



## Abstract

Lake Ohrid is likely of Pliocene age and thus commonly referred to as the oldest existing lake in Europe. In this study spatial variability of recent sediment composition is assessed using >50 basin wide distributed surface sediment samples. Analysis of biogeochemical bulk parameters, selected metals, pigment concentrations as well as grain size distributions revealed a significant spatial heterogeneity in surface sediment composition. It implies that sedimentation in Lake Ohrid is controlled by an interaction of multiple natural and anthropogenic factors and processes. Major factors controlling surface sediment composition are related to differences in geological catchment characteristics, anthropogenic land use, and a counter-clockwise rotating surface water current. In some instances processes controlling sediment composition also seem to impact distribution patterns of biodiversity, which suggests a common interaction of processes responsible for both patterns.

## 1 Introduction

Within the terrestrial realm large ancient lakes are known as favourable archives of climate and environmental change and further due to their long and often continuous existence widely recognized as hotspots of biodiversity. Situated within the northern Mediterranean borderland, with a presumed age between five and two million years (Stankovic, 1960), and its outstanding degree of endemism (Albrecht and Wilke, 2008) Lake Ohrid constitutes a valuable archive for studies of past climate changes (e.g. Wagner et al., 2008, 2009; Vogel et al., 2010a), ash dispersal (Vogel et al., 2010b, Sulpizio et al., 2010), and forces and mechanisms of speciation (e.g. Albrecht et al., 2006; Wilke et al., 2010).

As the setting and catchment characteristics differ from lake to lake and in order to employ lacustrine sediment records as archives of climatic and environmental change thorough knowledge of modern processes and factors controlling sedimentation in

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each particular lake is required. Although hydrological, limnological, physical, geological as well as faunal and floral settings of Lake Ohrid have been extensively studied over the last century (Cvijic, 1911; Stankovic, 1960; Anovski et al., 1992; Watzin et al., 2002; Matzinger et al., 2006a, b, 2007; Popovska and Bonacci, 2007; Albrecht and Wilke, 2008; Wagner et al., 2008), a comprehensive survey on how these factors influence modern sedimentation in the lake and their potential impact on biodiversity patterns is still lacking.

In this study we investigated 54 spatially distributed surface sediment samples using geochemical, physical, and granulometric methods. These data is used to provide important information on processes and factors influencing sedimentation including sediment transport, sources of minerogenic and organic sediment components and in lake productivity. Moreover, possible factors controlling both sedimentation and biodiversity patterns of benthic species (e.g. Hauffe et al., 2010) across the lake are also discussed.

## 2 Setting

Lake Ohrid (41°01' N, 20°43' E; Fig. 1), a transboundary lake shared by the Republic of Albania and the Former Yugoslav Republic of Macedonia, is situated at 693 m above sea level (a.s.l.) and surrounded by high mountain ranges of up to 2300 m a.s.l. The lake is approximately 30 km long, 15 km wide and covers an area of 358 km<sup>2</sup>. The lake basin has a tub-shaped morphology with steep slopes on its western and eastern flanks, more gentle inclined slopes at its northern and eastern terminations, and a flat basin centre. The deepest spot is situated in the southeastern part of the flat basin and exhibits a water depth of 289 m (Fig. 2). The average water depth accounts to 151 m, leading to a total volume of 50.7 km<sup>3</sup> (Popovska and Bonacci, 2007).

The topographic watershed of Lake Ohrid comprises an area of 2393 km<sup>2</sup> incorporating Lake Prespa, which is situated 10 km to the east of Lake Ohrid at an altitude of 848 m a.s.l. (Popovska and Bonacci, 2007). The two lakes are connected by karst

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aquifers passing through the Galicica and Suva Gora mountain range. Karst springs depleted in nutrients and minerogenic load represent the primary hydrologic inputs to Lake Ohrid (55%). Up to 50% of the water emerging from the inflow springs originates from Lake Prespa, with the remainder coming from precipitation on the surrounding mountain ranges (Anovski et al., 1992; Matzinger et al., 2007). Direct precipitation on the lake surface, river- and direct surface runoff together account for the remaining 45% of the hydrologic input to Lake Ohrid. Apart from temporary streams the rivers Sateska, Koselska, Cerava, Pogradec, and Verdova constitute the main riverine inflows with discharges between 0.20 (Verdova) and 5.5 m<sup>3</sup>/s (Sateska) (Fig. 1; Watzin et al., 2002). Nutrients are primarily delivered to Lake Ohrid by surface runoff and in particular by streams which pass agricultural or densely populated areas (Matzinger et al., 2007; Fig. 1). Surface outflow (60%) through the river Crn Drim to the north and evaporation (40%) are the main hydrologic outputs (Matzinger et al., 2006a, 2007).

Complete convective mixing of the water column of Lake Ohrid only takes place irregularly every seven years during severe winters when homothermy of the water body is established (Stankovic, 1960; Matzinger et al., 2006a). Wind driven convective mixing of the superficial 150–200 m of the water column throughout the year is, however, supported by a lack of stratification as common for deep, temperate lakes. Despite the irregular pattern of complete overturn, it is observed that dissolved oxygen (DO) concentrations remain above 6 mg/l below 200 m water depth throughout every year (Stankovic, 1960; Matzinger et al., 2007). Because of the overall low nutrient load of the hydrologic inputs, inhibited resuspension of nutrients from the sediment-water interface by incomplete and irregular mixing of the water body, and because of its large volume, Lake Ohrid is an oligomictic and highly oligotrophic lake (Stankovic, 1960; Matzinger et al., 2007).

Due to its sheltered position in a relatively deep valley surrounded by high mountain ranges and to its proximity to the Adriatic Sea, the climate of the Lake Ohrid watershed shows both Mediterranean and continental influences (Watzin et al., 2002), with an average annual air temperature for the period between 1961–1990 of 11.1 °C, maximum

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temperatures below 31.5°C, minimum temperatures above –5.7°C, and an average annual precipitation of 800–900 mm (Popovska and Bonacci, 2007). Prevailing wind directions follow the N-S axis of the Ohrid valley.

The Ohrid valley is located within an active tectonic graben system of the Western Macedonian geotectonic zone, which is part of the interior Dinaric Alps. Metasediments of Paleozoic (Cambrian-Devonian) ages are exposed to the north and northeast of the valley. Strongly karstified limestones of Triassic age are exposed along the northwestern, eastern, and southeastern shorelines (Watzin et al., 2002). Ultramafic extrusive rocks and associated weathering crusts containing chromium and iron-nickel ore deposits of Jurassic-Cretaceous age outcrop along the southwestern and western shorelines (Dilek et al., 2007). Quaternary lacustrine and fluvial deposits occupy the plains to the north and to the south of the lake (Watzin et al., 2002).

### 3 Materials and methods

#### 3.1 Surface sediment sampling

During 2005 and 2007 field seasons 54 surface sediment samples were collected from representative sites all over the lake basin (Fig. 3) using the research vessel of the Hydrobiological Institute in Ohrid and a gravity corer equipped with a 6 cm diameter Plexiglas liner. The sediment was vertically pressed out of the coring tube and the top-most 1 cm was sliced off. Samples were stored in a freezer prior to further processing.

#### 3.2 Analytical work

All samples were freeze-dried and aliquots were ground to a particle size below 63 µm using a planetary mill for subsequent geochemical analyses and x-ray diffractometry.

Total nitrogen (TN) concentrations were measured with a Vario Micro Cube combustion CNS elemental analyzer (VARIO Co.). TC was detected with an IR detector (Leco

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CS 125) after burning of 100 mg sediment. In a second step, 16% HCl was added to the ground sediment, Cl-gases were trapped and CO<sub>2</sub> was detected again with an IR cell. The amount of total organic carbon (TOC) was determined from the difference between TC and TIC.

5 For analysis of aluminium (Al), chromium (Cr), and nickel (Ni) concentrations in surface sediment samples 250 mg of sediment was treated with 8 ml of nitrous acid (HNO<sub>3</sub>) for 30 min in order to remove organic material. To dissolve the sample entirely 2 ml of hydrofluoric acid (HF) was added and samples were placed in a microwave set to 210 °C and 1200 W for 24 min. The emerged solution was neutralized using 10 ml  
10 boric acid (H<sub>3</sub>BO<sub>4</sub>) and a microwave setting of 180 °C and 1200 W for 25 min. Prior to quantitative measurement of Al, Cr, and Ni concentrations by inductive coupled plasma optical emission spectrometry (ICP-OES) using a Liberty 200 (Varian Inc.) device 50 ml of deionized water was added in order to obtain a diluted solution.

Algal pigment concentrations were estimated using a high performance liquid chromatography (HPLC) device coupled to a mass spectrometer (MS) with a setup of the  
15 device and sample pre-treatment according to Schmid and Stich (1995). Included in this general overview and Fig. 2 are only results for chlorophyll *a*, as indicator for algal biomass.

Bulk mineralogy of the sediment samples was determined with a X-Ray-diffractometer (Siemens D500) and steps of 0.05° 2theta. For visualization, we used  
20 counts per second (cps).

For grain-size analyses, 2 g of fresh sediment was treated with 10 ml 15% H<sub>2</sub>O<sub>2</sub> to remove organic material. Subsequently, 0.3 g of Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was added to prevent flocculation of the sample. After settling of the suspension, the clear supernatant water was removed, the sediment homogenized using a spatula, and transferred to a  
25 laser-diffractometer (Micromeritics DigiSizer 5200). Half a minute of ultrasonic treatment and flow rates of 10 l min<sup>-1</sup> resuspended the sediments prior to detection. The laser-diffractometer uses a 1 MB CCD and calculates 160 grain size classes with the average values of two runs. Calculations of grain-size parameters and statistics were

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made using the program GRADISTAT (Blott and Pye, 2001). The interpolation software SURFER was applied to visualize data.

## 4 Results and discussion

### 4.1 Sources of and processes controlling the sedimentation of clastic detritus

5 Grain-size distribution, selected metal concentrations, and the concentration of particular mineral phases show a strong spatial variability in surface sediments of Lake Ohrid, which seems to be closely tied to differences in catchment geology and transport processes. These parameters can therefore yield important information on transport energies and the direction of transport influencing the sedimentary composition in modern  
10 sediments of the lake.

The grain size distribution can be utilized as indicator for transport energy and flow velocity within the lake basin. In general surface sediments in Lake Ohrid exhibit a grain-size distribution with its maximum in the silt size fraction (>80 vol%; Fig. 3). While the amount of clay sized material is relatively low without significant variability  
15 the amount of coarse silt and fine to medium sand in surface sediments varies considerably. Highest amounts of coarser grain-size fractions occur in close proximity to river mouths of the major tributaries. Apart from this pattern, which can be explained by higher transport energies close to the riverine inlets as well as ample supply of clastic material, coarse grain sizes occurring in the basin centre and along the coastline  
20 point to significant transport by wind induced surface currents. The water flow velocity required for transport of suspended coarse silt to fine sand sized clastic matter is >0.4 m/s (Schäfer, 2005). Thus it can be assumed that wind driven surface currents in Lake Ohrid temporarily exceed 0.4 m/s, which correlates relatively well with qualitative  
25 own observation of a surface water current of >1 m/s in the years 2005, 2007, and 2009. These own observations are also in good agreement with observations made by Stankovic (1960) in the 1940's and 1950's who observed a wind-induced surface water

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flow velocity exceeding 0.1 m/s during days with wind speeds of less than 10 m/s.

The direction of transport in Lake Ohrid can be traced by using elements such as Al, Cr, and Ni as well as mineral phases such as feldspar, which originate from relatively confined sources. Al concentrations range from 20 to 65 g/kg in surface sediments of Lake Ohrid. Highest concentrations are found in the northern, southeastern, and central parts of the basin. The primary source of Al can be traced back to the rivers Cerava, Velgoska, and Koselska, which drain Paleozoic metasediments, Triassic limestones, and Tertiary to Quaternary fluviolacustrine sediments. Input of Al from rivers draining Jurassic and Cretaceous ultramafic extrusives to the southwestern/Albanian part of the Ohrid catchment is significantly lower. Concentrations of Cr and Ni range from 60–220 and 40–440 mg/kg in surface sediments of Lake Ohrid. As the highest concentrations can be observed in the southwestern part of the lake, it is apparent that Cr and Ni primarily originate from rivers draining the southwestern part of the catchment with ultramafic bedrock and associated weathering crust exposures (Fig. 1). Based on the distribution of feldspar in surface sediments with highest values in close proximity to the Cerava river mouth it can be assumed that the Cerava river is the most significant source for feldspar.

Apart from the highest concentration of these parameters in close proximity to their source areas further transport seems to be connected to a common mechanism. Cr and Ni are distributed from their source in the southwestern part of the lake along the southern and subsequently along the eastern shore. Northward transport along the western shore and to the northwestern part of the lake basin seems to be negligible (Fig. 3). Similarly, feldspar seems to be primarily transported from its southeastern source northward following the eastern shore line (Fig. 3). Due to the more ubiquitous occurrence of Al in sediments of Lake Ohrid the transport pattern as described by Cr, Ni, and feldspar concentrations is not as well expressed but generally points to a northward left diverted pathway of transport (Fig. 3). The common pattern of transport for these components implies that transport of suspended clastic matter is primarily driven by a counterclockwise current in Lake Ohrid. These data in combination with the

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observations of a counterclockwise rotating gyre (Stankovic, 1960; own observations; Fig. 4) probably explain the primary mechanism of sediment transport or suspended material in the water column of Lake Ohrid today.

## 4.2 Factors controlling productivity and sources of organic matter

5 Concentrations of TOC, TN, TIC, and chlorophyll *a* in surface sediments of Lake Ohrid were assessed in order to provide information on spatial differences in productivity and sources of organic matter (OM). The concentration of OM, as indicated by TOC concentrations, is relatively low in surface sediments of Lake Ohrid and shows a strong spatial variability with TOC values ranging from 0.3–4.1% (Fig. 3). Highest TOC concentrations occur in the northern, northeastern, southwestern and central-southeastern part of the lake basin. This apparent spatial variability is probably the result of a combination of differences in catchment characteristics, anthropogenic influences, and hydrology influencing productivity and the distribution and amount of allochthonous and autochthonous OM over the lake basin. In order to detangle variability in productivity and sources of OM, chlorophyll *a*, related degradation products and the ratio of organic carbon and nitrogen (C/N) were inferred. Chlorophyll *a* concentrations (Fig. 3) as well as related degradation products such as phaeophytin *a* and summed pheoporbide *a* (not shown) are highest in the northeastern and southwestern parts of the lake basin (Fig. 3). This in combination with the overall low C/N ratio (<12) implies high in-lake productivity and a primary autochthonous source of OM (Meyers and Ishiwatari, 1993). Strong productivity in these parts of the lake can best be explained by high input of soluble reactive phosphorus (SRP), a key nutrient (Wetzel, 2001) delivered by rivers and streams passing through agricultural and/or populated areas (Fig. 1; Watzin et al., 2002; Matzinger et al., 2007). Anthropogenic land-use seems thus to be a major factor facilitating productivity at shoreward sites in close proximity to populated areas around Lake Ohrid today. The central part of the lake, in contrast, seems not to be significantly affected by nutrients originating from anthropogenic land-use (Fig. 3). This indicates that most nutrients are already used up by primary producers in shoreward

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5 areas. Traceable amounts of allochthonous OM delivered to Lake Ohrid, as indicated by slightly raised C/N ratios of up to 14.5, are restricted to the Cerava, Velgoska, and Koselska river mouths (Fig. 3). However, the concurrence of high TOC, low chlorophyll *a* concentrations and C/N ratios of up to 14 for the central-southeastern part of the lake basin in close proximity to the deepest spot (Fig. 3) implies a somewhat stronger contribution of allochthonous OM, potentially originating from the Cerava river. Apart from few exceptions it can be assumed that OM in surface sediments of Lake Ohrid primarily originates from in lake productivity with only little contribution from terrestrial sources.

10 The amount of total inorganic carbon (TIC) in surface sediments of Lake Ohrid primarily originates from photosynthesis-induced calcite precipitation with only minor contribution of biogenic sources such as ostracod valves and mollusk shells. The amount of detrital calcite in sediments of Lake Ohrid is negligible (Matzinger et al., 2006; Wagner et al., 2008; Vogel et al., 2010a). TIC concentrations are in general highest in the northern, northeastern, and southwestern parts of the lake basin and thus strongly correlated to areas with enhanced productivity (Fig. 3). Exceptions from this general pattern comprise the areas in proximity or under influence of water discharge from the Koselska and Cerava rivers (Fig. 3). Both rivers drain a widely carbonate free catchment (Fig. 1) and are thus rather depleted with respect to  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ion concentrations. Since constant supply of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions is a necessity to maintain photosynthesis-induced calcite precipitation it can be assumed that discharge from these rivers leads to a dilution of surface waters and thus the photic zone with respect to  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ion concentrations, which in turn causes a less effective calcite precipitation. Another explanation could be dilution of calcite in the surface sediment by detrital clastic material from the Koselska and Cerava rivers. Overall the amount of endogenic calcite deposited in surface sediments of Lake Ohrid seems to be closely coupled to productivity with bias from riverine inflows depleted in  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ion load.

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### 4.3 Implications for biodiversity patterns and possible threats for endemic species

The distribution of benthic organisms in Lake Ohrid is extremely patchy. There are both depth related and horizontal gradients in diversity distribution (Albrecht and Wilke, 2008). Differences in benthos distribution exist on small scales. Sediment structure and thus habitat characteristics are believed to correlate to the distribution of sub-populations with ecological and geographical barriers in the lake potentially promoting speciation processes. The degree of habitat patchiness is still only fragmentarily understood (Hauffe et al., submitted). It is clear, however, that habitat heterogeneity is an important component that has triggered intralacustrine evolution of endemic benthic taxa of world-wide ancient lakes (Martens, 1997).

Increased sediment loads on the other hand have repeatedly been shown to significantly reduce habitat heterogeneity resulting in decreased densities of benthic organisms (Balata et al., 2007). The impacts of increased sediment loads have been summarized by Donohue and Molinos (2009). It is thus interesting to observe a lowered frequency of endemic molluscs in areas of highest productivity in Lake Ohrid, i.e. with the highest SRP load (Figs. 1, 3 and Hauffe et al., 2010, Fig. 4b,c). These are primarily the littoral surroundings of the inlets. Moreover, these are the areas of highest anthropogenic impact (Trajanovski et al., 2010). In those areas such as the Ohrid Bay, northern, and southwestern shores, proportions of non-endemic gastropod species were highest (Hauffe et al., 2010). It is also those parts of the lake where alpha diversity is generally low. For the time being, it is exactly those disturbed littoral localities (e.g. Ohrid Bay) where non-indigenous or even alien species start to penetrate the lake proper (Trajanovski et al., 2010).

Highly disturbed stretches exist along the western Albanian shore and Cr and Ni input are known to be enhanced by the mining facilities there (Watzin et al., 2002). Toxic effects and bioaccumulation tendencies of those trace metals are well known (e.g. Paquin et al., 2003; Kiffney and Clements, 2003), not yet studied in Lake Ohrid

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but demonstrated in other Balkan large lakes such as Lake Vegoritis (Skoulikidis et al., 2008).

It has been shown that an oligotrophic status is an important predictor for high mollusc diversity and endemism in world-wide ancient lakes (Albrecht, unpublished data).

5 Signs of eutrophication as indicated in this study as well as hydrological assessments (Matzinger et al., 2006, 2007) are important signals towards changes in the lakes ecosystem. Such a trend would have a multitude of consequences for biodiversity with effects ranging from biofilm changes and changing plankton communities and eventually to interrupted food chains. Other Balkan ancient and potentially ancient lakes  
10 have already experienced such recent anthropogenically induced ecosystem changes (e.g. Albrecht et al., 2009). Related oxygen depletion in sediments, mechanic abrasion, and clogging interstices threaten particular habitat types to which many endemic species have specifically adapted. One such particular habitat of Lake Ohrid is the so-called sublacustrine interlithon (Albrecht and Wilke, 2008). The increased silt loads  
15 combined with the identified prevailing counterclockwise direction of the surface current may present a threat to this Ohrid specific habitat and the associated biodiversity hotspot (Hauffe et al., 2010) on the southeastern shore of the lake. Alteration to habitat structure and reduced habitat quality in general have been hypothesized to pose a major threat to the survival of Lake Ohrid endemic species (Trajanovski et al., submitted).  
20 Changes in the sediments are directly or indirectly effecting most benthic organisms. This real or near-future threat is most severe for small-range endemics in many of the benthic taxa of the lake.

## 5 Conclusions

25 The investigation of >50 basin wide distributed surface sediment samples yielded important information on modern sedimentation in the Lake Ohrid basin. According to our investigations surface sediment composition varies significantly due to differing influences of catchment geology, anthropogenic land use and transport processes.

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Based on the grain-size distribution pattern, relatively strong wind driven surface currents were identified as the main process of transport in Lake Ohrid. Differences in the surrounding catchment geology have a strong impact on surface sediment composition and can be traced using Al, Cr, Ni, and feldspar concentrations. Due to the known sources of these components a counterclockwise rotating surface current can best explain the direction of transport of suspended clastic matter in Lake Ohrid.

The distribution of TOC, TN, and pigment concentrations over the lake basin revealed that organic matter in surface sediments of Lake Ohrid primarily originates from in lake productivity. Areas with highest productivity are situated in close proximity to riverine inlets with high SRP load originating from the drainage of agricultural and/or densely populated areas in the catchment. Nutrient load from these inlets seems to have only limited impact on productivity in more distal and basinward sites of Lake Ohrid.

Small-scale differences in sediment composition might have been responsible for habitat patchiness in related substructuring of predominantly benthic communities. Such heterogeneities might also be linked to evolutionary processes such as speciation. On the other hand, anthropogenic interference in sedimentation processes and particularly pollution with nutrients but also trace metals pose real threats to the primarily benthic endemic biodiversity of Lake Ohrid. Circumstantial evidence hints towards an already existing decline in habitat structure and species abundances. Conservation measures should therefore also focus on reducing anthropogenic effects on ecosystem processes such as sedimentation.

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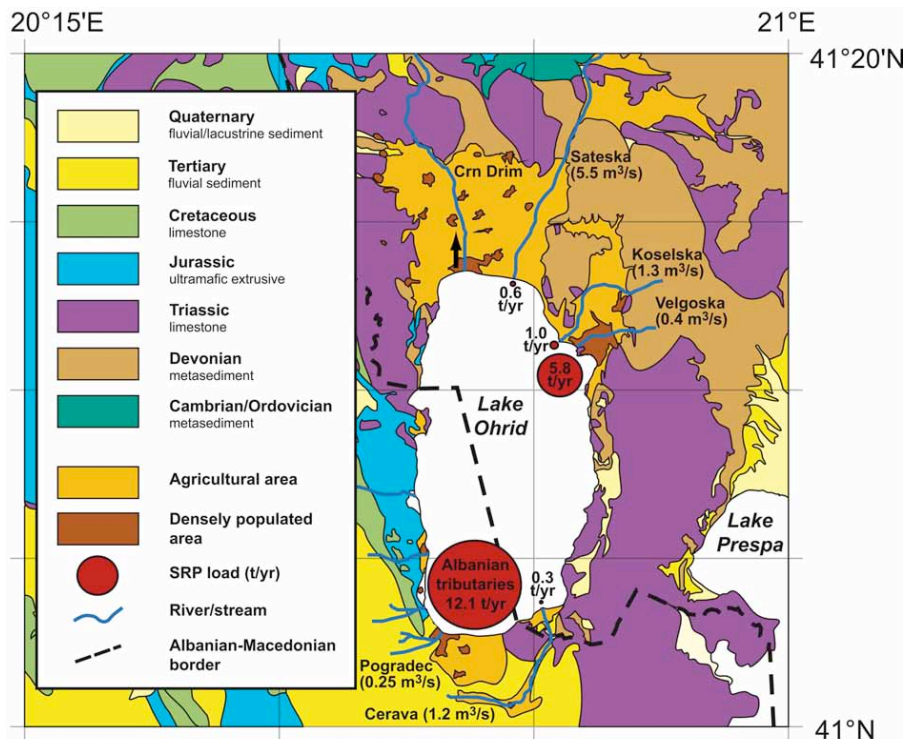






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**Fig. 1.** Geological overview map of the Lake Ohrid vicinity modified after Reicherter et al. (unpublished). Also shown are densely populated and agricultural areas, major streams and inlets including discharge rates and loads of soluble reactive phosphorus (SRP) according to Matzinger et al. (2007).

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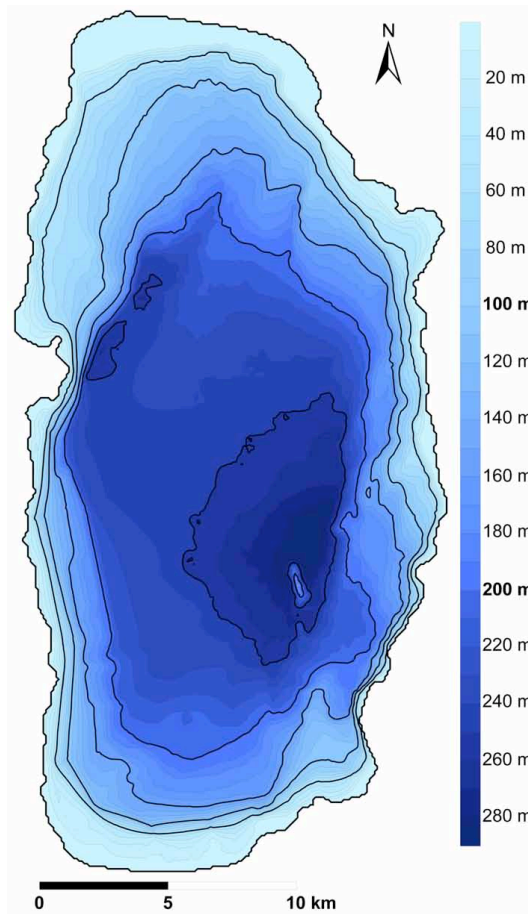
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**Fig. 2.** Bathymetric map of Lake Ohrid with 10 m contour intervals. Black lines denote 50 m intervals.

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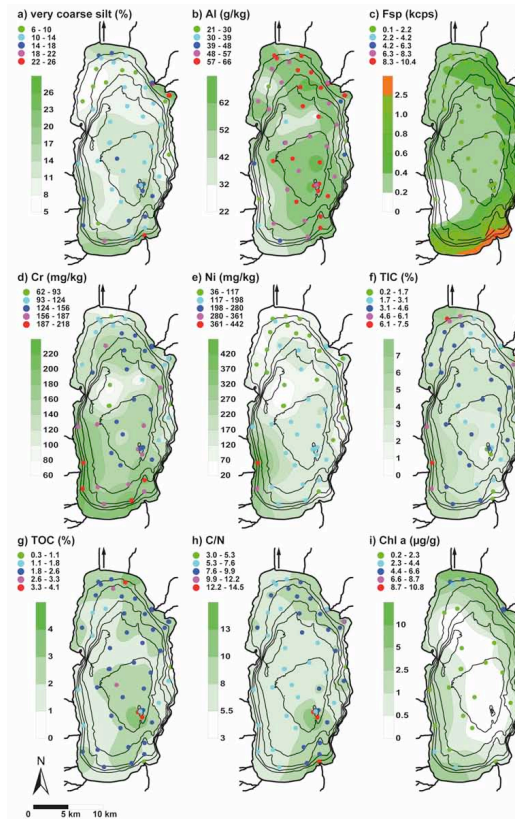
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**Fig. 3.** Simplified bathymetric maps showing the concentrations of very coarse silt (**a**), aluminium (Al; **b**), feldspar (Fsp; **c**), chromium (Cr; **d**), nickel (Ni; **e**), total inorganic carbon (TIC; **f**), total organic carbon (TOC; **g**), total organic carbon organic nitrogen ratio (C/N; **h**), and chlorophyll *a* (Chl *a*; **i**) in surface sediments of Lake Ohrid. Isopleths are interpolated using the interpolation program (SURFER).

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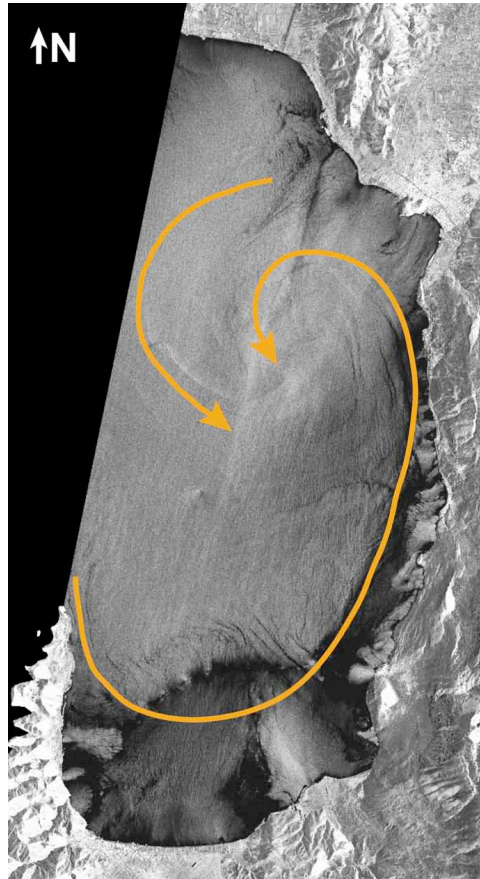
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**Fig. 4.** Radar satellite image taken on the early morning of 30 September 2009 (© DLR 2009). The image shows an apparent counterclockwise rotating surface current with its centre in the northeastern part of Lake Ohrid.

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