, flat-bottomed morphometry (Francke et al., 2013), suggesting that moisture balance and water chemistry are sensitive to and possibly respond linearly to climate and environmental change (Gasse et al., 1997; Fritz, 2008).

Two previous studies have been made of Holocene climate and environmental change in Lake Dojran. One is based on sedimentological and geochemical data (Francke et al., 2013) from the same core as our current study, and the other is based on pollen data from a separate littoral core Doirani-1/2 which covers the last 5,000 years (Athanasiadis et al., 2000). Francke et al. (2013) found that, during the Lateglacial period, high abundance of clay clasts, high mean grain size, an older shell fragment, and hydro-acoustic data indicated a low lake level and redeposition before ca. 12,100 cal yr BP. This was followed by a lake-level increase inferred from hydro-acoustic data, the absence of clay clasts, low mean grain size, and high potassium (K) concentration. During the earliest Holocene (ca. 11,500–10,700 cal yr BP), overall coarse sediment suggested high water inflow and high lake level, which led to high



Fig. 3. Map of the catchment of Lake Dojran with the coring sites Co1260 (this paper; Francke et al., 2013) and Doirani-1/2 (Athanasiadis et al., 2000).

evaporation as indicated by high $\delta^{18}O_{carb}$ values; lower K concentration indicated lower erosion, and low organic matter content suggested low in-lake productivity. During the early Holocene (ca. 10,700–8,300 cal yr BP), decreasing $\delta^{18}O_{carb}$ values suggested increasing humidity; lower K concentration implied less clastic input while increasing organic matter content was from more allochthonous supply. During the mid Holocene, relatively high lake level was inferred from hydro-acoustic data and finer grainsize distribution. After ca. 2,800 cal yr BP, hydro-acoustic data and fine grain-size distribution suggested a lake-level lowstand apart from around 1,000 cal yr BP (Francke et al., 2013), while pollen data indicated changes in the catchment from a natural landscape to one modified by intensified human impact (Athanasiadis et al., 2000).

4. Material and methods

In June 2011, based on a hydro-acoustic survey, a 717 cm-long core Co1260 was recovered from the deepest (6.7 m water depth), south-central part of Lake Dojran using UWITEC gravity and piston coring equipments (www.uwitec.at). The age model was established by Francke et al. (2013) by polynomial interpolation between the calibrated radiocarbon ages of six terrestrial plant macrofossils, one charcoal fragment, two bulk organic matter samples, and a regionally-correlated point of a CaCO₃ minimum. Three carbonate shell dates and one dislocated terrestrial plant date were not included into the calculations, and Francke et al. (2013) provided more detailed discussion of each age-control point (Table 1). This age model indicates that core Co1260 covers the last 12,500 years (Fig. 4), spanning the Younger Dryas and Holocene periods.

Diatom analysis was carried out on 107 subsamples, taken at 8 cm intervals but at a higher resolution of 4 cm for important phases comprising the bottom 30 cm, the 50 cm between ca. 11,800–11,400 cal yr BP, the 20 cm around ca. 8,200 cal yr BP, and the top 60 cm. The age resolution is ca. 70–150 years, except the top and bottom sections (ca. 30–40 years) and the middle section (ca. 200–500 years). The low age resolution between ca. 8,000–4,000 cal yr BP is correlated with low sediment accumulation rate indicated by the age model, and with a stable environment indicated by sedimentological and geochemical data (Francke et al., 2013).

Techniques in Battarbee et al. (2001) were adopted for diatom preparation of ca. 0.1 g dry weight subsamples, using 30% H₂O₂ to oxidise organics and a few drops of concentrated HCl to remove carbonates. Known quantities of microspheres were added to allow

Table 1

Ages from core Co1260. The calibration of radiocarbon ages into calendar ages is based on Calib 7.0.2 (Stuiver and Reimer, 1993) and IntCal13 (Reimer et al., 2013) and on a 2σ uncertainty.

16.5Bulk organic matter 140 ± 35 53.3Terrestrial plant remains 360 ± 70 111.3Terrestrial plant remains 840 ± 70 253.0Terrestrial plant remains $2,430 \pm 30$ $2,$	140 ± 140
287.3 Terrestrial plant remains $3,080 \pm 30$ $3,309.1$ 309.1 Charcoal $3,560 \pm 40$ $3,404.9$ 404.9 Carbonate shell $6,410 \pm 40$ $7,406.4$ 406.4 Terrestrial plant remains $8,020 \pm 150$ $8,400.9$ 502.9 Carbonate shell $9,840 \pm 40$ $11,520.9$ 521.9 Terrestrial plant remains $9,30 \pm 160$ $10,520.9$	$410 \pm 110 790 \pm 120 520 \pm 170 290 \pm 80 850 \pm 130 350 \pm 80^{a} 960 \pm 440 820 \pm 420^{a} 250 \pm 60^{a} 660 \pm 440 820 \pm 60^{a} 820 \pm 60^{a} \\ 820^{a} \\ 820^{a} \\ 820^{a} \\ 820^$
521.5 Friedmann (1975) 635.0 Bulk organic matter $10,220 \pm 70$ $11,$ 682.0 Carbonate shell $28570 + 170$ 32	920 ± 310 830 ± 650^{a}

^a Indicating the dates excluded into the calculations of the age model.

calculation of absolute valve concentration. Slides were mounted using NaphraxTM. Diatom valves were counted at \times 1000 magnification under oil immersion on an OLYMPUS BX51 light microscope. More than 500 valves per slide were counted, and around 100 valves for some slides where preservation was very poor. Diatom identification was based on a range of published literature (Krammer and Lange-Bertalot, 1986, 1988, 1991a, 1991b; Lange-Bertalot, 2001; Krammer, 2002; Levkov et al., 2007; Levkov, 2009) and diatoms of Lake Dojran (Levkov, unpublished data), adopting the nomenclature of the Catalogue of Diatom Names (online version) (Fourtanier and Kociolek, 2011). Following current taxonomic principles, Stephanodiscus minutulus (Kützing) Cleve & Möller and S. parvus Stoermer & Håkansson are merged into S. minutulus/parvus (Scheffler and Morabito, 2003; Cruces et al., 2010; Hobbs et al., 2011; Bennion et al., 2012). Diatom percentages were displayed using Tilia version 1.7.16, and zone boundaries were defined according to Constrained Incremental Sum of Squares (CONISS) cluster analysis (Grimm, 2011). Unconstrained ordination techniques were used to explore the variance in the diatom data using Canoco for Windows 4.5 (Ter Braak and Šmilauer, 2002). Detrended correspondence analysis (DCA) gave the largest gradient length of 3.91 SD units, and thus this unimodal model is better than linear methods such as principal components analysis (PCA) (Ter Braak, 1995; Lepš and Šmilauer, 2003).

Quantitative diatom-inferred total phosphorus (DI-TP) and conductivity (DI-Cond) reconstructions were performed based on the Swiss TP and Combined Salinity training sets, respectively, available within the European Diatom Database (EDDI; Juggins, 2001), using classic weighted-averaging regression (WA-Cla) with bootstrapping cross-validation in C2 version 1.7.3 (Juggins, 2007). Both the Swiss TP and Combined Salinity training sets have higher determination coefficients (R^2) and lower maximum bias values in WA-Cla than weighted-averaging with inverse deshrinking (WA-Inv) and weighted-averaging partial least squares (WAPLS) component 2. WA-Cla also performs better than WAPLS component 2 in terms of root mean squared error of prediction (RMSEP), and has a slightly higher RMSEP than WA-Inv (bootstrapped RMSEP: 0.26 and 0.23, respectively, for log₁₀-TP, and 0.48 and 0.47, respectively, for log₁₀-conductivity). WA-Inv is susceptible to edge effects (bias at the gradient ends) (Juggins and Birks, 2012), and thus WA-Cla was chosen. Some potential problems have been identified with the application of DI-TP transfer functions (Bennion et al., 2001, 2010; Sayer, 2001; Hall and Smol, 2010; Juggins et al., 2013) and some have suggested there are some fundamental problems with underlying assumptions in the transfer function approach (Sayer et al., 2010; Juggins, 2013), but the species TP optimum and tolerance estimates, particularly of planktonic taxa, may still be useful for trophic reconstruction. Among the EDDI TP transfer functions, the Swiss training set is predominantly from mesotrophic and eutrophic lakes (mean TP: 41.9 μ g l⁻¹), the Central European training set is mainly from oligotrophic and mesotrophic lakes (mean TP: 23.5 μ g l⁻¹), and the Combined TP training set spans the gradient from oligotrophic to hypereutrophic (mean TP: 98.6 μ g l⁻¹) but incorporates many non-karstic, hypereutrophic British and Danish lakes (Juggins, 2001). Although improving the likelihood of finding modern analogues, the merging in the Combined TP training set tends to extend the apparent distribution of species unevenly along the TP gradient, which not only affects species optimum estimates but also widens species tolerance ranges and makes them poor trophic indicators. Griffiths et al. (2002) suggested that Lake Dojran was mesotrophic in the recent past, and as shown above, it is currently eutrophic and occasionally hypereutrophic. Thus the Swiss training set was selected as more appropriate, although oligotrophic and hypereutrophic states are likely to be somewhat underestimated as they lie at the gradient



Fig. 4. Age-depth model of core Co1260 (modified from Francke et al., 2013).

ends. Importantly, the shifts between the dominance of centric (*Cyclotella ocellata* Pantocsek and *S. minutulus/parvus*) and fragilariod species in core Co1260 are well represented by their distributions along the TP gradient in the Swiss training set (Lotter et al., 1998).

5. Results and diatom interpretation

Six major diatom assemblage zones can be defined, which correlate clearly with lithostratigraphic boundaries from Francke et al. (2013) in Fig. 5. Diatom preservation quality is high with >500 valves counted and >10⁷ g⁻¹ concentration throughout until the late Holocene (Zone D-6). DI-TP log₁₀ values range from 1.02 to 2.18 (equivalent to 10.6–149.8 µg l⁻¹), estimated standard error of prediction (eSEP) ranges from 0.26 to 0.29, and the error range (2 × eSEP) varies from 0.51 to 0.58 (calculated as 13.7–210.8 µg l⁻¹). DI-Cond log₁₀ values range from 2.39 to 3.62 (equivalent to 0.2–4.2 mS cm⁻¹), eSEP ranges from 0.47 to 0.67, and the error range varies from 0.93 to 1.34 (calculated as 0.8–13.4 mS cm⁻¹). We treat the DI-TP and DI-Cond reconstructions with caution.

5.1. Zone D-1 (717-645 cm, ca. 12,500-12,000 cal yr BP)

In Subzone D-1a (717-696 cm, ca. 12,500-12,400 cal yr BP), the basal sample has relatively high abundance of benthic taxa (40%), possibly suggesting a lake-level lowstand at the base of the sequence, and this is followed at 713 cm depth by the dominance of planktonic taxa (50-70%), indicating relatively high lake level. Longer valves of Fragilaria crotonensis Kitton and Asterionella formosa Hassall have competitive advantages in deep waters for buoyancy and also prefer high nitrogen and silica concentrations (Bailey-Watts, 1986; Saros et al., 2005), and S. minutulus/parvus prefers high phosphorus concentration (Bennion, 1995; Kilham et al., 1996). Together, this also indicates a eutrophic state, presumably from high catchment runoff and nutrient erosion processes. The subsequent dominance of mesotrophic Stephanodiscus medius Håkansson and oligotrophic-mesotrophic C. ocellata suggests ongoing water inflow but declining nutrient enrichment, supported by declining DI-TP values. In Subzone D-1b (696-645 cm, ca. 12,400-12,000 cal yr BP), the increase in the relative abundance of facultative planktonic taxa, mainly comprising Pseudostaurosira brevistriata (Grunow) Williams & Round and Staurosira construens var. venter (Ehrenberg) Hamilton, and the clear increasing trend in benthic taxa from 667 cm depth suggest shallowing, starting with the peak concentration in the entire sequence at the 696 cm depth.

5.2. Zone D-2 (645-591 cm, ca. 12,000-11,500 cal yr BP)

Planktonic C. ocellata is at low abundance, and together with high relative abundance of benthos, this indicates a very low lake level. Facultative planktonic Pseudostaurosira, Staurosira and Staurosirella species are also rare. However, planktonic Cyclotella meneghiniana Kützing, S. minutulus/parvus and Cyclostephanos dubius (Fricke) Round (diameter <5 µm) are consistently present. C. meneghiniana lives in a wide range of habitats from shallow to deep waters (Gasse, 2002) and from fresh waters of high conductivity to saline conditions (Saros and Fritz, 2000). S. minutulus/ parvus and C. dubius (small) are eutrophic freshwater taxa but tolerate oligosaline conditions (Fritz et al., 1993). Benthic taxa are remarkably diverse, most of which are eutrophic and halotolerant, such as Nitzschia frustulum (Kützing) Grunow, Tryblionella constricta (Kützing) Poulin, Ctenophora pulchella (Ralfs ex Kützing) Williams & Round, Tabularia fasciculata (Agardh) Williams & Round (Fritz et al., 1993; Reed, 1998a; Gasse, 2002; Reed et al., 2012). Importantly, the presence of rare obligate saline taxa such as Biremis circumtexta (Meister ex Hustedt) Lange-Bertalot & Witkowski and Campylodiscus clypeus (Ehrenberg) Kützing indicates aridity in a closed basin due to enhanced evaporative concentration, since the groundwater influence on lake-water conductivity and salinity is insignificant. Maximum DCA Axis 1 scores also make this zone distinctive. In Subzone D-2a (645-611 cm, ca. 12,000-11,700 cal yr BP), eutrophic, halotolerant benthic taxa are dominant, and the DI-Cond reconstruction indicates a peak concentration of total dissolved solids (>3 mS cm⁻¹ conductivity). D-2b In Subzone (611 - 591)cm. ca. 11,700-11,500 cal yr BP), S. minutulus/parvus and C. dubius (small) increase distinctly. Since obligate saline taxa and eutrophic, halotolerant taxa indicate the maintenance of low lake level, enhanced nutrient input is inferred, supported by the peak in DI-TP.

5.3. Zone D-3 (591-525 cm, ca. 11,500-10,700 cal yr BP)

Zone D-3 exhibits a marked transition to the low-diversity dominance of planktonic oligotrophic-mesotrophic *C. ocellata* (70–90%), initially as a co-dominant with *P. brevistriata* (ca. 25%). The abundance of facultative planktonic taxa is <10% thereafter. Planktonic mesotrophic *S. medius* is consistently present at ca. 5% abundance. The abundance of benthic taxa is consistently <10%. A deep, oligotrophic to mesotrophic state can be inferred. A moderate, nearly stable nutrient level is shown by the DI-TP reconstruction. This zone is also clearly distinguished by stable, intermediate DCA Axis 1 scores.





5.4. Zone D-4 (525–407 cm, ca. 10,700–8,500 cal yr BP)

A shallow condition prevails in Zone D-4, clearly indicated by a transition to the co-dominance of C. ocellata, S. medius and F. brevistriata (ca. 20% each), to the dominance of F. brevistriata (up to 60%) and then to the relatively high abundance of S. construens var. venter (30-40%). Heavily-silicified facultative planktonic Staurosirella martyi (Héribaud) Morales & Manoylov and S. lapponica (Grunow) Williams & Round are consistently present. Benthic taxa are at higher abundance, including smaller Amphora pediculus (Kützing) Grunow and Mayamaea atomus (Kützing) Lange-Bertalot, and heavier Diploneis mauleri (Brun) Cleve and Eolimna rotunda (Hustedt) Lange-Bertalot, Kulikovskiy & Witkowski. A. pediculus is tolerant of oligotrophic to eutrophic conditions, D. mauleri and E. rotunda live mostly in mesotrophic waters, and *M. atomus* is a eutrophic species. A relatively high trophic level can also be inferred; this is not clear in the DI-TP reconstruction but is supported by high diatom concentration in this phase.

5.5. Zone D-5 (407-277 cm, ca. 8,500-3,000 cal yr BP)

The relatively high abundance of planktonic eutrophic Aulacoseira granulata (Ehrenberg) Simonsen and mesotrophic S. medius, the consistent presence of eutrophic Stephanodiscus hantzschii Grunow, and the short-lived peak of eutrophic C. dubius around 353 cm depth (ca. 5,700 cal yr BP), indicate a relatively deep and turbid state. It is supported by relatively high DI-TP and diatom concentration, particularly between 377 and 329 cm depth (ca. 7,200-4,500 cal yr BP), where it correlates with a broad peak of plankton and high in-lake productivity. Low light availability in the deeper water would reduce the growth of benthic diatoms, while tychoplanktonic Pseudostaurosira, Staurosira and Staurosirella species (maintained at 40-60%) are commonly transported into the water column (Battarbee et al., 2001) and are tolerant of disturbed environments (Anderson, 2000). Larger and heavily-silicified planktonic diatoms sink rapidly in the absence of mixing, even in a deep lake with a long settling distance (Bennion et al., 2010; Wolin and Stone, 2010), and in a shallow lake there is insufficient mixing to suspend these taxa for long growth periods (Bennion, 1995). Thus it is relatively high lake level and mixing that make robust planktonic A. granulata, C. dubius, S. hantzschii and S. medius and tychoplanktonic S. martyi remain in the photic zone. This supports an interpretation of the planktonic abundance both in terms of productivity and increased lake level.

5.6. Zone D-6 (277–0 cm, ca. 3,000 cal yr BP-present)

Diatom concentration is low, with high dissolution, particularly between 209 and 177 cm depth (ca. 1,900-1,500 cal yr BP) and between 81 and 21 cm depth (ca. 600-100 cal yr BP), where the diatom count is < 300 valves and assemblages are dominated by poorly-preserved valves of robust taxa. More fragile taxa such as P. brevistriata and A. pediculus are possibly dissolved. Despite the dissolution, the dominance of facultative planktonic taxa and low abundance of planktonic taxa indicate a shallow environment, possibly with the expansion of emergent vegetation, because the base of emergent macrophytes is a major habitat for small fragilaroid species (Sayer, 2001). After ca. 1,000 cal yr BP (in Subzone D-6b) there is a slight increase in Amphora species, but no major ecological shift occurs in the recent past. The topmost sample is distinguished by the relatively high abundance of A. granulata, which is probably a reflection of the incorporation of living diatoms rather than an indication of recent accelerated eutrophication. In the light of the lake's modern eutrophic to hypereutrophic state, the ecologically-consistent diatom assemblages suggest that high

trophic level possibly prevails in this zone, although nutrient reconstruction is not particularly sensitive here. There are several possible reasons for lack of diatom evidence for accelerated eutrophication in the recent past: 1) eurytopic diatoms with broad tolerance ranges tend to dominate at a high trophic state as an adaptation to wide fluctuations in water chemistry, compounding the aforementioned potential for poor reconstruction at the upper end of the nutrient gradient; 2) non-planktonic diatoms respond to water-column nutrient additions less directly than phytoplankton, and they are more sensitive to habitat availability as they can derive nutrients from sediments and macrophytes (Bennion et al., 2010; Hall and Smol, 2010); 3) other algae (chlorophytes, cyanobacteria and dinoflagellates) are the most important primary producers rather than diatoms in this lake at a high trophic level; and 4) a more turbid state due to increased phytoplankton growth in turn reduces diatom growth, while chlorophytes and cyanobacteria are better competitors for light (Tilman et al., 1986).

6. Multi-proxy, regional- and catchment-scale interpretation

The diatoms provide strong proxy data for Lateglacial and Holocene changes in lake levels and trophic status in Lake Dojran, and strengthen previous lake-level and palaeoclimate interpretation by comparison with extant sedimentological and geochemical data from the same core in Fig. 6. The diatom data are also important in disentangling regional climate effects from the influence of local catchment processes on Holocene hydrological variability, and we exploit extant regional pollen data with robust chronologies for vegetation change in the highlands and lowlands in Fig. 7. We compare with various proxy data from the northeastern Mediterranean, and assess the importance of seasonality in driving Holocene moisture availability by using the summer and winter latitudinal temperature gradient (LTG) to disentangle precipitation from temperature effects (Fig. 7).

6.1. Younger Dryas (ca. 12,400–11,500 cal yr BP)

Francke et al. (2013) suggested that the presence of clay clasts, the occurrence of a 32,830 cal yr BP old shell fragment, and an undulated reflector in the hydro-acoustic data probably indicate a low lake level and redeposition between ca. 12,500-12,100 cal yr BP. This interpretation of a shallow state may be consistent with the relatively high abundance of benthic diatoms at the base of the sequence at ca. 12,500 cal yr BP. Subsequently in Subzone D-1a, even if the presence of eutrophic plankton may relate more to high productivity than lake level, the well-preserved diatom flora are important in indicating the presence of permanent water. A viable interpretation is that redeposition may occur, but that diatoms indicate lake refilling after desiccation, from a shallow state with the relatively high abundance of benthos to a relatively high lake level and eutrophic state with the dominance of plankton just above the core base. In Subzone D-1b (ca. 12,400-12,000 cal yr BP), diatom-inferred shallowing appears inconsistent with redeposition, since diatoms are well preserved, with a clear shift from the dominance of facultative planktonic taxa (50–65%) to increasing abundance of benthos, and peak concentration at the base of this subzone. Diatoms can be preserved during redeposition, as in the mass wasting deposit from Lake Ohrid (Zhang, unpublished data), but they would be present at extremely low concentration and with enhanced dissolution.

The diatom-inferred shallowing culminates in an extremely low lake level and eutrophic, oligosaline condition in the endorheic lake between ca. 12,000–11,500 cal yr BP (Zone D-2), indisputably interpreted as peak aridity of the Younger Dryas due to enhanced evaporative concentration. Based on strong evidence for the



Age (cal yr BP)







presence of permanent water derived from hydro-acoustic data, grain-size composition and the absence of clay clasts, Francke et al. (2013) interpreted this zone as one of higher lake level than the shallow or even desiccated state at the base of the sequence. Since extremely shallow or even ephemeral lakes may be characterised by 'lacustrine' sediment (Reed, 1998a, 1998b), the data in conjunction indicate that this later phase (Zone D-2) can be interpreted as a stable and lacustrine state, but with the classic enhanced aridity of the Younger Dryas.

In the northeastern Mediterranean, there is growing palynological evidence for aridity during the Younger Dryas, commonly marked by a peak in steppic pollen taxa Artemisia and Chenopodiaceae throughout the altitudinal range (e.g. Lake Ribno, 2184 m a.s.l., Tonkov et al., 2013; Lake Prespa, 849 m a.s.l., Panagiotopoulos et al., 2013; Valle di Castiglione, central Italy, 44 m a.s.l., Di Rita et al., 2013), and including a peak in Ephedra in marine records (e.g. Kotthoff et al., 2008a; Desprat et al., 2013). Pollen-based biome reconstructions (Allen et al., 2002; Bordon et al., 2009) and quantitative temperature and/or precipitation reconstructions (e.g. Bordon et al., 2009; Dormoy et al., 2009) also provide evidence of a cold, arid steppe environment. Our results are important in strengthening the sparse regional palaeohydrological dataset, which to date only comprises a distinct decrease in planktonic diatoms (particularly C. ocellata) in Lake Ioannina (Wilson et al., 2008), a peak of the eutrophic diatom species A. granulata and facultative planktonic Staurosirella pinnata (Ehrenberg) Williams & Round in Lake Prespa, Macedonia/ Albania/Greece (Cvetkoska et al., 2014), a decrease in rubidium (Rb)/strontium (Sr) ratio in Lake Stymphalia, southern Greece (Heymann et al., 2013), and an increase in $\delta^{18}O_{carb}$ values and magnesium (Mg)/calcium (Ca) ratio in Lake Van, eastern Turkey (Wick et al., 2003; Litt et al., 2009).

6.2. The earliest Holocene (ca. 11,500–10,700 cal yr BP) (corresponding to the Preboreal period)

Diatom-inferred high lake level and relatively low trophic state during the earliest Holocene (Zone D-3) strengthens the previously tentative interpretation of high $\delta^{18}O_{carb}$ values. Francke et al. (2013) suggested that evaporation was promoted during this period by large lake surface area that was accompanied by lake-level increase in such a flat-bottomed basin. The high lake level in Lake Dojran is in accord with abrupt isotopic depletion at the Younger Dryas-Holocene transition in Lake Ioannina, Lake Van and Eski Acıgöl (central Turkey) (Roberts et al., 2008 and references therein). It is also in accord with the inference of high humidity from increased Rb/Sr ratio in Lake Stymphalia (Heymann et al., 2013). However, it is not in complete agreement with vegetation development in the northeastern Mediterranean during the earliest Holocene. Nonsteppic herb pollen increased rather than Quercus pollen in SL152 in the northern Aegean region at this time (Kotthoff et al., 2008a). Non-steppic herb pollen were abundant during this period although Quercus pollen increased rapidly at the onset of the Holocene in Nisi Fen (Lawson et al., 2005) and Lake Accesa (central Italy) (Drescher-Schneider et al., 2007). Non-steppic herb and steppe pollen were replaced by Quercus pollen gradually until its maximum around 10,500 cal yr BP in Lake Prespa (Panagiotopoulos et al., 2013) and Tenaghi Philippon (northeastern Greece) (Müller et al., 2011). Non-steppic herb pollen was dominant, with a gradual increase of Quercus pollen until ca. 10,500 cal yr BP in Eski Acıgöl (Roberts et al., 2001; Turner et al., 2008) and MD04-2797 (Siculo-Tunisian Strait) (Desprat et al., 2013). Non-steppic herb pollen replaced steppe pollen gradually during this period, along with a slightly increasing trend in Quercus pollen in Lake Van (Litt et al., 2009). Non-steppic herb taxa were more important in these records than the percentage data implied, because they are mostly lower pollen producers than *Quercus* (Broström et al., 2008).

The high lake level in Lake Dojran and isotopic depletion in the northeastern Mediterranean suggest that the increase in humidity during the earliest Holocene would be attributed to increased precipitation, since Younger Dryas mountain glaciations did not develop widely in this region (Hughes et al., 2006; Hughes, 2012) and meltwater input is an unlikely forcing function. However, the wide distribution of non-steppic herb taxa suggest that increased moisture availability was insufficient to support extensive forest development, since afforestation linked to soil development was asynchronous in this region. The limited increase in humidity is possibly the effect of high evaporation, corresponding to high pollen-inferred area-average summer and winter temperature in southeastern Europe (Davis et al., 2003) and high alkenoneinferred sea surface temperature (SST) at the beginning of the Holocene in the Mediterranean Sea (Abrantes et al., 2012). The comparison with the summer and winter LTG supports increased precipitation during the earliest Holocene. The negative (strong) winter LTG resulted in the negative phase of AO (Davis and Brewer, 2009), and promoted the penetration of more westerly moisture of North Atlantic origin in winter. The summer LTG suggests that the Subtropical High pressure was not strengthened and displaced northward (Davis and Brewer, 2009), and summer moisture was not scarce at this time. Thus the LTG and atmospheric moisture availability would contribute to the increase in precipitation during the earliest Holocene, modulated by high temperature-induced evaporation.

Changes in catchment vegetation and erosion can have a major influence on lake hydrology and nutrient input and hence diatom composition (Fritz and Anderson, 2013). At the catchment scale, the steppe vegetation was replaced by birch forest at high altitudes (Lakes Ribno and Trilistnika, the Rila Mountain, southwestern Bulgaria) (Tonkov et al., 2008, 2013) and by non-steppic herbs in the lowlands (SL152, northern Aegean Sea) (Kotthoff et al., 2008a). Despite increased precipitation and water inflow, the vegetation development restrained catchment erosion and nutrient input, which is supported by lower clastic input indicated by decreased K concentration (Francke et al., 2013). Together with the dilution effect of increased freshwater input, lower nutrient input resulted in the relatively low trophic level and in-lake productivity, which is supported by low organic matter content (Francke et al., 2013). In the northeastern Mediterranean, low trophic levels during the earliest Holocene were also indicated by pigment and diatom data in Lake Albano, central Italy (Guilizzoni et al., 2002). In all, increased precipitation was a major contributor to the high lake level in Lake Dojran and increased humidity in the northeastern Mediterranean during the earliest Holocene, although high evaporation reduced the effect of increased precipitation.

6.3. The early Holocene (ca. 10,700-8,500 cal yr BP)

The diatom data show a low lake level and relatively high trophic state during the early Holocene (Zone D-4), which is not in accord with decreasing $\delta^{18}O_{carb}$ values in Lake Dojran. Francke et al. (2013) suggested that the littoral zone might extend during this phase. If valid, epiphytic and epipelic diatoms can be similarly facilitated, and they could reach the coring site through water mixing and/or sediment redistribution. However, water mixing would cause nutrients to become well distributed in the water column as well as in the pelagic zone, conflicting with the rather low relative abundance of planktonic taxa at the coring site; sediment disturbance would be unfavourable to the settlement and preservation of smaller, fragile valves, conflicting with the relatively high percentages of *A. pediculus* and *M. atomus*.

The diatom-inferred low lake level is also inconsistent with low bulk carbonate δ^{18} O values in Lake Pergusa (Sicily) (Sadori et al., 2008), authigenic carbonate δ^{18} O values in Lake Gölhisar (southwestern Turkey) (Eastwood et al., 2007) and ostracod δ^{18} O values in Lake Ioannina (Frogley et al., 2001). Roberts et al. (2008) suggested that the freshening of surface water in the eastern Mediterranean Sea in parallel with sapropel formation would affect the isotopic composition of precipitation during the early Holocene. However, the low lake level in Lake Dojran is in line with relatively high δ^{18} O values of authigenic carbonates in Lake Ohrid (Macedonia/Albania) (Leng et al., 2010), Lake Prespa (Leng et al., 2013) and Lake Van (Litt et al., 2009), and mollusc $\delta^{18}O$ values in Lake Frassino (northern Italy) (Baroni et al., 2006). The apparent discrepancy in isotope proxy data is probably due to the control of different hydroclimatic parameters (Jones and Roberts, 2008) and the influence of catchment factors on the specific hydrology of each lake (Leng and Marshall, 2004). The diatom-based inferences in Lake Dojran are also in accord with the inference of low lake levels from low Rb/Sr ratio in Lake Stymphalia (Heymann et al., 2013) and high Ca/titanium (Ti) ratio in Lake Iznik, northwest Turkey (Roeser et al., 2012) at this time.

Palynological data are also complex, with the occurrence of different ecological pollen groups in this region (e.g. Roberts et al., 2011b; Sadori, 2013) and even in the same record (e.g. Peyron et al., 2011; Panagiotopoulos et al., 2013), which have been interpreted in different ways. The apparent discrepancy in the regional vegetation distribution was attributed to spatial and altitudinal variation in climatic factors (De Beaulieu et al., 2005; Sadori, 2013), and Roberts et al. (2011b) suggested that increased seasonality of climatic factors is an important factor. Willis (1992a) invoked the distance from mountain refugia of different taxa, and Sadori et al. (2011) linked this to edaphic conditions and water retention capacity suitable for different plant growth. With respect to the combination of ecologically-incompatible pollen groups in the same record, Panagiotopoulos et al. (2013) attributed this to a more even distribution of annual precipitation, while Magny et al. (2013) invoked high seasonality of precipitation. Roberts et al. (2011b) cautioned against interpreting this pollen flora too closely in terms of modern climate analogues. Despite this complexity, the Lake Dojran diatom data are supported by pollen-based quantitative reconstructions of higher winter precipitation and lower or consistently low summer precipitation in SL152 (Dormoy et al., 2009), Lake Accesa (Peyron et al., 2011), Lake Pergusa (Magny et al., 2012; Peyron et al., 2013) and MD04-2797 (Desprat et al., 2013). The low lake level and relatively high trophic state in Lake Dojran are probably driven by strong seasonal hydrological contrasts, and extreme summer aridity offset the effect of winter precipitation recharge. This is consistent with the wide distribution of Quercus ilex in the northern Aegean region rather than Quercus deciduous type (Kotthoff et al., 2008b), although moisture availability was sufficient to support tree growth.

The comparison with the summer and winter LTG supports this climatic interpretation as high seasonality. The negative (strong) winter LTG suggests that AO was in the negative phase (Davis and Brewer, 2009), the storm track was in a southerly path and moisture availability in winter was high during the early Holocene. The positive (weak) and increasing summer LTG suggests that the Subtropical High pressure was migrating northward (Davis and Brewer, 2009), blocking westerly moisture penetration in summer and leading to much drier summers than today. It is associated with the intensified African monsoon and the large number of lake records in the Sahara and Sahel (Lézine et al., 2011), and with sapropel formation in the eastern Mediterranean Sea since 10,800 cal yr BP (De Lange et al., 2008). Thus the LTG and high seasonality of moisture availability would contribute to the reduced

lake level and increased nutrient level in Lake Dojran during the early Holocene.

At the catchment scale, the Lake Dojran diatom data coincide with extensive forest development, mainly comprising deciduous oak forest (Quercus robur and Quercus cerris) at high altitudes (Lakes Ribno and Trilistnika, southwestern Bulgaria) (Tonkov et al., 2008, 2013) and evergreen oak forest (Q. ilex) in the lowlands (SL152, northern Aegean Sea) (Kotthoff et al., 2008a, 2008b). According to the contrasting growth requirements of deciduous and evergreen oaks (Roberts et al., 2011b), it can be posited that the dense, thick vegetation would reduce runoff and erosion in the catchment throughout the year through soil absorption and retention, which may contribute to the low lake level, high shell abundance and lower K concentration during this phase (Francke et al., 2013). However, forest vegetation would enhance chemical weathering and nutrient supply through soil development, which may contribute to the relatively high trophic level in spite of the limited water inflow. This is supported by high diatom concentration, as well as higher organic matter and carbonate content (Francke et al., 2013), indicating high in-lake productivity. In all, the low lake level and relatively high trophic state in Lake Dojran may result climatically from high seasonality of precipitation and locally from dense forest development and limited, nutrient-rich catchment runoff.

6.4. The mid Holocene (ca. 8,500-3,000 cal yr BP)

A relatively high lake level and maximum Holocene trophic level are inferred during the mid Holocene (Zone D-5). This is supported by decreased $\delta^{18}\text{O}_{carb}$ values. Francke et al. (2013) also discussed a relatively high lake level during this phase based on sedimentological data. The relatively high lake level in Lake Dojran is consistent with low $\delta^{18}O_{carb}$ values in Lake Prespa (Leng et al., 2013) and Lake Van (Litt et al., 2009), low mollusc $\delta^{18}\text{O}$ values in Lake Frassino (Baroni et al., 2006), and high lake levels in Lake Xinias, central Greece (Digerfeldt et al., 2007). However, in the northeastern Mediterranean, an aridification trend was shown by isotopic enrichment in Eski Acıgöl (Roberts and Jones, 2002), diatom succession in Lake Ioannina (Wilson et al., 2008; Jones et al., 2013), and lithological changes in Lake Pergusa (Sadori and Narcisi, 2001). Sadori et al. (2011) and Roberts et al. (2011b) improved understanding of this aridification process after ca. 8,000 cal yr BP based on a regional synthesis of pollen and isotope data, respectively. The comparison with the summer and winter LTG does not give support to increased humidity during the mid Holocene. Both the summer and winter LTG were more positive (weaker) during this period (Davis and Brewer, 2009), and the positive phase of AO and the northern position of the Subtropical High pressure suggest that winter was not influenced by the northward-shifted storm track and summer was controlled mostly by the downdraught of dry air, respectively. This would lead to low winter precipitation and much drier summers than today, although several regional syntheses of temperature (Davis et al., 2003; Finné et al., 2011; Abrantes et al., 2012) suggested cooling and decreased evaporation during the mid Holocene.

At the catchment scale, the relatively high lake level and high trophic state in Lake Dojran coincide with the dominance of coniferous forest (mainly firs) at high altitudes at ca. 8,500–7,800 cal yr BP (Lakes Ribno and Trilistnika, southwestern Bulgaria) (Tonkov et al., 2008, 2013) and the opening of the oak forest with an increase in non-steppic herbs in the lowlands (SL152, northern Aegean Sea) (Kotthoff et al., 2008a, 2008b). The reduction of forest density in the lowlands, most probably corresponding to the aridification process discussed above, was also clearly indicated by a distinct decrease in *Quercus* pollen concentration at ca. 8,400 cal yr BP (Kotthoff et al., 2008a), which would

cause an increase in nutrient mobility. The expansion of firs at high altitudes is a regional signal across the southern Balkans, including Rezina Marsh (1800 m a.s.l.) at ca. 8,600 cal yr BP (Willis, 1992b). Fir trees developed in more humid and organic soils (Sadori et al., 2011), and the wetting of the highlands and forest development enhanced runoff and nutrient supply. In all, the wetting of the highlands and associated local vegetation succession enhanced catchment runoff and nutrient erosion, and resulted in the relatively high lake level and eutrophic state in Lake Dojran.

6.5. The late Holocene (ca. 3,000–0 cal yr BP)

Despite low diatom concentration and high dissolution, a low lake level and high trophic state can be inferred during the late Holocene (Zone D-6). Late-Holocene aridity prevailed in the northeastern Mediterranean, indicated by isotope data (e.g. Roberts et al., 2008, 2011b; Leng et al., 2013) and lake-level reconstructions (e.g. Harrison and Digerfeldt, 1993; Digerfeldt et al., 2007; Magny et al., 2011). The comparison with the summer and winter LTG suggests that atmospheric moisture availability is not a determining factor, because the Subtropical High pressure regressed and AO index was slightly negative, which would not result in the obvious moisture deficit in this region. In contrast, the increase in regional temperature (Davis et al., 2003; Finné et al., 2011) and high evaporation may contribute to the aridity during the late Holocene, although one model simulation suggests that anthropogenic deforestation may itself have caused a decrease in summer and winter temperature in southern Europe due to increased albedo effect (Strandberg et al., 2014).

A previous late-Holocene palynological study in the littoral zone of Lake Dojran revealed that the oak forest in the lowlands and the conifer and beech forests in the mountain region were replaced by herb vegetation and secondary trees at ca. 2,800 cal yr BP as a result of intensified human impact (Athanasiadis et al., 2000). At the catchment scale, beech and spruce forests expanded widely at high altitudes, and beech trees were favoured by human agricultural and stock-breeding activities and resultant soil deterioration (Marinova et al., 2012; Tonkov et al., 2013). Non-steppic herbs expanded in the lowlands along with the further decline of the oak forest, and human disturbance was an important factor (Kotthoff et al., 2008a). Deforestation at mid-low altitudes during the late Holocene was also a regional event, for example, in Nisi Fen (475 m a.s.l.) the temperate forest declined at ca. 3,500 cal yr BP (Lawson et al., 2005; Kotthoff et al., 2008a), and in Lake Ohrid (693 m a.s.l.) it was reflected by the reduction of the coniferous forest at ca. 2,500 cal yr BP (Wagner et al., 2009). Thus human impact is possibly an important factor not only leading to the high trophic state during the late Holocene by deforestation and enhanced nutrient erosion, but also contributing to the low lake level through agriculture and irrigation.

7. Conclusions

The Lake Dojran diatom data, supported by extant sedimentological and geochemical data from the same core and late-Holocene palynological data from a separate littoral core, give a new insight into Younger Dryas and Holocene changes in lake levels and trophic status in the northeastern Mediterranean. The Lake Dojran diatom data provide more robust evidence and strengthen previous lakelevel interpretation based on sedimentological and geochemical data during the earliest, mid and late Holocene, and also clarify previous uncertainty in interpretation of Younger Dryas and early-Holocene lake-level change. Following a very shallow or even desiccated state at the core base at ca. 12,500 cal yr BP, indicated by sedimentological and hydro-acoustic data, diatoms indicate lake infilling, from a shallow state with abundant benthos to a planktondominated relatively high lake level and eutrophic state thereafter. Diatom-inferred shallowing between ca. 12,400-12,000 cal yr BP and a very low lake level and eutrophic, oligosaline state between ca. 12,000–11,500 cal yr BP provide clear evidence for aridity during the Younger Dryas. Although a slightly higher lake level was previously inferred during the second part of this period, the lacustrine state with permanent water does not conflict with the diatominferred salinity shift. Lake Dojran's water level increased markedly during the earliest Holocene (ca. 11,500–10,700 cal yr BP). A low lake level and relatively high trophic state are inferred during the early Holocene (ca. 10,700-8,500 cal yr BP), conflicting with the previous inference of increased humidity from decreasing $\delta^{18}O_{carb}$ values and sedimentological data. Lake Dojran was relatively deep and exhibited the maximum Holocene trophic level during the mid Holocene (ca. 8,500-3,000 cal yr BP), and it became shallow during the late Holocene (ca. 3,000–0 cal yr BP). Our results indicate that, being located at the juncture of the proposed boundaries between the west-east and north-south contrasting Holocene climatic domains, Lake Dojran cannot be classified simply into the western or eastern sector, or the northern or southern sector in the Mediterranean.

Our results are also important in disentangling regional climate effects from local catchment dynamics during the Holocene, and to this end we exploit extant regional palynological data for vegetation change in the highlands and lowlands. The importance of seasonality in driving Holocene climate change is assessed by reference to the summer and winter LTG model, linked to the Subtropical High pressure and AO, respectively. We suggest that diatom-inferred high lake level during the earliest Holocene was attributed to the increase in precipitation, in spite of high polleninferred, temperature-induced evaporation, and is coherent with high winter and summer atmospheric moisture availability inferred from the LTG. The relatively low trophic state at this time was possibly driven in part by vegetation development and reduced catchment erosion. The diatom-inferred early-Holocene lake-level reduction and increased trophic level may result climatically from high seasonality of precipitation, coherent with the contrasting summer and winter LTG, and locally from limited, nutrient-rich runoff in a densely-forested catchment. The relatively deep, eutrophic state in Lake Dojran during the mid Holocene shows strong affinity with palaeolimnological data from central Greece, northern Italy and eastern Turkey, but not with other records in the northeastern Mediterranean, where aridification is recognised. It is also not coherent with the LTG-inferred low atmospheric moisture availability. This may reflect local complexity of climate variability, but may also indicate that changes were driven more by local vegetation succession and associated changes in catchment processes than by climate change. During the late Holocene, diatominferred shallow and high trophic state is consistent with strong regional evidence for temperature-induced aridity, coupled with the influence of intensified human land use.

Overall, our study is important in strengthening existing multiproxy interpretation of Lateglacial and Holocene palaeohydrology and associated shifts in nutrient status. This study improves understanding of Younger Dryas and Holocene climate change in the northeastern Mediterranean, providing a coherent interpretation which suggests the important role of the LTG on moisture availability during the Holocene and clarifies the influence of catchment processes on Holocene hydrological variability.

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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 ²¹⁰Pb-dated sediment cores spanning the period from 1918 to 2009. According to the index of geoaccumulation, sediments were often moderately

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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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A. Schwalb Institut für Geosysteme und Bioindikation, Technische Universität Braunschweig, Langer Kamp 19 c, 38106 Brunswick, Germany e-mail: antje.schwalb@tu-bs.de 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. 1993; 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 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, northwest 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 ²¹⁰Pb and ¹³⁷Cs 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 km² belongs to Macedonia and 128.2 km² 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 km² (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 $0.4 \text{ m}^3 \text{ s}^{-1}$), Sateska $(5.5 \text{ m}^3 \text{ s}^{-1})$, Koselska $(1.3 \text{ m}^3 \text{ s}^{-1})$, and Čerava (0.2 m³ 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 grabenshaped 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 $\sim 1,500$ 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 \sim 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), 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 ²¹⁰Pb and ¹³⁷Cs 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.

Chronology

¹³⁷Cs, ²²⁶Ra, and ²¹⁰Pb 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 ²¹⁰Pb activities were obtained by level by level subtraction of ²²⁶Ra activities from total activities. Chronologies were established using the Constant Flux and Constant Sedimentation rate model (CFCS model) (Appleby and Oldfield 1992) for ²¹⁰Pb as well as the beginning of ¹³⁷Cs 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 freezedried, 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



Fig. 2 ¹³⁷Cs and total and unsupported ²¹⁰Pb (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 ¹³⁷Cs

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 NaphraxTM 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

¹³⁷Cs peaks (1955, 1963, and 1986) were first identified independently and then compared with results from sedimentation rates based on the ²¹⁰Pb data so that the three marker ages could be assigned to the ¹³⁷Cs 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 ²¹⁰Pb data was appropriate.

The total ²¹⁰Pb activities in core St09 (Fig. 2) ranged between 155 Bq kg⁻¹ (2.25 cm) and 26 Bq kg⁻¹ (39.50 cm). Unsupported ²¹⁰Pb 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 ²¹⁰Pb model, an average sedimentation rate of 0.40 cm year⁻¹ has been determined. Maximum ¹³⁷Cs 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 ¹³⁷Cs maximum in 1963. The onset of ¹³⁷Cs 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 ²¹⁰Pb 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 ²¹⁰Pb activities ranged from 138 Bq kg⁻¹ (0.25 cm) to 6 Bq kg⁻¹ (20.50 cm). Using the CFCS ²¹⁰Pb model, an average sedimentation rate of 0.47 cm year⁻¹ was

determined. ¹³⁷Cs activities in core Sv09 failed to display a sharp peak that might identify the onset of ¹³⁷Cs production in 1955 and the maximum fallout of 1963, nevertheless, the ¹³⁷Cs 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 ¹³⁷Cs and ²¹⁰Pb 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 grevish 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 (Igeo) (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 $(48.6 \text{ mg kg}^{-1})$ (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 $[1969-1972 \text{ AD } (58.04 \text{ g kg}^{-1}), 1986-1989 \text{ AD}]$ $(47.81 \text{ g kg}^{-1}),$ and 2003-2005 AD cm $(54.32 \text{ g kg}^{-1})$] 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



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 obligua 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.

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



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. (2012) 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 (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

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 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 Igeo 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 Igeo "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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The SCOPSCO drilling project recovers more than 1.2 million years of history from Lake Ohrid

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Abstract. The Scientific Collaboration on Past Speciation Conditions in Lake Ohrid (SCOPSCO) project is an international research initiative to study the influence of major geological and environmental events on the biological evolution of lake taxa. SCOPSCO drilling campaigns were carried out in 2011 and 2013. In 2011 we used gravity and piston coring at one of the five proposed drill sites, and in 2013 we undertook deep drilling with the Deep Lake Drilling System (DLDS) of Drilling, Observation and Sampling of the Earth's Continental Crust (DOSECC). In April and May 2013, a total of 2100 m sediments were recovered from four drill sites with water depths ranging from 125 to 260 m. The maximum drill depth was 569 m below the lake floor in the centre of the lake. By retrieving overlapping sediment sequences, 95% of the sediment succession was recovered. Initial data from borehole logging, core logging and geochemical measurements indicate that the sediment succession covers > 1.2 million years (Ma) in a quasi-continuous sequence. These early findings suggest that the record from Lake Ohrid will substantially improve the knowledge of long-term environmental change and short-term geological events in the northeastern Mediterranean region, which forms the basis for improving understanding of the influence of major geological and environmental events on the biological evolution of endemic species.

1 Introduction and goals

The Scientific Collaboration on Past Speciation Conditions in Lake Ohrid (SCOPSCO) project is an international research initiative to study the influence of major geological and environmental events on the biological evolution of aquatic taxa. The target site is Lake Ohrid, considered the oldest lake in continuous existence in Europe, and which contains more than 200 endemic species. The recovery of long sediment sequences from Lake Ohrid enables us to obtain information about the age and origin of the lake, and helps to improve our understanding of the regional climatic and environmental evolution including the history of Italian volcanic eruptions.

Lake Ohrid is ~ 30 km long, 15 km wide, covers an area of 358 km², and is located at an altitude of 693 m above sea level (a.s.l.) between Albania and Macedonia on the Balkan Peninsula (Fig. 1). The lake has a maximum water depth of 289 m and a volume of 55.4 km³. The total inflow of water can be estimated to $37.9 \text{ m}^3 \text{ s}^{-1}$, with ca. 25 % originating from direct precipitation and 25 % from riverine inflow. About 50 % of the total inflow derives from karst aquifers, of which ca. 8 m³ s⁻¹ are believed to come from Lake Prespa (Wagner et al., 2010, and references therein). Including Lake Prespa, the total catchment covers an area of 2393 km². Evaporation (40%) and the main outflow, the river Crni Drim (60%), balance the water budget of Lake Ohrid. Due to its large water volume and low nutrient availability, Lake Ohrid is highly oligotrophic today (e.g. Wagner et al., 2010). The surface water has a specific conductivity of $\sim 200 \,\mu S \, cm^{-1}$ and a pH of ~ 8.4 (Matter et al., 2010).

Lake Ohrid is renowned for having an outstanding degree of biodiversity for several groups of organisms, including 212 described endemic species. Endemic species are found in several groups, including bacteria, macrophytes, diatoms, and almost all animal groups such as crustacea, molluscs and fish (Albrecht and Wilke, 2008). There are very few lakes worldwide that contain species with this degree of endemism; examples include lakes Baikal, Tanganyika, Victoria and Malawi. However, all these lakes have a much larger surface area, meaning that Lake Ohrid is the most diverse lake in the world when the number of endemic species is related to surface area (Albrecht and Wilke, 2008). This intriguing characteristic contributed significantly to the establishment of Lake Ohrid as UNESCO World Heritage Site in 1979.

Lake Ohrid is considered to be the oldest lake in Europe and is one of the very few ancient lakes on earth that has likely existed continuously for more than 1 Ma. Geological studies suggest that the lake basin formed during the final phases of Alpine orogeny in an approximately N–S trending graben structure between ca. 10 and 2 Ma (cf. Lindhorst et al., 2014). Molecular clock analyses of several endemic species flocks (i.e. groups of closely related species) indicate

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Figure 1. Topographic and bathymetric map of Lake Ohrid on the Balkan Peninsula. ICDP coring sites are indicated by white dots. The red lines indicate the locations of seismic profiles shown in Figs. 2, 3 and 4.

that Lake Ohrid is probably 1.5 to 3 Ma old (Trajanovski et al., 2010).

Previous sedimentary records from Lake Ohrid are up to ca. 15 m long and span the last glacial/interglacial cycle with some minor hiatuses. These records indicate that Lake Ohrid sediments contain information on long- and shortterm climate change in this region (e.g. Vogel et al., 2010a; Wagner and Wilke, 2011). Other terrestrial records spanning more than 1 Ma are rare from the northern Mediterranean region. The most prominent study is likely the pollen record from Tenaghi Philippon, which covers the last ca. 1.35 Ma (Tzedakis et al., 2006). Continuous marine records of equivalent age are also rare and often analysed at too low temporal resolution (e.g. Kroon et al., 1998) to reliably reconstruct short-term events. In addition to generating proxy data on long- and short-term environmental change, our preliminary studies also revealed that Lake Ohrid is a distal archive of the activity of Italian volcanoes. Its sediments comprise ca. 10 tephra and cryptotephra (i.e. non-visible tephra) layers in the last ca. 140 ka. These volcanic event

Table 1. SCOPSCO drill sites.

Site	Water depth (m)	# of holes (planned)	Total drill metres (m)	Total recovery (m)	Deepest drill depth (m b.l.f.)	Length of composite record * (m)	Remarks
DEEP	243	6 (2)	2088.71	1526.06	568.92	544.88 (95.77%)	spot coring
Cerava	119/131	2 (2)	175.71	172.20	90.48	87.86 (97.10%)	site on a slope
Gradište	131	3 (2)	327.35	224.46	123.41	114.07 (92.43%)	
Peštani	262	1 (0)	194.50	177.90	194.50	177.90 (91.45%)	
Lini	260	1 (2)	10.08	10.08	10.08	10.08 (100.00 %)	drilled in 2011
Struga	0	0 (2)	0	0	0	0	skipped

* Composite field recovery is estimated based on field depths and magnetic susceptibility measurements.

layers provide information on ash dispersal from the prominent volcanic regions in Italy and contribute significantly to the construction of a robust chronology by comparison with other dated records in the region using tephrochronological cross-correlation of geochemical fingerprints (Sulpizio et al., 2010; Caron et al., 2010; Vogel et al., 2010b; Damaschke et al., 2013). In addition, analysis of Lake Ohrid sediments will generate information on tectonic events. The lake is located in a highly active seismic zone with frequent earthquakes (e.g. Muço et al., 2002; NEIC database, USGS), and the lacustrine sediments on the subaquatic slopes are subject to mass wasting and seismite formation (Wagner et al., 2008; Reicherter et al., 2011; Lindhorst et al., 2012). Studies from other lakes and marine basins have shown that these mass-wasting deposits can be used to reconstruct the longterm earthquake history of a region (e.g. Schnellmann et al., 2002; Beck et al., 2012).

Despite uncertainties in age estimation, its likely continuous existence over more than 1 Ma makes Lake Ohrid an extant hotspot of evolution and an evolutionary reservoir enabling relict species to survive (Albrecht and Wilke, 2008). These outstanding characteristics allowed Lake Ohrid to become one of the target sites within the scope of the International Continental Scientific Drilling Program (ICDP). The deep drilling of Lake Ohrid has four major aims: (i) to obtain precise information about the age and origin of the lake, (ii) to unravel the regional seismotectonic history including effects of major earthquakes and associated mass-wasting events, (iii) to obtain a continuous record containing information on Quaternary volcanic activity and climate change in the central northern Mediterranean region, and (iv) to evaluate the influence of major geological events on evolution and the generation of the observed extraordinary degree of endemic biodiversity.

2 Site selection

The site selection for the deep drilling project was based on hydro-acoustic surveys carried out between 2004 and 2008. Multichannel seismic data were collected using a Mini GI Air Gun (0.25 L in 2007 and 0.1 L in 2008) and a 16-channel 100 m long streamer, complemented by parametric sediment echosounder profiles (SES-96 light in 2004 and SES 2000 compact in 2007 and 2008, Innomar Co.). The theoretical vertical resolution of both types of seismic data can be estimated to be 2 m for the Mini GI gun and 0.2 m for the Innomar data.

Based on a dense grid of multichannel seismic data ($\sim 500 \text{ km}$ total length) and sediment echosounder profiles (> 900 km total length), five drill sites were originally proposed (Fig. 1; Table 1). They range from 80 to 260 m water depth and had target drilling depths between 20 and 680 m.

The "DEEP" site is located in the central basin of Lake Ohrid in ~250 m water depth. This master site is well suited to address most of our key research questions (Table 1). The seismic data from the central basin show a rough basement topography with numerous highs and lows (Figs. 2 and 3). The basement lows are characterized by onlap fills and therefore suggested possible recovery of the longest records. The DEEP site is located in a basement depression with an estimated maximum sediment fill of 680 m (Fig. 3). Seismic data show undisturbed sediments without unconformities or erosional features, thus suggesting that a continuous sediment record of maximum age and free of major hiatuses could be recovered. Strong multiples, however, mask the lower part of the sedimentary succession.

The "Struga" site is located close to the northern shore of Lake Ohrid (Fig. 1). It is the shallowest (80 m water depth) of all the sites. The objectives of this site are to investigate changes in the hydrological regime, to obtain information on lake level fluctuations, and potentially to obtain macrofossils for a cross-validation with the results obtained from molecular clock analyses. The intention to drill at the Struga site in the northern part of the lake was abandoned for logistical reasons during the drilling campaign. Instead, a new site was selected in the eastern part of the lake. This "Peštani" site (Fig. 1) had a water depth of 260 m and was chosen with the aim of reaching sediments deposited directly above the bedrock at ca. 200 m below lake floor (b.l.f.; Fig. 4).

The "Cerava" site (Figs. 1 and 4) is located on a lake terrace in 125 m water depth close to the southern shore of Lake Ohrid, 2–3 km off the southern feeder spring area and Cerava River, which are the main tributaries to Lake Ohrid. Several



Figure 2. Seismic profile crossing Lake Ohrid in N–S direction. The central basin shows thick undisturbed sediments, which were drilled at the DEEP site. The DEEP site is about 1 km to the west of the seismic line. Other prominent features include faults, slides, clinoforms and bright spots. See Fig. 1 for location.

clinoforms in the seismic data reflect the development of terraces, which are linked to lake-level fluctuations. The main objective of this site is to reconstruct these variations. In addition, data from this core will be used to support our interpretation of tectonic activities and related mass-movement events.

The "Gradište" site (Figs. 1 and 4) is located in 130 m water depth close to the eastern margin of the lake in the hanging wall of a major active lake-bounding normal fault. The bathymetry reveals a steep west-dipping major fault associated with a small graben on the lake floor, which suggests recent activity of this fault. The Gradište site is also characterized by high inflow from sublacustrine karstic springs and constitutes the most important hotspot of endemic biodiversity in the lake. Macrofossils from this site are expected to best reflect the evolutionary history of invertebrates and plants and should allow us to test the role of sublacustrine springs in generating and maintaining biodiversity.

The "Lini" site (Figs. 1 and 4) is off the Lini Peninsula in 260 m water depth close to the western shore of Lake Ohrid. This locality was selected to study fault activity on the west-

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ern basin bounding faults. Seismic profiles across the western coast show that the steepest gradient in front of the Lini Peninsula is due to active scarps of eastwards-dipping normal faults. The tectonic setting is comparable to the Gradište site with a set of active antithetic faults.

3 Coring results and borehole logging

Coring was originally planned for summer 2011 using Drilling, Observation and Sampling of the Earth's Continental Crust's (DOSECC) Deep Lake Drilling System (DLDS). Although this was postponed, a coring campaign using UWITEC (Austria) equipment was carried out in June 2011 in order to recover a 20 m long sediment sequence proposed for the Lini site and also surface sediment cores from the DEEP site. A gravity corer was used to obtain the undisturbed surface sediments, and deeper sediments were recovered with a piston corer. A re-entry cone, which was positioned on the lake bed, and extension rods of 2 m length controlled the exact release of the piston to ensure retrieval of a



Figure 3. Seismic profile crossing the DEEP site in W–E direction (only Macedonian part of Lake Ohrid due to missing Albanian permissions during the 2007 survey). See Fig. 1 for location. The green line in the seismic profile indicates the approximate maximum depth of cores recovered from DEEP site, whilst the black line indicates the originally proposed target depth.

continuous core sequence. Core recovery at the Lini site was around 100% including core catcher samples. Core loss or disturbance of sediment between the individual 2 m segments is therefore regarded as low (< 6 cm). However, bad weather and high waves on Lake Ohrid stopped the coring campaign at ca. 10 m depth in 2011. At the DEEP site, a 1.6 m long surface sediment sequence was retrieved.

A fire on the container vessel MV *MSC Flaminia*, which transported the DLDS from the US to Europe in summer 2012, caused a second delay for the start of the drilling operations. Finally, drilling started in late March 2013, and by late May 2013 a total of ~ 2100 m of sediment had been recovered from Lake Ohrid at four different sites. The SCOPSCO drilling operation is heralded as one of the most successful ICDP lake drilling campaigns ever.

At the DEEP site, six parallel holes were drilled with a maximum sediment depth of 569 m b.l.f. (Fig. 3). Pelagic sediments characterize the uppermost 430 m of the sediment column (Fig. 5). Below 430 m b.l.f., shallow water facies became increasingly dominant, including fine-grained material with high organic matter content, coarser sediments with shell remains, and distinct sand layers. Gravel and pebbles hampered penetration deeper than 569 m b.l.f. In total, 1526 m of sediment cores were recovered from the six parallel holes at the "DEEP" site. Taking into account sediment–core overlap, the total composite field recovery amounts to

95 % (545 m), being higher (99 %) for the uppermost 430 m (Fig. 5). At the Cerava site, two parallel cores were drilled with a maximum sediment depth of 90.5 m b.l.f. (Fig. 6). The composite field recovery was ca. 97 % (88 m). The basal sediments recovered consist of lithified sediments and shell fragments or whole shells. At the Gradište site, three parallel cores were drilled with a maximum sediment depth of 123 m b.l.f. (Fig. 6). The composite core recovery was 92 % (114 m). Coarse-grained sediments dominate below 82 m b.l.f. At the Peštani site only one hole with a maximum sediment depth of 194.5 m b.l.f. was recovered (Fig. 6). The core recovery was 91 % (178 m).

At all four drill sites, generation of high-quality continuous downhole logging data comprising spectral gamma ray, magnetic susceptibility (MS), resistivity, dipmeter, borehole televiewer and sonic data was achieved. Additional zerooffset vertical seismic profiling was conducted at the DEEP site. Spectral gamma ray was run through the drill pipe, and thereafter pipes were pulled gradually to maintain the borehole stability. All the other tools were run in about 40 m long open hole sections.

4 Preliminary scientific results

4.1 Downhole logging

Downhole logging data at the DEEP site reveal contrasting physical properties in spectral gamma ray (gamma ray, K, U, Th), MS, resistivity and seismic velocity (vp) data. The sediment sequence below 430 m b.l.f. is characterized by higher gamma ray values (mean: 70 gAPI) than pelagic sediments above, showing a cyclic alternation of low (20 gAPI) and high (65 gAPI) gamma ray values (Fig. 5).

4.2 Sedimentological work

In addition to borehole logging, some data have already been generated from the sediment sequences recovered. The age model and sediment stratigraphy of the 10 m long sediment sequence recovered from the Lini site in summer 2011 spans the Late Pleistocene to Holocene and contains two masswasting deposits (Wagner et al., 2012). The more significant uppermost mass-wasting deposit is almost 2 m thick and directly overlies the AD 472/512 tephra. The exact age of this mass-wasting deposit cannot be defined because the tephras from AD 472 and AD 512 indicate geochemical overlapping, and the sediments of Lake Ohrid are not annually laminated. However, the lack of any apparent erosional discordance at the base of the mass-wasting deposit and the small distance to the AD 472/512 tephra imply that the mass-wasting deposit occurred in the early 6th century AD (Wagner et al., 2012). A likely trigger for this mass-wasting event could be a historical earthquake that destroyed the city of Lychnidus (Ohrid). According to historical documents, this earthquake could have occurred at AD 518, AD 526, or AD 527.



Figure 4. Seismic cross sections at drill sites (A) Cerava, (B) Gradište, (C) Peštani, and (D) Lini. The green line in the individual seismic profiles indicates the approximate maximum depth of cores recovered, whilst the black line indicates the target depth.

Although the sediment sequence from the Lini site is shorter than proposed, the results indicate that one of the main scientific goals of the project – to reconstruct active tectonics and mass wasting (Table 1) – can be achieved.

MS was measured on all cores recovered in summer 2013 using a multi-sensor core logger (MSCL; Geotek, UK) in a field laboratory. Logging started immediately after the transportation of the cores from the drilling platform to the laboratory in order to ensure best possible overlap between individual holes. The volume-specific MS was measured over 10 s for every 2 cm of each core section with a whole core loop sensor (internal diameter: 10 cm). The data show a pronounced cyclic pattern most likely related to glacial/interglacial cycles and demonstrate the excellent potential of Lake Ohrid for palaeoenvironmental reconstructions (Fig. 5). We also identified a similar cyclic pattern in the seismic data and interpreted them as a climatic signal (Lindhorst et al., 2014). A preliminarily correlation between seismic and MS data using a simple time–depth chart constructed out of available p wave velocity data for the DEEP site allows an optical correlation between the cyclicity of seismic and MS data (Fig. 5), demonstrating the great potential to integrate physical properties, sedimentological and seismic data. Distinct peaks of MS are most likely correlated with the occurrence of tephras or cryptotephras in the sedimentary succession.

Small aliquots of core catcher material from the DEEP site were freeze-dried and homogenized. This material was used for measurements of total carbon (TC) and total inorganic carbon (TIC) using a DIMATOC 200 (DIMATEC Co.). Total organic carbon (TOC) was calculated as the difference between TC and TIC. Studies of the sediment cores recovered



Figure 5. Core recovery and lithology from DEEP site. Colours indicate the different coring tools used for the four parallel holes 1B, 1C, 1D, and 1F with deeper penetration. A hydraulic piston corer (HPC, blue) was used for the recovery of the upper sediment sequences. The relatively soft consistency of these sediments allows penetration of a 3 m long piston corer by hydraulic pressure. Rotation drill tools were used for the deeper and more consolidated sediments and comprise the extended nose (XTN, green), where the drill bits stand back by about 12 cm from the core barrel front, and the Alien (ALN, red), where the drill bits are placed directly at the core barrel front. 1A and 1E are not displayed as coring was restricted to surface sediments (< 5 m) using the HPC. The core composite (cc) is based on core correlation of individual holes based on field depth measurements. White parts indicate no core recovery due to gaps. The lithology (lith.), total organic carbon (TIC), and stable isotope ($\delta^{18}O_{calc.}$, red dots in the TIC curve, and $\delta^{13}C_{calc.}$ to the right) measurements are based on core catcher samples. Magnetic susceptibility (MS) was measured in 2 cm intervals on a multi-sensor core logger (MSCL) equipped with a whole core loop sensor. Spectral gamma ray (GR) is based on downhole logging data run through the drill pipe with 10 cm vertical resolution. The grey bar indicates tentatively the Middle Pleistocene transition (MPT). Marine isotope stages (MIS) 11 and 31 are extrapolated from glacial/interglacial changes in TIC contents.

during pre-site surveys between 2005 and 2009 have already shown that TIC is a valuable proxy for short-term and longterm climate change over the last ca. 135 ka (Vogel et al., 2010a; Wagner et al., 2010). TIC is high during interglacials and primarily originates from calcite precipitation. During glacial phases carbonate is almost absent. In the core catcher samples from the DEEP site, very low TIC characterizes the coarser sediments below 430 m b.l.f. (Fig. 5). This indicates that fluvial conditions prevailed at the onset of the existence of Lake Ohrid and that the clastic detrital matter supplied does not originate from the calcareous Galiçica mountain range to the east of the lake (Fig. 1), where the main inlets are located today. At 430 m b.l.f. TIC significantly increases upcore to slightly more than 10%. This implies that the lake had established and relatively warm conditions in combination with higher productivity that caused intense calcite precipitation. Between 430 and 315 m b.l.f. TIC, data show distinct high-frequency fluctuations. This can probably be attributed to the dominant 41 ka obliquity cycle prior to 920 ka (Mudelsee and Schulz, 1997; Tzedakis et al., 2006), and the




Figure 6. Core recovery and lithology from Cerava (2A and 2B), Gradište (3A, 3C, and 3D), and Peštani (4A) sites. Colours indicate different coring tools used (cf. Fig. 5). White sections in the core composites (cc) of each site indicate no core recovery.

highest TIC peak at ca. 360 m b.l.f. is tentatively correlated with the Marine Isotope Stage (MIS) 31 (Fig. 5). The sequence between 315 and 250 m b.l.f. exhibits a decrease in TIC frequency, which probably corresponds to the Middle Pleistocene transition (MPT) between 920 and 640 ka. The uppermost 250 m indicate similar amplitudes in TIC fluctuations, ranging between almost 0% and 10%, but fluctuating at a lower frequency. This variability can be attributed to 100 ka cycles, which have dominated since 640 ka. As interglacial periods should correspond with high TIC, the MIS 11 and MIS 5 sediments in the DEEP site record would occur at ca. 175 and 50 m b.l.f., respectively (Fig. 5). This is supported by the occurrence of several tephras, which are identical to those identified previously during analysis of cores from presite surveys (Sulpizio et al., 2010; Vogel et al., 2010b). For example, a coarser horizon at 18 m b.l.f., which is characterized by a maximum in MS and gamma ray data (Fig. 5), corresponds with the Y-5 tephra (Campanian Ignimbrite). This is the most prominent tephra in all other records from Lake Ohrid and was deposited 39.3 ka (e.g. Sulpizio et al., 2010). Numerous peaks in the MS data suggest that the DEEP site will become an outstanding distal record of the activity of Italian eruptive volcanoes and perhaps the "Rosetta Stone"

for regional tephrostratigraphy. The low organic matter content in all core catcher samples from the DEEP site sequence, such as reflected by TOC values of < 3% (Fig. 5), suggests that the lake has had an oligotrophic state throughout its entire existence.

4.3 Diatom data

Preliminary diatom data were generated from core catcher samples at ca. 3 m resolution from two boreholes (1B and 1C) at the DEEP site. Results for 1C are presented here (Fig. 7). A total of 173 smear slides was prepared, and ca. 100 diatom valves per slide were counted under oil immersion at $\times 1500$ magnification with a Nikon Eclipse 80i light microscope (LM) equipped with a Nikon Coolpix P6000 digital camera. Counts were converted into percentages and displayed using Tilia and TGView v. 2.0.2. (Grimm, 2004). Diatom identification was aided by reference to the taxonomic keys of Krammer and Lange-Bertalot (1986-1991) and dedicated Ohrid and Prespa taxonomic works (Hustedt, 1945; Jurilj, 1954; Levkov et al., 2007, 2012; Cvetkoska et al., 2012). Diatoms were preserved throughout the uppermost 480 m of the sediment sequence, comprising 122 diatom taxa. Although the benthic group is the most speciesrich (60 % of taxa), the sequence above 430 m b.l.f. is dominated by planktonic species (> 85 %). At the base of the sequence, the initially poor preservation in a coarse substrate (480-430 m b.l.f.) strengthens the interpretation of a shallow water body; the gradual increase in relative abundance of planktonic taxa from 430 to 320 m b.l.f. probably reflects the initial infilling of the lake basin, with a stable and deep water body thereafter. Major shifts at 430 m, 320 m, 230 m and 80 m b.l.f. are likely to represent key stages of evolution and/or environmental change, the first of which corresponds to the key boundary identified between shallow and deeper lake states. There is clear evidence for evolution within the dominant planktonic genus, Cyclotella. The replacement of C. iris by C. fottii/hustedtii, the similar morphological characteristics of which indicate that they are likely to have similar ecological niches, probably represents an excellent example of rapid species turnover. Apparently close correlation with geochemical proxies, and carbonate in particular, suggests that major shifts in diatom-species assemblage composition are driven by glacial/interglacial climate cycles in the latter part of the record. Our previous diatom-based palaeoclimate analysis of sequences spanning the last 134 ka, from the last interglacial to present (Wagner et al., 2009; Reed et al., 2010; Cvetkoska et al., 2012), demonstrates the high sensitivity of diatoms to glacial/interglacial and interstadial climate change, driven primarily by temperature-induced productivity shifts. This is supported by modern ecological data, which define the epilimnetic vs. hypolimnetic life habit of dominant planktonic taxa (Allen and Ocevski, 1976). The same suite of dominant taxa prevails in the DEEP sequence above 230 m b.l.f., giving good modern analogues for future

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Figure 7. Preliminary diatom data from smear slides of core catcher samples (hole 1C, DEEP site).

palaeoenvironmental reconstruction. Analogues are poor below this depth, underlining the degree to which Quaternary diatom evolution has probably occurred, but the presence of dominant taxa such as *Cyclotella iris* in oligotrophic fossil assemblages (Krammer and Lange-Bertalot, 1991a) provides a strong baseline from which to reconstruct earlier Quaternary palaeoclimates in the lower record.

4.4 Stable isotope data

Stable isotope analysis of carbonate was conducted using sediment aliquots from 69 samples with >1% TIC (hole 1B, core catchers). Subsamples were processed to remove organics and measured for stable isotope ratios. The data show $\delta^{18}O_{\text{calcite}}$ values increasing through the core, ranging between -7.6 ‰ and -2.9 ‰, and averaging -5.2 ‰ ± 1.1 ‰ (Fig. 5), which is most likely the result of greater freshwater input and lower lake-water residence times in earlier interglacials. From modern calibration data sets, $\delta^{18}O_{calcite}$ in Lake Ohrid is known to be a function of inflow and evaporation (Leng et al., 2010), so significant positive excursions suggest periods of exceptional aridity and potentially lower lake levels (for example at 50, 210 and 310 m b.l.f.), which coincide with high TIC phases (interglacial periods). δ^{13} C_{calcite} ranges (-2.1 % to +2.1 %, mean =0.0 % ± 0.8 %) are consistent with the catchment geology providing a major source of inorganic carbon ($\delta^{13}C_{catchment} = +1 \%$) enhanced by longer residence times allowing increased exchange with atmospheric CO₂ towards the top of the sequence.



Figure 8. Rounded gravel and pebbles in core catcher material (DEEP site, hole 1D at 569 m b.l.f.) indicate fluvial transportation.

Overall, the patterns seen in borehole logging, MS and core-catcher data imply that the record from the DEEP site covers the entire history of extant Lake Ohrid. Rounded pebbles and gravel from the base of the sediment record (Fig. 8) imply that fluvial sedimentation prevailed in the Lake Ohrid basin before the basin was filled, culminating in the development of the deep modern lake. A stepwise decrease in grain size from the base to 430 m b.l.f. is attributed to the establishment of lacustrine conditions and increasing lake levels. According to TIC, MS, and borehole gamma ray values, the

uppermost 430 m b.l.f. cover probably > 1.2 Ma. Major hiatuses or mass-wasting deposits were not observed at this site.

5 Ongoing and future work

The sediment cores recovered during the SCOPSCO 2013 field campaign at Lake Ohrid are stored at the University of Cologne, Germany, where core opening, description, documentation, and initial analyses such as MSCL and X-ray fluorescence (XRF) scanning are taking place. The primary focus of current studies is the sediment sequence from the DEEP site. For the XRF scanning, intervals are set to 2.5 mm, which likely provides a decadal resolution. Visual inspection, MS and XRF scanning data will be used to identify horizons with tephras or cryptotephras. Such horizons will be sampled and tephra identification will be carried out (cf. Vogel et al., 2010b; Damaschke et al., 2013). The results combined with palaeomagnetic measurements and chronostratigraphic tuning will be applied to establish an age model.

Subsampling for geochemical, pollen and diatom analyses will be carried out at consistent intervals of 16 cm on the composite core after core correlation based on visual inspection and XRF data. Based on an estimated average sedimentation rate of ca. 30 yrs cm^{-1} (430 m sediment column corresponding to ca. 1.2 Ma), the 16 cm intervals correspond to a resolution of ca. 500 years. Shorter intervals with higher temporal resolution are envisaged for future studies to investigate, for example, glacial to interglacial transitions or other selected events.

Core opening, description and documentation, and analyses of the Cerava, Gradište and Peštani sediment sequences will be carried out after the DEEP site. Combining the DEEP site with the peripheral drill sites will allow us to achieve the main goals of the SCOPSCO project. Altogether, this makes Lake Ohrid a key site of global importance for improving our understanding of Quaternary environmental change in the northern Mediterranean and general triggers of evolutionary events.

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