Eutrophication of ancient Lake Ohrid: Global warming amplifies detrimental effects of increased nutrient inputs

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Abstract
Lake Ohrid in southeastern Europe is one of the few ancient, long-lived lakes of the world, and contains more than 200 endemic species. On the basis of integrated monitoring of internal and external nutrient fluxes, a progressing eutrophication was detected (~3.5-fold increase in phosphorus (P) concentration in the lake over the past century). The lake is fortunately still oligotrophic, with high concentrations of dissolved oxygen (DO) in the deep water that are requisite for the unique endemic bottom fauna. Hypolimnetic DO is not only very sensitive to changes in anthropogenic P load—via mineralization of organic material—but also to global warming via decrease of vertical mixing and less frequent complete deep convection. Moreover, these two human effects amplify each other. To keep DO from falling below currently observed minimal levels—given the predicted atmospheric warming of 0.04°C yr⁻¹—the P load must be decreased by 50% in coming decades. However, even with such a reduction in P load, anoxia is still expected toward the end of the century if the rate of warming follows predictions.

There are but a few ancient lakes that have provided favorable living conditions for freshwater organisms over time periods far beyond the usual. These ancient systems allowed the persistence and speciation of fauna and flora, acting as literal centers of evolution (Martens et al. 1994). Compared to short-lived lakes, they often developed extensive species endemism (Table 1). Most of the lakes in Table 1 are potentially threatened by cultural eutrophication (Beeton 2002); for Lake Victoria and Lake Biwa even possible species extinction has been reported (Seehausen et al. 1997; Tsugeki et al. 2003). Moreover, shifts toward nonendemic species have been observed in the vicinity of polluted inflows to oligotrophic Lake Ohrid. To prevent future irreversible losses, it is therefore important to detect trends toward eutrophication in ancient lakes as early as possible to react in time (e.g., Bootsma and Hecky 1993).

Once the extent of cultural eutrophication is known, the choice of mitigation measures may be complicated by interactions with other impacts. Of particular concern is the predicted global warming, which will affect a wide range of lakes and may aggravate effects of eutrophication (Matzinger et al. 2006b; Schindler 2006). In summary, appropriate lake management needs to address the three questions (i) to what extent eutrophication has occurred, (ii) what are the timescales of past changes and steady-state conditions, and (iii) what P loads are acceptable and whether this limit is sensitive to global warming or other expected changes.

However, eutrophication is difficult to identify for most of the unique lakes listed in Table 1, due to (1) low phosphorus (P) concentrations with variations in the range of measurement errors and (2) excessively long residence times. Thus it would take decades of high-quality measurements to detect eutrophication in the water column. Alternatively, nutrient input can be monitored. However, sensible input assessment again requires an enormous effort and may still be unreliable (Moosmann et al. 2005). Finally, the analysis of sediments provides an option to look into the history of eutrophication, but...
Lake Ohrid eutrophication

Table 1. Comparison of ancient lakes.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Age (10^3 yr)</th>
<th>Endemic species described (Number)</th>
<th>Residence time* (Yr)</th>
<th>Max. depth (m)</th>
<th>TP (mg m⁻³)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baikal</td>
<td>25–30</td>
<td>982</td>
<td>350</td>
<td>1,636</td>
<td>~8†</td>
<td>Shimaraev et al. 1994; Martens et al. 1994; Goldman et al. 1996</td>
</tr>
<tr>
<td>Tanganyika</td>
<td>~20</td>
<td>632</td>
<td>7,000 (1,600‡)</td>
<td>1,470</td>
<td>1.9†</td>
<td>Martens et al. 1994; Järvinen et al. 1999; Bootsma and Hecky 2003</td>
</tr>
<tr>
<td>Malawi</td>
<td>&gt;2</td>
<td>~620</td>
<td>650 (450‡)</td>
<td>700</td>
<td>9.3‡</td>
<td>Martens et al. 1994; Guildford and Hecky 2000; Bootsma and Hecky 2003</td>
</tr>
<tr>
<td>Victoria</td>
<td>0.015–0.75‡</td>
<td>~240</td>
<td>140</td>
<td>79</td>
<td>77.5</td>
<td>Martens et al. 1994; Guildford and Hecky 2000; Bootsma and Hecky 2003</td>
</tr>
<tr>
<td>Titicaca</td>
<td>~3</td>
<td>61</td>
<td>660</td>
<td>284</td>
<td>24‡</td>
<td>Wurtsbaugh et al. 1992; Martens et al. 1994; Grove et al. 2003</td>
</tr>
<tr>
<td>Biwa</td>
<td>0.4–1</td>
<td>54</td>
<td>5.5</td>
<td>104</td>
<td>9</td>
<td>Martens et al. 1994</td>
</tr>
<tr>
<td>Ohrid</td>
<td>2–3</td>
<td>210</td>
<td>70</td>
<td>289</td>
<td>4.6</td>
<td>Stankovic 1960; updated for selected groups by Jerkovic 1972; Kenk 1978; Gilbert and Hadzisce 1984; Martens et al. 1994</td>
</tr>
</tbody>
</table>

* Defined as volume per outflow.
‡ SRP during main mixing in July (L. Baikal) and September (L. Titicaca).
‡ Upper, oxygenated layer.
§ Large range due to different opinions regarding extent of past desiccation events.

The present paper advances by the next two logical steps to quantify the potential severity of worsened DO conditions in Lake Ohrid.

In the first part of the paper the extent and dynamics of eutrophication is assessed. It is based on P, the limiting element in Lake Ohrid, with total phosphorus (TP) concentrations ~4.6 mg m⁻³ and molar ratios of total nitrogen TN:TP > 50 (Guildford and Hecky 2000). P measurements in inflows, water column, and sediments are used to establish the contemporary lake-internal P balance. In a second step, timescales of past changes and a potential steady state are discussed on the basis of a linear P model to answer questions (i) and (ii) above.

In the second part of the paper, a dynamical model is established on the basis of the P balance (1) to quantify DO availability for different future eutrophication and global warming scenarios, as well as their interactions and (2) to define allowable P loads depending on these human impacts and DO requirements (question iii).

Lake Ohrid

Lake Ohrid is a transboundary lake shared by Macedonia and Albania (Fig. 1), situated between mountain ranges to the east and west. It is oligotrophic, deep (max. depth ~289 m), large (surface area ~358 km²), and one of the most voluminous lakes (~55 km³) in Europe (Table 2). The water balance is dominated by inflow from karst aquifers (~50%) with smaller shares from runoff and direct precipitation (Matzinger et al. 2006b). The fraction of river runoff had even been less than 10% before 1962, when River Sateska was deliberately diverted into the lake to reduce siltation in downstream reservoirs (Fig. 1). The karst aquifers are charged from mountain range precipitation and from Lake Prespa, which has no surface outflow (Fig. 1; Eftimi and Zoto 1997; Matzinger et al. 2006a). Via this underground connection to Lake Prespa the lake catchment extends also to Greece.

The top 150- to 200-m water column of Lake Ohrid follows the usual thermal stratification seasonality of deep, temperate lakes, whereas the lower hypolimnion is stably stratified by salinity (Fig. 2a). The stability due to the salinity gradient—although very weak—allows complete, deep convective mixing (in the following referred to as “complete overturn”) only roughly once every 7 yr during
cold winters (Hadzisce 1966; Matzinger et al. 2006b). Figure 3 shows the change in different water properties for such an event in winter 2003/2004. In the absence of cold winters, geothermal heat input and turbulent vertical exchange steadily raise hypolimnion temperature, making complete overturn more probable as time progresses (Fig. 3b). In turn salinity (S) and DO show a seasonal trend because of summer productivity and increased turbulence in winter (Fig. 3c,d). DO stays always high throughout the water column with a maximum between 20 and 40 m depth as a result of phytoplankton production (Fig. 2b).

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude</td>
<td>°N</td>
<td>41.1</td>
</tr>
<tr>
<td>Longitude</td>
<td>°E</td>
<td>20.7</td>
</tr>
<tr>
<td>Altitude</td>
<td>m asl</td>
<td>690</td>
</tr>
<tr>
<td>Catchment area (including Lake Prespa)</td>
<td>km²</td>
<td>2,600</td>
</tr>
<tr>
<td>Surface area</td>
<td>km²</td>
<td>358</td>
</tr>
<tr>
<td>Volume</td>
<td>km³</td>
<td>54.9</td>
</tr>
<tr>
<td>Maximal depth</td>
<td>m</td>
<td>288.7</td>
</tr>
<tr>
<td>Average depth</td>
<td>m</td>
<td>155</td>
</tr>
<tr>
<td>Average annual inflow</td>
<td>m³ s⁻¹</td>
<td>38</td>
</tr>
<tr>
<td>Average annual outflow</td>
<td>m³ s⁻¹</td>
<td>25</td>
</tr>
<tr>
<td>Mean water residence time</td>
<td>yr</td>
<td>70</td>
</tr>
<tr>
<td>Average phosphorus concentration</td>
<td>mg m⁻³</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Fig. 1. Geographical overview. The inset maps indicate the location of Lake Ohrid within Europe and the Macedonian-Albanian-Greek triangle.

Fig. 2. Typical summer profiles of (a) salinity and temperature, and (b) chlorophyll $a$ and DO saturation from Lake Ohrid (30 Jun 2003).
Cyclotella fottii analyses, using the relation proposed by.

Three sediment cores OHR03-1, after acidifying the sample with 3 mol L\(^{-1}\) HCl at.

Values were measured by weight loss after freeze-drying. TP was measured photometrically after digestion with K\(_2\)S\(_2\)O\(_8\) in an autoclave for 2 h at 120 °C (DEW 1996). Total carbon (TC) and TN were analyzed with a combustion CNS-analyzer (EuroVector Elemental Analyzer). Total inorganic carbon (TIC) was measured by infrared absorption of CO\(_2\) after acidifying the sample with 3 mol L\(^{-1}\) HCl (Skoog et al. 1996). Total organic carbon (TOC) was calculated as TOC = TC − TIC.

For consistency check, four additional cores Lz1083 to Lz1086 were taken from 270-250-, 232-, and 85-m depths in 2004 (Fig. 1, Table 3). Vertical 2-cm segments were equally freeze-dried and analyzed using a VARIO elemental CNS analyzer for TC and TN. TOC content was measured with a Metalyt CS 1000S (ELTRA Corp.) analyzer, after pretreating the sediment with 10% HCl at 80 °C to remove carbonate. Finally TIC was calculated indirectly from TOC and TC.

For the dating of the core OHR02-1 \(^{137}\)Cs and \(^{210}\)Pb activities were established from gamma-counting in Ge-Li borehole detectors (Hakanson and Jansson, 1983). As no clear peaks could be identified in the \(^{137}\)Cs profile, only \(^{210}\)Pb was used. In the top 2 cm of the core, the \(^{210}\)Pb activity was practically constant, probably because of bioturbation by benthic organisms. Below the homogeneous layer, the \(^{210}\)Pb signal decreased exponentially to background activity.

Plankton sampling—Plankton samples for quantitative analysis were taken with Niskin bottles covering the whole water column of Lake Ohrid down to 150 m (Table 3). Species were identified and counted under the microscope. Phytoplankton biomass was calculated from photometric chlorophyll \(a\) analyses, using the relation proposed by Marshall and Peters (1989) (detailed methods in Patceva 2005). Zooplankton biomass was based on detailed assessment of numbers and biovolumes of all major zooplankton species and their different stages (Eudiaptomus gracilis, Arctodiaptomus steindachneri, Cyclops ochridanus, Mesocyclops leuckarti, Daphnia pulicaria) for the year 2000 (detailed methods in Guseska 2003).

Sediment analysis—Three sediment cores OHR03-1, OHR03-2, and OHR02-1 were retrieved from 122-, 202-, and 280-m depths, along the north-south axis of the lake (Fig. 1, Table 3), using a gravity corer (Kelts et al. 1986) and subsequently sectioned to 0.5- to 2-cm-long vertical segments. For each segment, the water content was measured by weight loss after freeze-drying. TP was measured photometrically after digestion with K\(_2\)S\(_2\)O\(_8\) in an autoclave for 2 h at 120 °C (DEW 1996). Total carbon (TC) and TN were analyzed with a combustion CNS-analyzer (EuroVector Elemental Analyzer). Total inorganic carbon (TIC) was measured by infrared absorption of CO\(_2\) after acidifying the sample with 3 mol L\(^{-1}\) HCl (Skoog et al. 1996). Total organic carbon (TOC) was calculated as TOC = TC − TIC.

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In addition, profiles were taken in Lake Ohrid with a Seabird SBE 19 CTD. Parameters included water temperature, in situ conductivity \(k_T\), pH, and DO. On the basis of an analysis of major ionic composition of Lake Ohrid water (IC 690 equipped with a Super-Sep column for cations, IC 733 with 753 suppression module for anions; all Metrohm; methods in Weiss 2004), \(k_T\) values were transformed to conductivity at 20°C and to salinity (Wüest et al. 1996). CTD DO values were calibrated using the Winkler method.

Materials and methods

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Sediment mass flux was calculated using:

\[ S_M = (1 - \text{POR}) \times \text{sed} \times \rho_{\text{sed}} \]  

where \( S_M \) (kg m\(^{-2}\) yr\(^{-1}\)) is sedimentation of dry matter, POR (no units) is porosity calculated from the water content, sed (m yr\(^{-1}\)) is the sediment accumulation rate from \(^{210}\)Pb dating, and \( \rho_{\text{sed}} = 2,600 \text{ kg m}^{-3} \) is the sediment density from Ohrid cores established by pycnometer. The average \( S_M \) in the dated section of the core (top 8 cm, \( \sim 100 \text{ yr} \)) was used to calculate sedimentation of TP, TN, TOC, and TIC by multiplication with their respective measured mass fractions.

Apart from cores, sediment was collected by six sediment traps at the main sampling site (Fig. 1, Table 3). Traps were emptied twice per year from 2001 to 2003. Before chemical analysis, as for the OHR cores, sediment mass was determined after drying the samples at 30°C.

**Assessment of phosphorus loads**—For the three main tributaries, rivers Velgoska, Koselska, and Sateska (Fig. 1), discharge measurements have been performed with a SEBA Universal Current Meter F1. To reach a higher resolution of river discharge, water levels were read regularly and calibrated with occasional discharge measurements (Table 3). For the calculation of TP loads, rating curves were established using a linear fit for River Velgoska, which is influenced mainly by point sources, and the concentration (C)-discharge (Q) relation \( C = k_1/Q + k_2 \times \ln(Q + k_3) \) (Moosmann et al. 2005) for rivers Koselska and Sateska, which are influenced both by point and diffuse sources. On the basis of the rating curves, P loads were calculated and integrated using daily flow readings for rivers Velgoska and Koselska and average monthly discharge for River Sateska from Ivanova (1974) and the Macedonian Hydrometeorological Institute (unpublished data). For a second estimate of P loads, measured \( C-Q \) pairs since 1996 [from this monitoring, Naumoski (2000) and Veljanoska-Sarafiloska (2002)] were combined and integrated over 1 yr.

Eight Albanian tributaries were sampled on one excursion after several rainy days. Flow was estimated through water speed and cross-sectional river area.

Finally rain samples were collected on the roof of the Hydrobiological Institute in Ohrid using a funneled plastic collector, which was emptied after every rain event (Fig. 1).

**Linear phosphorus model**—To check the calculated P budget and estimate historic concentrations, the linear model by Vollenweider (1969) was used:

\[ \frac{\dot{e}\langle \text{TP} \rangle}{\dot{e}t} = \frac{1}{V} \times P_{\text{inp}} - \sigma \times \langle \text{TP} \rangle - \beta \times \langle \text{TP} \rangle \]  

where \( \langle \text{TP} \rangle \) (mg m\(^{-3}\)) is the volume-averaged concentra-
Table 4. Phosphorus balance.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Total P* (t yr⁻¹)</th>
<th>Potential bioavail. P* (t yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>External balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>External P loads from rivers, rain, groundwater</td>
<td>C-Q measurements</td>
<td>32±5</td>
<td>27±5</td>
</tr>
<tr>
<td><strong>Internal balance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P input</td>
<td>From balance</td>
<td>99±15</td>
<td>47±15</td>
</tr>
<tr>
<td>P outflow</td>
<td>Surface TP × outflow</td>
<td>3.0±1.8</td>
<td>3.0±1.8</td>
</tr>
<tr>
<td>P gross sedimentation</td>
<td>Sediment traps</td>
<td>110±19</td>
<td>58±19</td>
</tr>
<tr>
<td>P net sedimentation</td>
<td>Sediment core 0–2 cm</td>
<td>128±11</td>
<td>76±11</td>
</tr>
<tr>
<td>P release from sediment</td>
<td>Sediment core 2–4 cm</td>
<td>96±15</td>
<td>44±15</td>
</tr>
<tr>
<td></td>
<td>SRP increase in lake</td>
<td>25±4</td>
<td>25±4</td>
</tr>
<tr>
<td></td>
<td>Sediment core</td>
<td>32±16</td>
<td>32±16</td>
</tr>
</tbody>
</table>

*Indicated errors are standard deviations among different profiles, cores, sediment trap periods, or P load estimates.

A summarized overview of the following P balance is given in Table 4.

**External phosphorus loads**—P was monitored in the catchment (1) to quantify P inputs and (2) to identify the main contributors. Inputs are expected from direct precipitation, dry deposition, groundwater inflows, tributaries, and diffusive sources, such as agricultural activities and settlements close to the lake shore. The calculated P loads are summarized in Table 5. In total, an integrated SRP input of ~27 t yr⁻¹ from tributaries, groundwater, and rain was found.

In rain samples collected close to the town of Ohrid over 1 yr (Fig. 1), average SRP of ~8.4 ± 1.6 mg m⁻³ was found, which is in the range of sites with minor anthropogenic influence, such as Lake Malawi (Bootsma and Heeky 1993) or northeastern Crete (Markaki et al. 2003). The measured value also contains SRP that may have leached from dry deposition, given the time between rain event and actual sample collection, which was typically several hours (Herut et al. 1999). Few samples on which also TP was measured (though without prior stirring) indicate that the load of inert particulate P is at least one order of magnitude larger than for SRP.

The contribution of groundwater depends on the amount of water stemming from Lake Prespa and the P retention capacity of the underground karst connection. Matzinger et al. (2006a) found SRP ~10.9 ± 2.6 mg m⁻³ for the 7.8 m³ s⁻¹ flow from Lake Prespa and SRP ~4.0 ± 0.9 mg m⁻³ for the precipitation-fed remainder, which add up to a total groundwater load of ~4.2 t yr⁻¹.

P load of River Velgoska is dominated by point sources, as can be observed in P dilution with discharge (Fig. 4), leading to an extreme increase in SRP over the mere 5 km from source to mouth (Fig. 5). In contrast, River Sateska—by far the largest tributary—shows an increase in P with higher flow in Fig. 4, indicating that leaching and erosion from agricultural soils are important (Gächter et al. 2004). Finally, River Koselska is influenced both by agriculture and point sources with increased concentrations at low and high discharge (Fig. 4). The expected moderate SRP increase along the river is diluted effectively by more pristine tributaries (Fig. 5).

For all three rivers, differences between P loads from direct integration and rating-curve estimates were smaller than 10%. These small deviations may be attributed to a reduced influence from agriculture-based pollution.
compared to central European streams examined by Moosmann et al. (2005). For the remaining Macedonian tributaries, rough estimates are given using average Sateska P concentrations or based on measurements for River Cerava (Naumoski 2000). The Albanian catchment consists mainly of small creeks with large seasonal flow variations, some of which are severely polluted. As a result, two creeks at the town of Pogradec contribute, 90% of the SRP input from Albanian tributaries. Given this dominance of permanent point sources on the Albanian side, it can be assumed that the measurements after several days of rain reflect the daily household pollution quite accurately.

Table 5. External P loads to Lake Ohrid.

<table>
<thead>
<tr>
<th>Source</th>
<th>Status quo Mean annual inflow (m$^3$s$^{-1}$)</th>
<th>SRP load (t yr$^{-1}$)</th>
<th>Historic situation (&gt;200 yr ago) Mean annual inflow (m$^3$s$^{-1}$)</th>
<th>P-load (t yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation on lake surface</td>
<td>8.8</td>
<td>2.3 ± 0.4</td>
<td>8.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Groundwater inflow</td>
<td>20.2</td>
<td>4.2 ± 0.7†</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tributaries:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>River Velgoska</td>
<td>0.4</td>
<td>5.8 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River Koselska</td>
<td>1.3</td>
<td>1.0 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>River Sateska</td>
<td>5.5</td>
<td>0.6 ± 0.6</td>
<td>(5.8 ± 0.6 TP)</td>
<td></td>
</tr>
<tr>
<td>River Cerava</td>
<td>0.2</td>
<td>0.3 ± 0.15§</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small creeks from Macedonia</td>
<td>1.0</td>
<td>0.9 ± 0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Albanian tributaries</td>
<td>0.5</td>
<td>12.1 ± 4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total tributaries</td>
<td>8.9</td>
<td>25.9</td>
<td></td>
<td>37.1 ± 3.9</td>
</tr>
<tr>
<td>Total</td>
<td>37.9</td>
<td>32.4</td>
<td></td>
<td>13.5</td>
</tr>
</tbody>
</table>

*From Matzinger et al. (2006b).
† Errors represent standard deviation among measurements for precipitation and groundwater, and deviations among methodologies for tributaries.
‡ From Matzinger et al. (2006a).
§ Based on Naumoski (2000).
|| Including point sources.

Fig. 4. Measured TP and SRP concentrations versus discharge of three tributaries (Fig. 1). Data from 1996 to 2000 are from Naumoski (2000) and Veljanoska-Sarafiloska (2002). Bold lines are least-square fitted rating curves using the concentration (C)-discharge (Q) relation $C = k_1/Q + k_2 \times \ln(Q + k_3)$ and a linear relation for River Velgoska. Thin lines are 95% confidence limits. For River Sateska SRP concentrations are on a separate axis (right) and the respective fitted curve and confidence limits are shown with dashed lines.

Fig. 5. Change in SRP concentrations of three tributaries as a function of distance from their mouth (Fig. 1). Note breaks on y-axis in top two graphs. Missing symbols for River Sateska in July 2003 indicate that riverbed was dry at the sampling point.
Phosphorus outputs—The P balance can be alternatively calculated via its loss terms. P output via the only outflow, the River Crn Drim (Fig. 1), amounts to ~3 t yr\(^{-1}\), calculated from surface concentrations and flow rate. In comparison, P loss to the sediment requires a more elaborate analysis.

Sediment traps were placed in Lake Ohrid over two full annual cycles to estimate gross P sedimentation and to better understand internal lake cycling (Fig. 6). As the top trap was still in the trophogenic zone and the lowest was subject to focusing, the intermediate four traps were used for the estimation of lake-wide vertical fluxes. Sedimentation was unexpectedly constant throughout the seasons as well as interannually (Fig. 6a), with an average gross P sedimentation of 110 t yr\(^{-1}\). Surprisingly, almost 60% of this amount was found during the less productive winter season (Fig. 6e), when phytoplankton density in the lake drops to about 10% of its summer maximum (Patceva 2005) and TIC amounts to 1/3 of the sedimentation in summer (Fig. 6b). The three times higher TIC values during summer season (Fig. 6b) can be explained through increased temperature and photosynthetically driven calcite precipitation. The increased summer productivity is verified by phytoplankton counts and chlorophyll \(a\) measurements; however, phytoplankton never drops below 10% of its maximum density (Patceva 2005). This comparably high standing crop can also partly explain the similar summer and winter sedimentation of TOC and TN (Fig. 6c,d). However, higher TP sedimentation in winter (Fig. 6e) is most likely the result of allochthonous material over the winter months, when about 70% of annual precipitation is occurring. The low corresponding molar ratios of TOC : TP and TN : TP (Fig. 6g,h) indicate as well that a large share of the allochthonous P input is of inorganic, apatite-bound form (Downing and McCauley 1992).

Compared with trap results, cores provide an averaged picture of sedimentation, both spatially and temporally. Net sedimentation estimates are based on the three OHR sediment cores that have been taken along the north-south axis of Lake Ohrid (Fig. 1). The results for TIC, TOC, and TN contents are in excellent agreement with four additional cores taken and analyzed in 2005 (Fig. 7), despite the numerous thrusts and folds that have been observed at the lake bottom in a seismic survey (Wagner et al. in press). As a result the three OHR cores can be assumed to give a representative picture of lake sedimentation.

\(^{210}\)Pb dating of core OHR02-1 provided an average sediment accumulation of sed ~0.09 ± 0.02 cm yr\(^{-1}\). This result is in line with the 0.08 cm yr\(^{-1}\) reported by Roelofs and Kilham (1983) for cores taken in 1973. Thus 0.09 cm yr\(^{-1}\) should be reliable, covering at least the topmost 8 cm (~100 yr) of the core, if we assume that \(^{210}\)Pb dating is appropriate for the past ~70 yr (~three times the half-life of \(^{210}\)Pb). Using \(^{14}\)C dating, Roelofs and Kilham (1983) found 0.045 cm yr\(^{-1}\) for sediment layers beyond 10,000 yr of age, which indicates that no dramatic changes in sed occurred even over long time spans. Gross sedimentation from sediment traps ~1.0 g m\(^{-2}\) d\(^{-1}\) (Fig. 6a) would lead to a sed ~0.07 cm yr\(^{-1}\), assuming a water content of ~60% as found in the top 8 cm of the cores. Total sedimentation (Eq. 1) is ~26% higher in the cores than for the sediment traps, consistent with 0.02 cm yr\(^{-1}\) difference in sed. In contrast, individual material sedimentation in the top 2 cm of the cores was found on average 30% lower.

![Fig. 6. Data from sediment traps. Squares for winter season (three periods: 07 Feb 2001 to 25 Apr 2001, 27 Dec 2001 to 14 May 2002, 21 Oct 2002 to 27 Mar 2003), circles for summer season (two periods: 23 May 2002 to 21 Oct 2002, 27 Mar 2003 to 16 Sep 2003). Error bars show standard deviations of averaged periods. (a) shows sedimentation as dry mass per area and time; (b) to (h) describe contents of trap material. Dashed lines in (f) to (h) indicate Redfield ratio (C:N:P = 106:16:1).]
than in the sediment traps for TIC, TOC, and TN, and 16% higher for TP. The results imply that—in contrast to TOC and TN—release of TP is relatively weak during settling and takes place mainly at the sediment (Fig. 6c–e). This is also indicated by the sharp TP decrease within the top sediment layer (Fig. 7d). The P release during early diagenesis was estimated to be 32 t yr$^{-1}$, by comparing sedimentation from 0–2 cm with 2–4 cm depth. The 32 t yr$^{-1}$ represent a maximum estimate, as it also contains a potential eutrophication signal of the past two decades.

Molar TOC : TN : TP ratio stayed almost constant over the past 100–200 yr (Fig. 7f,g). The abrupt change in TOC : TP and TN : TP at 15–20-cm sediment depth is the result of the increase in TOC and TN with depth of the core (Fig. 7b,c). This increase might stem from a change in allochthonous organic material input, but cannot be interpreted on the basis of the available data. However, TOC : TP and TN : TP are below Redfield, contrary to expectations for a P-limited lake (Fig. 7g,h). The low ratios can be explained by a significant fraction of nondecomposable, possibly apatite-bound P.

Below 20-cm core depth (>220 yr old), the cores show background P sedimentation of ~66 t yr$^{-1}$, far higher than estimated current SRP input (Table 4) and therefore mostly consisting of inorganic P. For the organic P cycle, core data were corrected in Fig. 7e to an estimated natural, bioavailable P input of 14 t yr$^{-1}$ for a roughly 10 times smaller population. On the basis of this correction we find a recent gross sedimentation of noninert P of 76 t yr$^{-1}$ in the top 2 cm of the cores. Below this top layer between 2- and 4-cm sediment depth or ~30 yr before present, when major early diagenetic processes are terminated, recent net P sedimentation is ~44 t yr$^{-1}$. During these three decades about 76–44 = 32 t yr$^{-1}$ are released to the water column. This 42% release rate is in the range of observations by Hupfer et al. (1995) and Moosmann et al. (2006). The high background of inorganic P—typical for mountainous, oligotrophic regions—is imported by surface runoff following heavy rain events (Müller et al. 2006) and by dry deposition (Herut et al. 1999).

P dynamics in the water column—Over the period of observation average lake concentrations TP $< 4.6 \pm 0.8$ mg m$^{-3}$ and SRP $< 2.1 \pm 0.5$ mg m$^{-3}$ were found. Average concentrations and molar fractions in the euphotic zone of TN : TP $= 54$ and dissolved inorganic N : P = 220 indicate an oligotrophic, P-limited situation (Guildford and Hecky 2000). It is important to mention that the euphotic zone extends down to 150 m depth because of the exceptionally high water clarity of the lake (Fig. 2b; Ocevski and Allen 1977; Patceva 2001). Because of the relatively low P concentrations in Lake Ohrid measurement errors are large, with 41% and 29% for TP and SRP, respectively; hence short-term P content variations cannot be interpreted.

TP and SRP concentrations in the deep hypolimnion below 150 m are consistently higher than in the euphotic layer above (Fig. 8b,c), indicating SRP release from settling particles despite the aerobic water column, as has been observed by Hayes and Phillips (1958) or more recently by Gächter and Müller (2003) and Moosmann et al. (2006). Indeed, SRP makes up ~60% of the average difference $\Delta$TP$_{150–270 m} – \Delta$TP$_{0–150 m}$ = 1.7 mg m$^{-3}$. The role of
mineralization and consequent SRP release is evidenced by parallel maximum SRP and minimum DO concentrations close to the lake bottom (Fig. 9). Annual hypolimnetic SRP increase can be estimated from observations to $21 \pm 2$ t yr$^{-1}$ and $28 \pm 2$ t yr$^{-1}$ for the years 2002 and 2003, respectively (Fig. 8b).

**Overall phosphorus budget**—The overall budget (Table 4) is consistent regarding gross sedimentation (top of sediment cores vs. sediment traps) and P release during early diagenesis (sediment cores vs. SRP in water column).

Adding up the P net sedimentation and the P outflow amounts to an annual input of bioavailable phosphorus of $44 + 3 = 47$ t yr$^{-1}$. The difference of $20 \pm 1$ t yr$^{-1}$ from the measured SRP input in Table 4 could be explained by "diffusive" point sources. According to Foy et al. (1995) a P load of $20 \pm 1$ t yr$^{-1}$ is equivalent to the urban P discharge of about 20,000 people. In 1995 the households of 9,000 people living in villages directly at the lake shore and up to 100,000 people throughout the catchment were without connection to any sewage treatment. The same is valid for several hotels and campsites. Moreover, sewage pumps were reported to overflow regularly during heavy rainstorms. Thus $20 \pm 1$ t yr$^{-1}$ of additional P sources seem more than plausible.

**Eutrophication assessment**

*Detection of eutrophication*—Population in the Lake Ohrid catchment has more than doubled (+100,000 inhabitants) since the late 1940s. Moreover, up to 50,000 tourists visit the area annually. Thus changes in the nutrient balance of the lake could be expected despite the installation of a limited sewer and treatment system in Macedonia in the 1970s and its improvement since 1995.

Concurrent increase in TOC, TN, and TP in the top sediment (Fig. 7b–d) is a clear sign of ongoing eutrophication (Schelske and Hodell 1995). The increase can be split into a period of slow eutrophication, which started about 150–200 yr ago, and an accelerated phase over the past $50 \pm 1$ yr (Fig. 7e).

**Timescales**—On the basis of P monitoring and the net sedimentation of organic and bioavailable P in Table 4, a linear P model can be set up according to Eq. 2. It was assumed that the current TP concentration of $4.6 \pm 0.8$ mg m$^{-3}$ is near steady state. On the basis of the parameters $\beta = 0.84$ and $\sigma = 0.18$ yr$^{-1}$ derived from the observations, $\tau_P^* = 5.3$ yr was found, which is the average time that bioavailable P will remain in the water column before being buried in the sediment or leaving via outflow. After an increase in P input, new equilibrium concentration will be reached to $95\%$ after $3 \times \tau_P^* = 16$ yr and will thus lag behind significantly.

Having estimated historic P loads of $14 \pm 1$ t yr$^{-1}$ (see P outputs above), Eq. 2 can be used to calculate corresponding P concentrations. Using current parameters $\beta$ and $\sigma$ we find an equilibrium TP concentration of $1.3 \pm 0.5$ mg m$^{-3}$, 3.5 times less than today.

**Answers to questions (i) and (ii)**—On the basis of the assessment above, the two first questions can be answered:

(i) Lake Ohrid is clearly in the process of eutrophication, given the sediment records. On the basis of a linear model the P concentration in the lake may have
increased by a factor of \( \sim 3.5 \), from historic \( \sim 1.3 \text{ mg m}^{-3} \) to current \( \sim 4.6 \text{ mg m}^{-3} \). The most probable reason for eutrophication is the increase in domestic sources due to growing population.

(ii) Different timescales are important. Eutrophication is relatively slow but ongoing since \( \sim 150 \) to 200 yr ago. Since the late 1940s its speed seems to have accelerated. Average P residence time is \( \sim 5.3 \text{ yr} \). As a result it takes many years before increased P inputs can be detected.

**Definition of sustainable phosphorus load**

*Scenario development*—Given its importance for the endemic fauna of Lake Ohrid, hypolimnetic DO is applied for the definition of sustainable P load. However, it is unknown which level of DO might be critical for the endemic species of Lake Ohrid. During the period of observation average DO below 200 m, referred to as \( \text{DO}_{\text{hyp}} \) in the following, never dropped below \( 6.2 \text{ mg L}^{-1} \) (Fig. 3d), which seems to be sufficient for profound bottom fauna and deep-living fish species (S. Trajanovski and Z. Spirkovski pers. comm.). Directly above the lake bottom DO levels down to \( 4.3 \text{ mg L}^{-1} \) have occurred over short time periods (Fig. 9). However, the following analysis concentrates on \( \text{DO}_{\text{hyp}} \) because the phenomenon concerns only a small volume of the lake.

\( \text{DO}_{\text{hyp}} \) in Lake Ohrid has been shown to be sensitive to changes in lake stratification because of global warming (Matzinger et al. 2006b). Thus several scenarios were used for the next decades, from no warming to the expected 0.04 \( \text{C yr}^{-1} \) increase in air temperatures for the Balkan Peninsula (Table 6), on the basis of a two- to threefold increase in atmospheric \( \text{CO}_2 \) level over the next century (Giorgi et al. 2004). Following model results by Mortsch and Quinn (1996) and observations by Livingstone and Lotter (1998), increase in air temperature was directly transferred to the surface of Lake Ohrid and its tributaries. Global warming is expected to affect lake mixing through enhanced stratification during the warming process and, in contrast, stronger convective mixing because of increasing thermal expansivity with water temperature (Matzinger et al. 2006b). Reduced vertical mixing will lead to a decrease in upward transport of SRP and thus lake productivity. Consequently \( \text{DO}_{\text{hyp}} \) would be enhanced by lower lake productivity and sedimentation of organic matter but limited by reduced downward flux of DO. Finally, higher temperatures will positively affect biological processes such as algal growth and decomposition of organic matter but reduce DO solubility in water.

Unlike global warming, lake eutrophication can be controlled by local measures. Thus both increased as well as decreased anthropogenic P loads, relative to the current situation, are considered in separate scenarios (Table 6). Changes in P input are expected to affect the entire biogeochemical cycle and thus DO production in the trophogenic layer as well as DO consumption at the lake bottom. Moreover, increased salt transfer to the hypolimnion is anticipated from eutrophication via mineralization of settled organic matter and calcite. This salt transfer was assumed to be changing linearly with gross P sedimentation.

It is not clear, a priori, which of the competing processes above dominate under different boundary conditions. To test their relative importance the above scenarios are discussed in the following, on the basis of the results of a coupled physical, biogeochemical lake model, calibrated to observations (Fig. 3; Web Appendix 1). The term “status quo” is used to refer to current P loads and no warming, although an atmospheric warming of \( \sim 0.006 \text{ C yr}^{-1} \) has been observed over the past decades (IPCC 2001).

---

Table 6. Simulated scenarios and their effects on Lake Ohrid.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>P load (% of status quo)</th>
<th>( z_{\text{mix}}^* ) (m)</th>
<th>( K_z ) at 200 m depth( \dagger ) (cm² s⁻¹)</th>
<th>( z ) above which ( \text{DO} &gt; 6.2 \text{ mg L}^{-1} ),( \ddagger ) (m)</th>
<th>Average TP( \dagger ) (mg-P m⁻³)</th>
<th>Gross primary production( \dagger ) (% of status quo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0. 01</td>
<td>50</td>
<td>289</td>
<td>2.6</td>
<td>289</td>
<td>1.0/2.2</td>
<td>70</td>
</tr>
<tr>
<td>100</td>
<td>0.02</td>
<td>289</td>
<td>2.2</td>
<td>288</td>
<td>1.8/4.6</td>
<td>100</td>
</tr>
<tr>
<td>0.04</td>
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<td>289</td>
<td>2.1</td>
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<td>247</td>
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<td>97</td>
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<td>102</td>
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<td>129</td>
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<tr>
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<td>50</td>
<td>125</td>
<td>1.3</td>
<td>289</td>
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<td>71</td>
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<tr>
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<td>1.1</td>
<td>114</td>
<td>1.7/7.1</td>
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<td>1.5/11.3</td>
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<td>0.5</td>
<td>69</td>
<td>2.7/23.4</td>
<td>129</td>
<td></td>
</tr>
</tbody>
</table>

\( * \) Maximum convective mixing depth in 2067.
\( \dagger \) Averaged from 2053–2067.
\( \ddagger \) \( 6.2 \text{ mg L}^{-1} \) is the minimal observed (2001–2004) mean DO level below 200 m depth.
\( \times \) Bold numbers are status quo.
Vertical mixing and stratification—Vertical exchange through occasional complete overturns and the exchange between the annually mixed layer—stretching as deep as 200 m—with the lower, stratified hypolimnion are crucial for biogeochemical cycling. Vertical mixing at the 200-m boundary is about one order of magnitude larger from December to March ($K_{z,\text{win}} < 2.5 \text{ cm}^2 \text{s}^{-1}$) compared to strong stratification from April to November ($K_{z,\text{sum}} < 0.25 \text{ cm}^2 \text{s}^{-1}$), in agreement with indirect measurements by Matzinger et al. (2006b). Under status quo complete overturn is occurring roughly once every 7 yr (Hadzisice 1966; Matzinger et al. 2006b). Consequently the most probable situation was simulated with regular complete overturns at 7-yr intervals on the basis of observed meteorological forcing (Fig. 10).

The vertical mixing pattern changes significantly for the different scenarios in Table 6. At an atmospheric warming of $T_t = 0.04 \degree C \text{ yr}^{-1}$, temperature and salinity gradients increase with time, rendering stratification more and more stable (Fig. 10b). As a result the water body below $\sim 64$ m is basically secluded from the regularly mixed top layer after 60 yr of simulation, even in comparably cool winters. The exchange between this upper layer and the hypolimnion—important for transport of nutrients and DO—is on average more than three times lower compared with the status quo (Table 6). It is interesting that hypolimnetic mixing does not decrease linearly with increasing atmospheric warming rates $T_t$. The strongest change occurs between $T_t = 0.01 \degree C$ and $0.02 \degree C \text{ yr}^{-1}$, where $K_z$ is reduced by 50% (Table 6) and maximal convective mixing depth decreases from $\sim 250$ m to merely $\sim 90$ m. Up to a certain warming rate, obviously between $0.01 \degree C$ and $0.02 \degree C \text{ yr}^{-1}$ for Lake Ohrid, bottom water temperature can cope with the pace through geothermal heating and vertical exchange. Once $T_t$ goes beyond that threshold, bottom temperature lags behind, leading to an increase in stratification with time. Thus the warming rate rather than the absolute temperature increase is crucial for the extent of deep water isolation.

Under predicted $T_t$, eutrophication is of secondary importance for vertical mixing. However, at $T_t = 0.01 \degree C \text{ yr}^{-1}$, eutrophication-induced salt input from mineralization would lead to a deepwater isolation of similar extent as an increase to $T_t = 0.02 \degree C \text{ yr}^{-1}$.

In situ biogeochemical processes—As for the physical parameters, an excellent agreement of the model was found with observed P and TOC balances, primary productivity, and DO concentrations (Fig. 3; Web Appendix 1). During periods without complete overturn $\text{DO}_{\text{hyp}}$ continuously decreases, whereas total dissolved phosphorus (TDP) is increasing because of release during mineralization (Fig. 11a,b). After complete overturn both DO and TDP are distributed almost homogeneously throughout the water column. As a result productivity in the trophogenic layer increases, which consequently leads to high sedimentation of organic particles and consumption of DO in the hypolimnion. It is interesting to note that raised primary productivity after complete overturns can well be seen in simulated $\text{DO}_{\text{hyp}}$, sedimentation of organic matter, or zooplankton biomass (Fig. 11a,d). However, TP concentration shows but minor fluctuations and phytoplankton abundance is not a reliable indicator at all (Fig. 11b,c).
but switches between two main states: A first, where basically the whole lake is above DO_{ref} (DO_{DO>DO_{ref}} = 250–289 m) and a second, where only the top third of the water column (z_{DO>DO_{ref}} = 70–114 m) fulfills this requirement. Under status quo P load, DO switches states between T_{i} of 0.01 °C yr^{-1} and 0.02 °C yr^{-1}. However, a similar switch in DO occurs between T_{i} of 0.02 °C yr^{-1} and 0.04 °C yr^{-1} for a 50% reduction of P loads but already at 0 or 0.01 °C yr^{-1} for doubled P loads. The worst-case scenario—an air temperature increase of 0.04 °C yr^{-1} coupled with a doubling of anthropogenic P input—would lead to DO < DO_{ref} below 69-m depth and practically anoxic conditions below 110 m. In that case the sediment area for which DO > DO_{ref} would be reduced by at least 50% to find DO_{hypo} just around the minimum observed bottom concentration of 4 mg L^{-1} after ~60 yr (Fig. 12).

Another important aspect, not shown in Fig. 12, is the temporal dynamics of DO_{hypo}. While DO_{hypo} approaches equilibrium under status quo and for moderate warming scenarios, it simply decreases for T_{i} = 0.04 °C yr^{-1}, anthropogenic P load has to be reduced by at least 50% to find DO_{hypo} just around the minimum observed bottom concentration of 4 mg L^{-1} after ~60 yr (Fig. 12).

Answer to question (iii)—Lake Ohrid is highly sensitive to increased P loads, as well as global warming. In particular DO_{hypo} is reduced both by increased productivity from higher P loads as well as reduced mixing due to global warming. As a result, sustainable P load cannot be defined by a constant but has to be expressed as a function of global warming. A reduction of current anthropogenic P loads by 50% must be achieved to keep most of the lake above 4 mg L^{-1} for the next decades.

Discussion

Lake Ohrid—The analysis of Lake Ohrid nutrient balance clearly points to a eutrophication process, which has led to more than a threefold increase in average P concentration over the past century. Although Lake Ohrid is a slower reacting (P residence time ~5 yr) and oligotrophic system, the ongoing eutrophication was traced and quantified with low-cost monitoring, thanks to a combination of information on river inputs, lake concentrations, sediment cores, and population development in the catchment.
On the basis of simulation results, increase in P loads to Lake Ohrid leads to higher lake productivity and consequently higher sediment fluxes and mineralization. As a secondary effect water column stratification is stabilized because of an increase in salt transfer to the hypolimnion by mineralization. However, mixing is reduced to a much larger extent by anticipated global warming, since the temperature of the deep water lags behind, increasing the density difference to the surface layer. Both processes—higher mineralization at the sediment and reduced mixing of the water column—lead to a decrease in DO in the deep water. If air temperatures increase by 4°C over the next century as predicted, current anthropogenic P load would have to be reduced by at least 50% to maintain sufficient oxygen conditions for the endemic bottom fauna for the next decades.

Lake management is challenged to reduce P loads to Lake Ohrid and keep them on a low level, as global warming seems to be already occurring and is likely to accelerate. Positive steps in that direction have been taken in Macedonia over the past 5 yr by extending the sewerage system and limiting the P content in washing agents (G. Traub pers. comm.).

Timescales of expected changes are relatively long, on the order of decades: e.g., even at worst-case scenario of 0.04°C yr⁻¹ atmospheric warming and doubling of anthropogenic P input, P concentration in Lake Ohrid would increase at a rate of only 0.4 mg m⁻³ yr⁻¹. As a result long-term, regular monitoring of basic parameters is a necessity to track such slow changes and plan or evaluate protection measures. Still, P makes a sensible monitoring parameter as it reacts primarily to higher P loads. Temperature (T), on the other hand, allows the assessment of the effect of global warming both in terms of absolute T as well as the potential isolation of deep layers. Finally DO is the most complete parameter, as it is most sensitive to both global warming and higher P input. For Lake Ohrid a long-term monitoring of the three parameters DO, P, and T would allow detection of changes as well as the evaluation of their main causes. While the monitoring of those “simple” parameters is suggested, one should not forget that the reaction of the endemic species, the main treasure of this unique lake, cannot be anticipated and thus their observation should not be neglected.

General implications—While local human pressures may differ, global atmospheric warming would affect most deep lakes by reducing vertical exchange. Deepwater isolation would be expressed most severely in lakes without alternative deepwater renewal, such as turbidity-driven, plunging rivers. Regarding biogeochemical cycling we found that lakes are most sensitive to the rate of warming via vertical mixing, whereas higher temperature showed only secondary effects via biological processes. This phenomenon is very important when discussing temporal stability of the ancient lakes of Table 1. These lakes have certainly experienced warmer as well as cooler periods than today over their long history; however, predicted global warming rates for the next century may be unprecedented regarding the past million years (Bintanja et al. 2005).
Many special lakes, such as the ones in Table 1, are equally clean as Lake Ohrid and no urgent eutrophication control measures seem necessary. Nevertheless our analysis shows that it is important to react in time, (1) when dealing with slow-reacting systems and (2) because anticipated global atmospheric changes will amplify effects of eutrophication. The presented analysis is a first important step to assess this interaction. It is suggested that similar monitoring programs be established for other precious ancient lakes.

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Lake Ohrid eutrophication


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