

**A Late Glacial to Holocene record of
Holocene record of
environmental
change**

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A Late Glacial to Holocene record of environmental change from Lake Dojran (Macedonia, Greece)

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Abstract

A Late Glacial to Holocene sediment sequence (Co1260, 717 cm) from Lake Dojran, located at the border of the F.Y.R. of Macedonia and Greece, has been investigated to provide information on climate variability in the Balkan region. A robust age-model was established from 13 radiocarbon ages, and indicates that the base of the sequence was deposited at ca. 12 500 cal yr BP, when the lake-level was low. Variations in sedimentological (TOC, CaCO₃, TC, N, S, grain-size, XRF, $\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$) data were linked to hydro-acoustic data and indicate that warmer and more humid climate conditions characterized the remaining period of the Younger Dryas until the beginning of the Holocene. The Holocene exhibits significant environmental variations, including the 8.2 ka and 4.2 ka cooling events, the Medieval Warm Period, and the Little Ice Age. Human induced erosion processes in the catchment of Lake Dojran intensified after 2800 cal yr BP.

1 Introduction

Although several paleoenvironmental records spanning the entire Holocene already exist from the Balkan region (e.g. Bordon et al., 2009; Wagner et al., 2009; Vogel et al., 2010a; Peyron et al., 2011; Panagiotopoulos et al., 2012), some suffer from poor radiocarbon chronologies (Wagner et al., 2009; Vogel et al., 2010a), or are inconsistent in terms of spatial variability and short-term climate events (Magny et al., 2003, 2009; Tzedakis, 2007; Berger and Guilaine, 2009). Additional records with high-resolution sedimentary information from this region can help to get a better understanding of Late Glacial and Holocene climatic change and anthropogenic activity and their spatial variability. In the Balkan region, it is assumed that significant anthropogenic impact started during the early Holocene (Holtvoeth et al., 2010) and increased distinctly during the late Holocene (Willis, 1994; Wagner et al., 2009; Aufgebauer et al., 2012;

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Panagiotopoulos et al., 2012), which complicates the reconstruction of climate change (Vogel et al., 2010a).

Lake Dojran is located at the boarder of the Former Yugoslav Republic of Macedonia (FYROM) and Greece (Fig. 1). A lake-level lowering of 6 m between 1955 and 2000 was mainly caused by irrigation and canalization of the former outlet, River Doiranitis (Griffiths et al., 2002; Zacharias et al., 2002; Sotiria and Petkovski, 2004; Manley et al., 2008). This lake level decrease led to eutrophication and is well recorded in the chemical, biological and stable isotope data of the surface sediments (Veljanoska-Sarafiloska et al., 2001; Griffiths et al., 2002). Increasing anthropogenic influence at Lake Dojran from the mid to late Holocene has been inferred from pollen assemblages in sediment cores recovered close to the lakeshore (Athanasiadis et al., 2000). However, the sediments are poorly dated and variable change in their sedimentation rates imply major hiatuses, probably due to significant lake level changes, particularly in the lateral coring locations. As a comparison of records from lakes Prespa and Ohrid has shown that shallower lakes can amplify climatic and anthropogenic signals (Leng et al., 2010; Wagner et al., 2010), we can assume that the even shallower Lake Dojran provides a valuable record of climatic change and anthropogenic impact at the Balkan region.

2 Site descriptions

Lake Dojran (Fig. 1, 41°12' N, 22°44' E) is considered to be a relict of the Plio-Pleistocene Peonic Lake, which was formed by volcanic and tectonic activities (Cvijic, 1911; Stojanov and Micevski, 1989). Lake Dojran is located at 144 m above sea level (a.s.l.) in a carstic depression formed by Paleozoic marble intercalated with phylites (Stojanov and Micevski, 1989). The lake catchment predominantly comprises Paleozoic mica gneiss, muscovite-gneiss and amphibolite, Tertiary volcanic and volcanic-sedimentary rocks, and Quaternary alluvial and limnic sediments (Stojanov and Micevski, 1989; Sotiria and Petkovski, 2004). Only 18% of the total catchment area of 275 km² exceeds an elevation of 500 m a.s.l., and that is in the Northeast of

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Lake Dojran where the Belisca Mountain range is up to 1870 m a.s.l. high (Sotiria and Petkovski, 2004). Small rivers, creeks and groundwater drain the catchment area and feed Lake Dojran, particularly during winter and spring (Griffiths et al., 2002; Sotiria and Petkovski, 2004). The former outlet of Lake Dojran, River Doiranitis, which connected the lake to the Axios/Vardar River, is located some meters above the present lake-level. Current water loss from Lake Dojran is due to evaporation and probably to groundwater outflow.

The climate at Lake Dojran is influenced by the Mediterranean Sea via the connection of the Thessaloniki Plain, continental influences and local morphology (Sotiria and Petkovski, 2004). The mean annual air temperature was +14.3 °C between 1961 and 2000, with monthly average summer and winter temperatures of +26.1 °C and +3.7 °C, respectively (Sotiria and Petkovski, 2004). The highest proportion of the annual precipitation (612 mm) falls during mild winters (Sotiria and Petkovski, 2004), leading to warm and dry summers.

In 2004, Lake Dojran had a lake water surface area of 40 km² with water depths between 3 to 4 m (Sotiria and Petkovski, 2004), however, there are seasonal and longer-term progressive change that affected the surface area and water depth (cf. Athanasiadis et al., 2000; Manley et al., 2008). Thermal stratification occurs during the summer months (Zacharias et al., 2002) and it is presumed that lake water mixing occurs during winter, similar to Lake Prespa (Matzinger et al., 2006). Due to its location in the karstic depression, Lake Dojran is bicarbonate- and chloride-rich, alkaline and productive (Stankovic, 1931; Griffiths et al., 2002). Today, the littoral area of the lake comprises a fringe of up to 30 m wide reed beds.

3 Material and methods

3.1 Fieldwork

Fieldwork at Lake Dojran was carried out in June 2011. A hydro-acoustic survey (Innomar SES-2000 compact, 10 kHz) on the Macedonian part of the lake (Fig. 1) was used to provide more detailed information on the lake bathymetry and the sediment architecture. At coring location Co1260 (41°11.703' N, 22°44.573' E) undisturbed, horizontal bedded sediments and a water depth of ~ 7 m were observed (Fig. 2). Core Co1260 was recovered from a floating platform using a gravity corer for undisturbed surface sediments, and a percussion piston corer for deeper sediments (both UWITEC Co., Austria). After recovery, the overlapping 300 cm long sediment cores were cut into up to 100 cm long sections. Core catcher samples were transferred at 2 cm resolution in plastic vials.

3.2 Analytical work

In the laboratory, the cores were split into two halves and one half was sealed airtight for archiving. On the other half, X-Ray Fluorescence (XRF) scanning was carried out in 2 mm resolution with an ITRAX core scanner (Cox Analytical Systems, Sweden), equipped with a Cr-tube and a Si-drift detector in combination with a multi-channel analyzer. Voltage and amperage were set to 30 kV and 30 mA, respectively. The measured count rates can be used as semi-quantitative estimates of relative concentrations of the detected elements (Croudace et al., 2006). Inaccuracies in comparison to conventional XRF analyses rise due to different resolutions and variations in grain-size, porosity, water content and surface structure of the core.

The sediments were then subsampled in 2 cm intervals and half of each sample, including those from the core catchers, was freeze-dried. The water content was calculated from the weight loss after freeze-drying. Approximately 1 g of the dry sediment was treated with hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), sodium hydroxide

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(NaOH), and $\text{Na}_4\text{P}_2\text{O}_7$ for grain-size analysis (8 cm resolution) of terrigenous clastic material. Grain-size measurements were carried out with a Saturn DigiSizer 5200 laser particle analyzer and a Master Tech 52 multisampler (Micromeritics Co., USA) after one minute of ultrasonic treatment. The data processing of each sample was based on three runs and the GRADISTATv8 program (Blott and Pye, 2001).

An aliquot of the freeze-dried samples was ground to $< 63 \mu\text{m}$ and homogenized for biogeochemical analysis (2 cm resolution). Total nitrogen (TN) and total sulfur (TS) were determined with a Vario Micro Cube combustion CNS elemental analyzer (ELEMENTAR Co., Germany). Total carbon (TC) and total inorganic carbon (TIC) were measured with a DIMATOC 200 (DIMATEC Co., Germany). The calcite content (CaCO_3) was calculated from TIC by multiplying with 8.33 and total organic carbon (TOC) was determined by subtracting TIC from TC.

Isotope studies included modern lake and spring waters (O, H, C isotopes) and wet sediment samples (O, C isotopes) at 4 cm resolution. For O isotope composition of modern lake and spring water, the water was equilibrated with CO_2 using an Isoprep 18 device for oxygen isotope analyses with a VG SIRA mass spectrometry. A EuroPyrOH-3110 system, which based on an on-line Cr reduction method, was used for hydrogen isotope analysis. For C isotope analysis of total dissolved inorganic carbon (TDIC), the inorganic carbon was precipitated during the field work from ca. 85 mL water using ca. 15 mL of NaOH- BaCl_2 . In the laboratory, the precipitated barium carbonate (BaCO_3) was washed with deionized water. For isotope analyses, CO_2 was extracted from BaCO_3 with anhydrous phosphoric acid (H_3PO_4) under vacuum and the isotope was analyzed using a VG Optima dual inlet mass spectrometer.

For inorganic carbon and oxygen isotope analysis of endogenic calcite, horizons with more than 1 % TIC were bleached with sodium hypochlorite (NaOCl), neutralized and sieved to $80 \mu\text{m}$. After the $< 80 \mu\text{m}$ fraction was ground, the extraction of gaseous CO_2 and the subsequent measurement followed that described above for TDIC.

Samples for organic carbon isotope analysis were treated with HCl to remove CaCO_3 , neutralized, filtered to $20 \mu\text{m}$ and the supernatant was dried at 50°C . After

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the > 20 μm fraction was ground and homogenized, it was combusted by an Elemental Analyser (Costech Co., USA) on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer. CaCO_3 adjusted TOC content was determined by the elemental analyzer. Modern water and sediment isotopic ratios are reported as per mill (‰) deviations from the VSMOW (O and H water) and VPDB (O, C barium carbonate, calcites; C organics) scales.

Radiocarbon dating on bulk sediment samples, terrestrial plant material, charcoal, and biogenic carbonates were carried out by accelerator mass spectrometry (AMS) at the University of Cologne Centre for AMS and the ETH Laboratory of Ion Beam Physics in Zurich (Switzerland). Previously, sample pre-treatment and graphitization was carried out according to Rethemeyer et al. (2012). Organic carbon from bulk sediment, terrestrial plant material, and charcoal samples was chemically extracted by acid-alkali-acid extraction (AAA). The alkali extraction was omitted for small samples sizes to avoid loss of sample material. Combustion and graphitisation was carried out with a Vario Micro Cube elemental analyzer (ELEMENTAR Co., Germany) coupled to a graphitization system, where the CO_2 is converted to graphite with hydrogen over iron as catalyst. The surface of biogenic carbonates was leached with 1M H_2SO_4 and the carbonate sample was subsequently converted to CO_2 by hydrolysis with 99% H_3PO_4 under He. CALIB 6.1.1 (Stuiver and Reimer, 1993) and the IntCal09 dataset (Reimer et al., 2009) were used for conversion of the conventional radiocarbon ages into calendar ages (cal yr BP) on an uncertainty level of 2σ . Based on the calibrated ages a polynomial age model was established and sedimentation rates were calculated.

4 Results and discussion

4.1 Hydro-acoustic survey

From the hydro-acoustic survey, profiles 1 and 2 were selected to show the bathymetry and sediment architecture of Lake Dojran (Fig. 2). The bottom morphology of Lake

Dojran is relatively simple, with a mean water depth of ca. 6.6 m and slightly inclining slopes towards the shores (Fig. 2).

The maximum penetration depth of the hydro-acoustic signal only sporadically exceeds 7 m sediment depth. One of the spots with deeper penetration is close to the northern shore, where onlap structures and tilted sedimentation below ca. 7 m sediment depth suggest tectonic activity (profile 2, Fig. 2). In the central basin, a hard reflector occurs at 7 m. This reflector is close to the surface multiple, but has a more undulated shape, particularly in northern part of the basin. In addition, the multiple in the central basin is slightly deeper, as observed in spots, where hyperbolic reflections with transparent areas underneath indicate the occurrence of gas. At coring location Co1260, parallel, but somewhat undulated reflectors particularly below 7 m imply sediment thickness of at least ~ 13.4 m and do not indicate underlying bedrock. Below this depth, the reflectors are too weak or are overlain by multiples (Fig. 2). The undulated shape of the hard reflector at 7 m (reflector 1) and the weaker reflections below suggest somewhat disturbed sedimentation as it might have occurred during a lake level lowstand. A terrace in the northern part of the lake (Fig. 2) probably represents a paleo-shoreline. The hard reflector at coring location Co1260 is overlain by reflector 2 at 6.05 m sediment depth, which indicates onlap structures to the hard reflector in the central to northern part of the lake and close to the terrace (profile 2, Fig. 2). Reflector 3 (4.46 m) indicates onlap structures only at the terrace close to the northern shore (Fig. 2). Reflector 4 (4.00 m) pinches out in central areas of the lake and suggests minor lake level fluctuations or the occurrence of lake internal currents, such as observed in Lake Prespa (Wagner et al., 2012). Reflectors 5 (3.57 m) and 6 (2.25 m) span almost the entire lake basin and were likely formed when the lake level was higher. Reflector 7 (1.92 m) pinches out again, whilst reflector 8 (1.3 m) can be observed in marginal parts of the lake and thus indicates a somewhat higher lake-level.

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4.2 Lithostratigraphy and biogeochemistry

Based on visual core description, XRF data and water content, the correlation of the overlapping segments of core Co1260 led to a composite profile of 717 cm length, which has been subdivided into four lithofacies (Fig. 3).

Lithofacies 1 (717 to 658 cm) is grey, has a low water content, and a crumbly structure due to a high abundance of clay clasts. The sediment is poorly sorted, with mainly coarse silt with sporadic drop stones. Aquatic or terrestrial macrophyte remains are not apparent, and the amount of finely dispersed organic material (OM) is low, as indicated in $\text{TOC} < 1\%$ and $\text{TS} < 0.5\%$. TOC/TN varies between 3 and 12 and suggests that OM is mainly of aquatic origin, however, ratios < 4 can be associated with selective decomposition of TOC (Leng et al., 1999). A high TOC/TS in the lowermost 17 cm of lithofacies 1 indicates well-oxygenated bottom water conditions and surface sediments (cf. Müller, 2001; Wagner et al., 2009). The CaCO_3 content of lithofacies 1 varies between 5% and 20%, and is mainly derived from endogenic calcite, as shown by SEM (Fig. 4). Additional sources of CaCO_3 include ostracodes and shells or shell fragments of bivalves, such as at ~ 664 cm depth. Post-sedimentary dissolution of calcite can be excluded at least for the upper part of lithofacies 1 (ca. 682–658 cm), because the sediments contain well-preserved ostracodes (determined by F. Viehberg). Potassium (K) and iron (Fe) counts from XRF analyses, which can be associated with clastic sediment supply (Cohen, 2003; Arnaud et al., 2005), are low, but might be an artifact of the crumbly structure of the core surface. The lowermost section of lithofacies 1, where CaCO_3 is $< 9\%$ and the mean grain size is highest (Fig. 3), corresponds to the hard reflector (reflector 1) in the hydro-acoustic profiles at 7 m sediment depth.

Lithofacies 2 (658 to 520 cm) is grey to olive grey, has an increasing water content, and a massive structure. The grain-size composition is dominated by medium to very coarse silt, which indicates high transport energy due to low water depth or high inflow. Sporadic fine sand lenses are interpreted as ice rafted detritus (IRD). Lithofacies 2 has been sub-divided into lithofacies 2a (658 to 590 cm) with fine-grained sediments,

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relatively high OM and TOC/TN and lithofacies 2b (590 to 520 cm) with coarser sediments, lower OM and TOC/TN. Similar patterns of TOC and TS suggest that TS derives mainly from OM, however, a low TOC/TS and a good correlation between TOC/TS and Fe throughout lithofacies 2 suggest that TS is partly derived from pyrite (Wagner et al., 2006, 2009). Plant remains or carbonate fossils are not apparent in lithofacies 2a and 2b. The transition of lithofacies 2a to 2b likely corresponds to reflector 2 (6.05 m) in the hydro-acoustic profiles.

Lithofacies 3 (520 to 265 cm) is olive grey, has a water content between 55 and 70 %, and a massive or marbled structure. Grain-size is dominated by medium and coarse silt. A TOC increase from around 1 % at the base to ca. 3 % at the top implies decreasing decomposition or increasing lake productivity, which is, however, only partly reflected in small variations in TOC/TN. Increasing lake productivity is better indicated in CaCO₃ of up to 40 %, which anti-correlates with K and Fe counts. The variations in CaCO₃, K, and Fe counts form the sub-division of lithofacies 3 (Fig. 3). Lithofacies 3a (520 to 401 cm) is massive or marbled and has high CaCO₃ and low K counts. Shell fragments and well-preserved *Dreissena* bivalves occur sporadically between 505 and 404 cm and are more common at 503 and 404 cm (Fig. 3). In the lower part of lithofacies 3a (520 to 460 cm) TS increases to 1 %. SEM analyses showed a high abundance of pyrite (Fig. 4), although this does not correlate with Fe counts, which probably indicates that Fe is bound in other chemical compounds above and below. Lithofacies 3b (401 to 390 cm) is massive, has minimum CaCO₃, which is anti-correlated with K and Fe counts, and has a maximum in grain-size distribution. In lithofacies 3c (390 to 265 cm), which is also massive, CaCO₃ increases to around 40 % at 350 cm, before it drops to negligible values at the top. Although the CaCO₃ content is similar to lithofacies 3a, shell and shell fragments are absent. The decrease of CaCO₃ at the top of this sub-lithofacies correlates with increasing K and Fe counts and a decrease of the mean grain-size from ca. 310 cm. The change in sedimentary characteristics in lithofacies 3 are also reflected in the hydro-acoustic data, as reflector 3 (4.46 m) corresponds

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with the upper limit of the TS peak, and reflectors 4 (4.00 m) and 5 (3.57 m) represent distinct change in mean grain size.

Lithofacies 4 (265 to 0 cm) is dark olive brown to dark olive black, has a water content of 60 to 76 % and a massive, marbled, or laminated structure. Medium and coarse silt dominate the grain-size composition. A high abundance of shell fragments and some well-preserved *Dreissena* bivalves occur between 195 and 100 cm. CaCO₃ in general is low, but shows some distinct peaks, where shells or shell fragments occur (Fig. 3). The occurrence of these shell layers seems to be irregular, as a layer of well-preserved *Dreissena* bivalves was found at 32 cm in one core segment, but did not occur in the overlapping segment. Variations in sediment structure, color, associated CaCO₃, and OM, allow a sub-division of lithofacies 4. Lithofacies 4a occurs between 265 and 152 cm, is massive or marbled, dark olive brown in color, has a low CaCO₃, and decreasing TOC content and TOC/TN. The mean grain size is the lowest for the entire sequence, whereas K and Fe reach maximum counts. This suggests pelagic sedimentation and a low productivity, or dilution by relatively high clastic input. Low productivity is confirmed by low TS and high TOC/TS, implying good mixing of the water column and potentially additional decomposition of OM. CaCO₃ dissolution can be excluded, as ostracodes are well preserved. Lithofacies 4b, from 152 to 116 cm, is massive or irregularly laminated, has a dark olive grey to very dark brown color, a relatively high CaCO₃, TS and TOC/TN, mean grain size and a relatively low TS. TOC increases throughout lithofacies 4b. Lithofacies 4c comprises the uppermost 116 cm of core Co1262 and is massive, with a dark olive brown color. Some faint black laminations occur between 18 and 8 cm, where a peak in TS occurs. Whereas CaCO₃ is negligible, TOC is the highest of the entire core. High TOC implies high productivity, which is probably triggered rather by high nutrient input than temperatures. The mean grain size is constant around 20 μm, but K and Fe counts show some distinct fluctuations in the uppermost ca. 60 cm. Distinct change in sedimentological characteristics of lithofacies 4 can be correlated with the reflectors in the hydro-acoustic profile. Reflector 6 (2.25 m) coincides with a broad maximum in TOC and water content, reflector 7

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(1.92 m) is, where the maximum in K and Fe counts can be observed and reflector 8 (1.3 m) marks the maximum in mean grain size and CaCO₃.

The overall massive to marbled structure of the entire sediment succession suggests bioturbation. This is confirmed by a relatively high abundance ostracodes in the sediments. The occurrence of the ostracode *Darwinula stevensoni* (determined by F. Viehberg), which was observed in sandy groundwater-influenced sediments (Meisch, 2000), substantiates that Lake Dojran is influenced by an aquifer.

4.3 Isotope record

$\delta^{18}\text{O}_{\text{water}}$ and $\delta\text{D}_{\text{water}}$ of samples from springs, which enter Lake Dojran, plot close to the global meteoric water line (GMWL, Fig. 5, Table 1). $\delta^{18}\text{O}_{\text{water}}$ and $\delta\text{D}_{\text{water}}$ of modern lake water have higher values and plot on a local evaporation line (LEL). The isotope data also show that the evaporation of the lake water was lower in 2011 compared to 1997 (cf. Griffiths et al., 2002), which corresponds with an increasing lake-level in the last few years. Because the present lake level of Lake Dojran is below the outlet, the data also imply that aquifers play an important role in the water balance. Similarly to the water isotopes (O, D), $\delta^{13}\text{C}_{\text{TDIC}}$ of total dissolved inorganic carbon (TDIC) in the lake has higher values than the marginal springs (Table 1), most likely due a long residence time enabling the dissolved bicarbonates to exchange with isotopically heavier atmospheric CO₂. This is a common feature in lakes, in which the water isotope geochemistry is dominated by evaporation (Leng and Marshall, 2004; Leng et al., 2012).

In core Co1260, the sediments from lithofacies 1 and 4 with TIC < 1% could not be analyzed for carbon isotope composition. The rest of core Co1260 shows moderate fluctuations in $\delta^{18}\text{O}_{\text{carb}}$ between -4.6‰ and -1.2‰. These moderate values with relatively low variability (ca. 3‰) suggest that the lake has not experienced complete hydrologic closure during the deposition of these sequences (cf. Roberts et al., 2008). Variations in $\delta^{18}\text{O}_{\text{carb}}$ can be caused by change in the isotopic composition of precipitation (linked to source and/or temperature variation), in the precipitation/evaporation (P/E) ratio, or in the lake water residence time (cf. Roberts et al., 2008; Leng et al.,

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2012). $\delta^{13}\text{C}_{\text{carb}}$ varies between -3.2‰ and $+1.4\text{‰}$, with the lowest values in lithofacies 2a and at the top of lithofacies 3c. These low values are probably due the greater contribution of soil derived CO_2 or decomposition of OM relative to the amount of carbon from the karst and the atmosphere (cf. Leng et al., 2010).

5 The pattern of $\delta^{13}\text{C}_{\text{org}}$, with values between -27.1‰ to -24.2‰ , corresponds only partly with $\delta^{13}\text{C}_{\text{carb}}$. Therefore, TDIC cannot be the only carbon pool for OM in the Lake Dojran sediments, which suggests that variations in $\delta^{13}\text{C}_{\text{org}}$ could also derive from change in allochthonous versus autochthonous OM deposition.

4.4 Chronology

10 The age model for core Co1260 is based on 13 radiocarbon ages and cross correlation with other lacustrine sediment cores from the Balkan region (Fig. 6, Table 2).

The 7 samples with terrestrial plant material and charcoal provide a robust basis for the age model, as these samples are considered to have no reservoir effect. However, there is an age reversal in samples COL 1320.1.1 (460.9 cm, $10\,820 \pm 420$ cal yr BP) and COL 1321.1.1 (521.9 cm, $10\,660 \pm 440$ cal yr BP, Table 2). Both samples are of
15 terrestrial plant material and originate from the same core section, but sample COL 1320.1.1 was probably dislocated during opening of the cores, as it was found on the surface of the core halves. In contrast, sample COL 1321.1.1 was from the inner part of one of the core halves and is therefore considered to provide the accurate age.

20 In addition to the terrestrial plant samples, 2 bulk organic carbon and 3 carbonate samples were used for the establishment of the age-depth model. Both materials can be influenced by reservoir effects, i.e. incorporation of fossil/old organic matter from bedrocks or other sources not in equilibrium with atmospheric $^{14}\text{CO}_2$. This can result in depleted radiocarbon ages (Cohen, 2003 and references therein; Ramsey, 2008 and references therein), such as also reported from lakes Prespa and Ohrid (Vogel et al., 2010b; Aufgebauer et al., 2012). However, we cannot assume a constant off set, as reservoir effects can vary over time (e.g. Aufgebauer et al., 2012). A
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low reservoir effect is suggested by the small age difference of COL 1312.1.1 (bulk organic carbon: 140 ± 140 cal yr BP) at 16.5 cm depth, and a terrestrial plant residue from 53.3 cm (COL1324.1.1: 410 ± 110 cal yr BP) and the sediment surface. Samples from 502.9 cm (ETH 44957.1.1, carbonate: $11\,250 \pm 60$ cal yr BP) and 521.9 cm depth (COL 1321.1.1, terrestrial plant: $10\,6620 \pm 440$ cal yr BP) suggest a reservoir effect of several hundred years. The large difference between bulk organic C and carbonate ages at 635 and 682 cm depth (ETH 46615.1.1: $11\,920 \pm 310$ cal yr BP and ETH 44958.1.1: $32\,830 \pm 650$ cal yr BP) could indicate an even higher reservoir effect. On the other hand, a high TOC/TN of sample ETH 46615.1.1 indicate a predominantly terrestrial origin and suggest that the age of this sample could be reliable and that sample ETH 44958.1.1 is probably re-deposited. Re-deposition can also be assumed for the shell fragment sample at 404.9 cm (ETH 44956.1.1; 7350 ± 80 cal yr BP). This sample is significantly younger than the 2 cm underlying terrestrial plant fragment COL 1319.1.1 (8960 ± 440 cal yr BP) and there was no lithological indication for a hiatus or a distinct change in sedimentation rates. The age of sample COL 1319.1.1 has a large uncertainty, because the carbon weight is very low (0.28 mg) and the calendar age is located on a ^{14}C plateau. Within these uncertainties, the age of plant fragment COL 1319.1.1 seems to be reliable, because cross correlation with other lacustrine sediment cores from the Balkan region including the nearby lakes Prespa and Ohrid indicates that a minimum in CaCO_3 around 397 cm depth in core Co1260 likely corresponds with the 8.2 ka cooling event (Wagner et al., 2009, 2010; Vogel et al., 2010a; Aufgebauer et al., 2012).

For the polynomial interpolation of the age depth model of core Co1260, the sediment surface was adjusted to -61.5 cal yr BP and 6 terrestrial plant material samples, the charcoal sample, the two bulk organic carbon samples, and the cross correlation point at the 8.2 ka cooling event were included (Fig. 6; Table 2). The calculated age model of core Co1260 yields a basal age of ca. $12\,500$ cal yr BP. According to the established age model, the sedimentation rate of core Co1260 is high at the bottom and the top of the core and low between 390 and 330 cm sediment depth (Fig. 6).

5 Interpretation

5.1 Late Glacial (> 11 500 cal yr BP)

The Late Glacial part of core Co1260 is represented by deposits of lithofacies 1 and 2a (717–590 cm) and covers the period between 12 500 and 11 500 cal yr BP.

The deposits of lithofacies 1 between 717 cm and 658 cm represent the period 12 500 to 12 100 cal yr BP. The high abundance of clay clasts, which are most likely formed under subaerial conditions, implies that the deposits were formed to a certain amount from redeposited lacustrine material. This is confirmed by the undulated morphology of reflector 1, which corresponds to the lower 17 cm of lithofacies 1, and by the occurrence of the shell fragment with an age of $32\,830 \pm 650$ cal yr BP at 682 cm depth. Low lake level, redeposition, and intensive wave action are also indicated by a high mean grain-size and the overall poor sorting. The poor sorting is enhanced by the occurrence of drop stones from ice floe transport. As drop stones do not occur in the surface sediments of Lake Dojran and the modern lake is only occasionally covered by ice (Zacharias et al., 2002), winter temperatures during the deposition of lithofacies 1 must have been lower than today. Lower temperatures are also suggested by the relatively low OM and CaCO_3 . In the modern lake, low lake levels during relatively warm conditions correspond with periods of algal blooms and eutrophication (cf. Griffiths et al., 2002). Intensive macrophyte growth, such as often occurs during low lake levels (cf. Coops et al., 2003; Beklioglu et al., 2006), is also not evident in lithofacies 1. However, there are some smaller fluctuations in OM and CaCO_3 , which indicate minor variations in local temperatures or lake level. A minimum of $\delta^{13}\text{C}_{\text{org}}$ and a maximum in TOC/TN suggest increased allochthonous OM input at this time. A low lake level could have promoted the degradation of OM, particularly in the lowermost 17 cm of lithofacies 1, where a high TOC/TS indicates higher oxygen supply to the surfaces sediments. Relatively low $\delta^{18}\text{O}_{\text{carb}}$ values until 12 250 cal yr BP and subsequent higher values at the top of lithofacies 1 imply increased evaporation and correspond to a subtle finer

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grain-size distribution. A higher lake level could reduce the wave action at Co1260 and enlarge the surface area of the lake water while the water volume would only increase marginally due to the flat-bottomed nature of Lake Dojran. Greater surface area promotes more evaporation of the lake water.

5 The deposits of lithofacies 2a from 658 to 590 cm depth represent the period 12 100 to 11 500 cal yr BP. The absence of clay clasts and a lower mean grain size imply less redeposition, low wave action, and a higher lake level, which corresponds with the onlap structure of reflector 2. Fine sand lenses, which are interpreted as IRD, indicate that the lake was still ice covered during winter. During summer, higher temperatures are indicated by enhanced productivity as reflected in a higher OM and CaCO₃ content. Maxima in OM occur around 11 900 and 11 560 cal yr BP and are probably caused by increased allochthonous nutrient and sediment supply, such as indicated in high K and Fe counts, high TOC/TN, and low $\delta^{13}\text{C}_{\text{org}}$. Enhanced erosion and input of soil derived CO₂ is also suggested by low $\delta^{13}\text{C}_{\text{carb}}$, as a low TOC/TS suggest that oxidation of OM was negligible. Despite the higher inflow, the higher $\delta^{18}\text{O}_{\text{carb}}$ values till 11 800 cal yr BP imply a longer residence time and that evaporation of lake water was important. Isotopic depletion at the end of the Younger Dryas, such as described from various lacustrine isotope records from the Mediterranean region (Roberts et al., 2008 and references therein), is also seen in Co1260 as $\delta^{18}\text{O}_{\text{carb}}$ decreases between 20 11 800 and 11 500 cal yr BP.

Cold and dry climate between 12 500 and 11 500 cal yr BP at Lake Dojran can be attributed to the Younger Dryas, when 6 °C lower temperatures and arid conditions with 50 % less annual precipitation are reported from the northern Aegean region (Kotthoff et al., 2008a, 2011) and the Sea of Marmara (Valsecchi et al., 2012), and from other terrestrial records in Italy (Allen et al., 2002), Macedonia (Bordon et al., 2009; Panagiotopoulos et al., 2012) and Greece (Digerfeldt et al., 2000; Lawson et al., 2004). However, the cold and dry climate during the Younger Dryas is barely visible in geochemical and hydrological data from lakes Prespa and Ohrid, probably because 25 lower winter temperatures and moisture deficits have only minor effects on lake internal

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processes (Vogel et al., 2010a; Aufgebauer et al., 2012; Panagiotopoulos et al., 2012) and the long lake water residence time in Ohrid (Leng et al., 2012). Lake Dojran with its low volume to large surface area is likely more sensitive to hydrological change. The transition from a low lake level and low temperatures towards higher lake level and warmer temperatures at Lake Dojran around 12 100 cal yr BP corresponds well with marine records from the western Mediterranean Sea and the North Atlantic, and with terrestrial archives from the Iberian Peninsula and northwest Europe (Cacho et al., 2001 and references therein).

5.2 Early Holocene (11 500 to 7900 cal yr BP)

The deposits of lithofacies 2b, 3a and 3b (590–390 cm) in core Co1260 represent the early Holocene between 11 500 and 7900 cal yr BP.

Lithofacies 2b (590–520 cm) covers the period 11 500 to 10 700 cal yr BP. The sporadic occurrence of sand lenses indicates that the winter temperatures at Lake Dojran remained low. Low winter temperatures during the early Holocene are also reported from Lake Ohrid and are explained by movement south of cold polar air (Vogel et al., 2010a; Wagner et al., 2010). Although the occurrence of the sand lenses leads to distinct variations in grain-size distribution, the overall coarser sediments suggest relatively high transport energy at coring location Co1260. The high transport energy is most likely due to stronger inflow and not triggered by a lake-level low stand, because clay clasts are absent and there is no indication for a very low lake level in the hydro-acoustic profile (Fig. 2). A constant CaCO_3 along with lower allochthonous clastic and organic sediment input, indicated by lower K, Fe, TOC/TN, and higher $\delta^{13}\text{C}_{\text{org}}$, implies somewhat lower productivity in the lake, which corresponds with lower TOC. Thereby, the higher $\delta^{13}\text{C}_{\text{org}}$ are probably rather a result of less allochthonous OM than of more productivity. The discrepancy between relatively high inflow and low erosion can be explained by the development of a dense vegetation cover in the catchment, such as observed around lakes Prespa and Maliq to the west (Bordon et al., 2009; Aufgebauer et al., 2012; Panagiotopoulos et al., 2012) and the Aegean region to the south and

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southeast (Kotthoff et al., 2008a). Extensive reed beds in the littoral areas of Lake Dojran could also have restrained allochthonous clastic and organic sediment supply and limited the productivity in the lake center despite rapidly increasing temperatures in the Mediterranean region (Allen et al., 1999; Bordon et al., 2009; Kotthoff et al., 2011) by nutrient consumption (cf. Yin and Lan, 1995; Wang et al., 2002). Despite more humid conditions, the low TOC/TS implies oxygen depletion in the bottom waters and stratification of the lake during summer. Summer stratification was probably promoted by higher summer temperatures in the early Holocene, such as reported from various records in the central and eastern Mediterranean region (e.g. Allen et al., 1999; Lawson et al., 2004; Kotthoff et al., 2008a; Vogel et al., 2010a; Peyron et al., 2011; Aufgebauer et al., 2012). Increased humidity in the early Holocene conflicts with the high $\delta^{18}\text{O}_{\text{carb}}$ values, which would normally be interpreted as indicating a low *P/E* ratio. Enhanced evaporation however is enabled by higher lake level when this is accompanied by increasing lake water surface area especially in lakes like Dojran, which is located in a flat-bottomed basin (cf. Leng et al., 2005; Hernández et al., 2008). A large surface area also promotes greater exchange of TDIC with atmospheric CO_2 , and therefore tends to lead to both higher $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{13}\text{C}_{\text{carb}}$ as seen in lithofacies 2b.

In lithofacies 3a (520–401 cm), which covers the period 10 700 to 8300 cal yr BP, the grain-size distribution is dominated by medium and coarse silt, but is less variable due to the lack of fine sand lenses. The lack of the sand lenses indicates that the lake was not significantly covered by ice during winter. The decreasing $\delta^{18}\text{O}_{\text{carb}}$ after 10 200 cal yr BP could be associated with a greater through flow due to further increasing humidity. This corresponds with increasing moisture in southern Italy until 9400 cal yr BP (Joannin et al., 2012), but in particular with increasing $\delta^{18}\text{O}_{\text{carb}}$ after 9400 cal yr BP at Lake Prespa, which was explained by increasing summer wetness (Leng et al., 2010). Despite this increasing humidity during the early Holocene, which incidentally coincides partly with the formation of sapropel 1 in the Mediterranean Sea (Kotthoff et al., 2008b), K and Fe imply decreasing catchment erosion until 9000 cal yr BP. Less input from the catchment could be due to denser vegetation in the

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littoral areas and catchment, which while filtering clastic material might cause greater delivery of more allochthonous OM to the lake, as indicated by increasing TOC/TN. Another explanation for increasing allochthonous OM supply could be as a result of lake level increase and flooding of shallow, littoral parts of the lake. This is indicated by reflector 3 in the seismic data, which is the oldest reflector that covers the lacustrine terrace in the northern part of profile 2 (Fig. 2). The flooded shallow lake parts would have formed suitable habitats for Mollusca, which probably explains the high abundance of shells and shell fragments in lithofacies 3a. The increase in lake surface and volume was apparently correlated with a distinct change in redox conditions, such as indicated in the TS peak and the shift of TOC/TS. The larger surface could have led to higher wind fetch and thus a better mixing of the water column after 9500 cal yr BP. More nutrient and allochthonous OM supply from the flooded parts likely promoted productivity in the lake, and can be inferred from a minimum of $\delta^{13}\text{C}_{\text{org}}$ and maxima in CaCO_3 adjusted TOC and CaCO_3 around 9000 cal yr BP. Decreasing CaCO_3 and CaCO_3 adjusted TOC contents after 8700 cal yr BP suggests decreasing lake productivity, which goes along with increasing erosion, such as indicated by increasing K and Fe.

In lithofacies 3b from 401 to 390 cm, which covers the period 8300 to 7900 cal yr BP, the coarser grain-size distribution implies relatively high transport energy. Increased transport energy is probably due to a lower lake level and increased wave action, which is indicated by the pinching out of the hydro-acoustic reflector 4 in the central area of the lake. A low lake level implies dry conditions at Lake Dojran, which is however inconsistent with low $\delta^{18}\text{O}_{\text{carb}}$ unless the lower lake levels and smaller surface area (which reduce evaporation) is the main driver of the isotopic composition of the lake water. Another explanation for low $\delta^{18}\text{O}_{\text{carb}}$ is increasingly lower $\delta^{18}\text{O}$ of rainfall from the Atlantic (cf. Zanchetta et al., 2007a) or eastern Mediterranean origin (cf. Develle et al., 2010). Despite the presumed arid conditions, high K and Fe imply enhanced clastic sediment supply and erosion in the catchment, which is probably associated with a less dense vegetation cover in the catchment. Less dense vegetation could have reduced the availability and supply of allochthonous OM to the lake as suggested by

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low TOC/TN and high $\delta^{13}\text{C}_{\text{org}}$, and could also be triggered by lower temperatures. This is also suggested by subtly lower TS and higher TOC/TS, indicating less pronounced thermal stratification and improved oxygen supply to the surface sediments. Furthermore, low CaCO_3 and CaCO_3 adjusted TOC contents in lithofacies 3b imply low productivity, such as also reported from lakes Prespa and Ohrid (Wagner et al., 2009, 2010; Vogel et al., 2010a; Aufgebauer et al., 2012). The low temperatures are most likely associated with the 8.2 ka cooling event, which covers a broad period in Mediterranean paleoclimate records varying between 8500 and 8000 cal yr BP (e.g. Magny et al., 2003 and references therein; Berger and Guilaine, 2009 and references therein). The 8.2 ka cooling is associated with an interruption of the sapropel 1 formation in the Mediterranean Sea (Kotthoff et al., 2008b; Siani et al., 2012) and a hydrological tripartition of Europe. Whilst wet conditions have predominated between 43° to 50° N, dry conditions persisted north and south of this corridor (Magny et al., 2003), which is in line with low lake level and dry conditions at Lake Dojran. Pollen analyses from Lake Maliq (Bordon et al., 2009) and Tenaghi Philippon (Peyron et al., 2011) suggest that the dryness is predominantly due to restricted winter precipitation.

5.3 Mid Holocene (7900 to 2800 cal yr BP)

The deposits of lithofacies 3c from 390 to 265 cm of core Co1260 represent the mid Holocene between 7900 and 2800 cal yr BP. The finer and relatively stable grain-size distribution implies lower wave action at Co1260 during this period. This implies a high lake level and humid conditions, with only minor fluctuations and more inflow at least until 4300 cal yr BP. A relatively high lake level between 7900 and 4300 cal yr BP is also suggested by reflector 5 in the hydro-acoustic data. The onlap structures to reflector 3 in the lateral parts of the lake imply that the lake level did not exceed that of the early Holocene. The onset of broad maxima in CaCO_3 and mean grain-size at ca. 6000 cal yr BP correlates with a minimum K and Fe and suggests slightly increased productivity, slightly reduced lake level, and lower supply of clastic material.

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This modification in environmental conditions is likely correlated to warmer temperatures and the end of humid conditions in the Mediterranean region during the early and mid Holocene, which caused the formation of S1 and are also observed in other paleoclimate records in the Mediterranean region (e.g. Wick et al., 2003; Kotthoff et al., 2008a, b; Roberts et al., 2008; Wagner et al., 2009; Leng et al., 2010; Vogel et al., 2010a; Aufgebauer et al., 2012; Joannin et al., 2012). However, relatively stable OM, TS, TOC/TS, TOC/TN and $\delta^{13}\text{C}_{\text{org}}$ in core Co1260 suggest that the shift from more humid to more arid conditions had only minor impact on lake productivity, thermal stratification, and allochthonous OM supply. This is supported by stable and low $\delta^{18}\text{O}_{\text{carb}}$, which indicates a period of humidity and/or enhanced ^{18}O depleted rainfall at Lake Dojran persisted through this period. Low and stable $\delta^{18}\text{O}_{\text{carb}}$ during the mid Holocene is a common feature in central Mediterranean isotope lake sediment records, although there are some differences in the exact timing (e.g. Zanchetta et al., 2007b; Roberts et al., 2008; Develle et al., 2010; Leng et al., 2012 and references therein).

Between 4300 and 2800 cal yr BP, more fluctuations and a distinct change in some of the proxies suggest greater instability during a period of gradual environmental change at Lake Dojran. A minimum in mean grain-size around 4000 cal yr BP suggests low inflow and dry conditions for a short period and coincides with low lake productivity, as indicated by CaCO_3 adjusted TOC and CaCO_3 . Low productivity is likely caused by low temperatures, as low TOC/TS imply less intensive thermal stratification. Restricted nutrient availability is less likely, as increasing K and Fe counts imply increasing clastic supply and erosion in the catchment. The short period of low temperatures and arid conditions around 4000 cal yr BP is most likely associated with the 4.2 ka cooling event, which has been described in other records from the Mediterranean region (e.g. Bar-Matthews et al., 1999; Weiss and Bradley, 2001; Magny et al., 2009; Wagner et al., 2009; Vogel et al., 2010a). Subsequent to the 4.2 ka cooling event, increasing K and Fe and a higher mean grain size imply higher erosion in the catchment, stronger inflow, and more humid conditions. More humid conditions between 3500 and 2500 cal yr BP are also suggested by a quantitative pollen reconstruction from southern Italy (Joannin

et al., 2012). Erosion processes could also have been promoted by human induced deforestation, as pollen analyses indicate first permanent settlements at Lake Dojran during this period (Athanasiadis et al., 2000). The anthropogenic deforestation was probably intensified until ca. 2800 cal yr BP as indicated by increasing K and Fe and decreasing $\delta^{13}\text{C}_{\text{carb}}$, the latter a proxy for enhanced soil derived CO_2 or enhanced remineralisation of OM in the lake. The enhanced clastic sedimentation coincides with decreasing CaCO_3 . Comparable human-induced modifications of the environmental setting and the sedimentological properties around the same time are also reported from Lake Prespa (Aufgebauer et al., 2012; Panagiotopoulos et al., 2012) and Lake Ohrid (Wagner et al., 2009; Vogel et al., 2010a, Fig. 8).

5.4 Late Holocene (2800 cal yr BP to present)

The deposits of lithofacies 4 (265–0 cm) in core Co1260 represent the late Holocene between 2800 cal yr BP and today.

In lithofacies 4a (265 to 152 cm), which covers the period 2800 to 1200 cal yr BP, the decreasing mean grain-size indicates declining inflow and a decreasing lake level. A decreasing lake level is also suggested by the hydro-acoustic data, where reflector 6 (2.25 m) occurs in lateral parts of the lake, whereas the overlaying reflector 7 (1.92 m) pinches out in these parts. Relatively arid conditions in the Mediterranean region during the late Holocene are also reported from other records, including Lake Prespa (Schilman et al., 2001; Roberts et al., 2008 and references therein; Joannin et al., 2012; Siani et al., 2012; Leng et al., 2012). A lower lake level at Lake Dojran could have resulted in a relative enlargement of shallow lake areas covered by reed beds. The reed beds likely restricted the productivity in the lake (low TOC, CaCO_3 , and TS), as they retain the supply of allochthonous OM and nutrients (decreasing TOC/TN, high $\delta^{13}\text{C}_{\text{org}}$). The reed beds, however, did not lead to less supply of clastic material (high K, Fe and sedimentation rates), probably because human induced wood clearance and anthropogenic impact in the catchment increased (cf. Athanasiadis et al., 2000), as it is also reported from other records in the Eastern and Northeastern Mediterranean region

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(Willis, 1994; Denèfle et al., 2000; Kotthoff et al., 2008a; Bordon et al., 2009; Valsecchi et al., 2012; Panagiotopoulos et al., 2012). A lower lake level could also have promoted the occurrence of shells and shell re-deposition (Bially and Macisaac, 2000) by greater exposure of the shell beds to wave action, which would explain the high abundance of shells or shell fragments in upper parts of lithofacies 4a. The low lake level is also indicated in a distinct shift of sedimentation rates in a sediment core from the lateral parts of the lake (Athanasiadis et al., 2000). This shift could be caused by a hiatus, when lateral parts of the lake became sub-aerially exposed. Despite the anthropogenic overprint, the period between 2800 to 1200 cal yr BP apparently was characterized by a slight cooling, which resulted in reduced thermal stratification and is suggested by relatively high TOC/TS.

In lithofacies 4b (152 to 116 cm), which covers the period from 1200 to 900 cal yr BP, the coarser mean grain-size implies higher transport energy, which is probably associated with more inflow and humid conditions and a higher lake level. The higher lake level is also indicated by the occurrence of the hydro-acoustic reflector 8 in lateral parts of Lake Dojran. A lower proportion of reed likely covered the lateral parts of the lake leading to a reduced filter effect and enhanced supply of allochthonous OM, as seen in high TOC/TN and lower $\delta^{13}\text{C}_{\text{org}}$. Flooding of reed-covered areas would have enlarged the surface area of the lake, which would again promote the exchange of TDIC with atmospheric CO_2 , such as suggested by the high $\delta^{13}\text{C}_{\text{carb}}$. The enlarged surface area also intensified summer evaporation, as indicated by high $\delta^{18}\text{O}_{\text{carb}}$. The gradual increase of OM and CaCO_3 is likely due to higher lake productivity, and could be additionally caused by declining anthropogenic activities, less erosion, and supply (dilution) of clastic material from the catchment. A similar observation was made at Lake Prespa and explained by a denser vegetation cover between 1500 and 600 cal yr BP (Aufgebauer et al., 2012). Lake productivity was likely promoted by a warmer climate associated with the Medieval Warm Period (cf. Crowley and Lowery, 2000), which resulted in an intensification of the thermal stratification during summer and in high TS, low TOC/TS and the faintly lamination structures in lithofacies 4b.

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In lithofacies 4c (116 to 0 cm), which covers the period from 900 cal yr BP until today, the subtle finer grain-size distribution suggests lower transport energy, inflow and lake level. Significant lake level fluctuations, such as reported from lakes Prespa and Ohrid (Matzinger et al., 2006; Wagner et al., 2009; Vogel et al., 2010a; Aufgebauer et al., 2012), are not recorded in Lake Dojran. We can assume that anthropogenic impact affected the lake hydrology and the catchment dynamics significantly during this period. Nevertheless, reduced precipitation of CaCO_3 along with high OM implies high productivity but low temperatures subsequent to the Medieval Warm Period. Low temperatures are also indicated by high TOC/TS in lithofacies 4c, which implies restricted thermal stratification during summer. The colder temperatures after the Medieval Warm Period are also observed in other records from the Balkan areas and are commonly attributed to the Little Ice Age (Wagner et al., 2009; Vogel et al., 2010a; Aufgebauer et al., 2012). The lake level lowstand of Lake Dojran about 2–3 decades ago, when the maximum water depths was < 4 m, is not obvious in the sediment record. The only hint for the lake level lowstand could come from a sub-surface peak in TS. The lake level lowstand was likely caused by a combination of dry climate and by high water use for irrigation, which likely promoted the eutrophication, as shown by the increasing TOC and CaCO_3 in the upper few centimeters of core Co1260 and confirmed by other surface sediment cores (Griffiths et al., 2002).

6 Conclusions

The investigation of sediment architecture and sediment properties of Lake Dojran provides valuable information on climate variability and human impact in the Balkan region. As Lake Dojran is a relatively shallow lake for its size, paleoclimatic change and human interactions seem to have had a significant impact on lake hydrology, allochthonous supply of OM and clastic material, and lake productivity. The shallow morphology of Lake Dojran causes greater evaporation of the lake water when lake levels are relatively high and supports that reed beds in littoral areas of the lake are apparently crucial

for in-lake processes, as these reed beds consume nutrients from the catchment and reduce lake internal productivity. The following interpretations, based on analysis of the data presented here, for climate variability and human impact from the Lake Dojran sediment sequence can be drawn for the Late Glacial and Holocene:

- Cold and dry conditions with low productivity and a low lake-level persisted between 12 500 to 12 100 cal yr BP and are followed by slightly higher temperatures and more humid conditions with subtle enhanced productivity and a higher lake level until 11 500 cal yr BP. This entire period is attributed to the Younger Dryas. The separation of the Younger Dryas into a cold and dry early period and a warmer and more humid later period has been described already from western Mediterranean region, but not explicitly from the Balkan region.
- The temperatures during the early Holocene (11 500 to 8300 cal BP) increased, but nutrient availability and productivity in the lake were restricted until 10 700 cal yr BP likely due to the impact of filtering of the inflow through littoral reed beds. More humid conditions and higher lake level coincide with the formation of sapropel 1 in the marine realm and improved the nutrient supply to the lake by more runoff and smaller reed beds. Highest productivity occurred around 9000 cal yr BP and implies a thermal maximum in the region. Lake level lowering and lower productivity between 8300 and 7900 cal yr BP implies a return to drier conditions and lower temperatures during the 8.2 ka cooling event.
- Stable conditions between 7900 and 4300 cal yr BP suggest that the more arid conditions after the formation of sapropel 1 had only minor impact on hydrology and productivity of Lake Dojran. More unstable conditions and gradual environmental change occurred between 4300 and 2800 cal yr BP. Dry and cold conditions around 4000 cal yr BP are correlated with the 4.2 ka cooling event, whereas increasing erosion is most likely associated with human induced wood clearance of the catchment of Lake Dojran.

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- Intensive anthropogenic impact occurs during the late Holocene (2800 cal yr BP to today) as seen by intensive erosion and enhanced nutrient supply. Despite this anthropogenic overprinting, the sediment characteristics of Co1260 clearly indicate temperature variations associated with the Medieval Warm Period and the Little Ice Age.

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Table 1. Modern isotope data of spring and lake water as standard deviations from VSMOW (O, H isotopes) and VPDB (TDIC), collected in June 2011 (own data) and in September 1997 (Griffiths et al., 2002).

| location | collection | $\delta^{18}\text{O}_{\text{water}}$ (‰VSMOW) | $\delta\text{D}_{\text{water}}$ (‰VSMOW) | $\delta^{13}\text{C}_{\text{TDIC}}$ (‰VPDB) |
|-------------|----------------|--|---|--|
| spring | June 2011 | −9.51 | −62.8 | −11.6 |
| spring | June 2011 | −8.08 | −50.5 | −13.0 |
| lake center | June 2011 | −0.91 | −13.0 | −5.9 |
| lake margin | June 2011 | −0.86 | −13.3 | −4.7 |
| lake margin | June 2011 | −0.86 | −13.1 | −4.8 |
| spring | September 1997 | −7.9 | −50.4 | −7.9 |
| lake center | September 1997 | +2.0 | +1.1 | +0.2 |
| lake margin | September 1997 | +2.1 | +1.9 | +0.6 |

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Table 2. Radiocarbon and calendar ages from core Co1260. The calibration of radiocarbon ages into calendar ages is based on Calib 6.1.1 (Stuiver and Reimer, 1993) and INTCAL09 (Reimer et al., 2009) and on a 2σ uncertainty.

| AMS Lab ID | core depth (cm) | material | C weight (mg) | ^{14}C age (yr BP) | calendar age (cal yr BP) |
|---------------|-----------------|-------------------|---------------|-----------------------------|--------------------------|
| COL 1312.1.1 | 16.5 | bulk organic C | 0.44 | 140 ± 35 | 140 ± 140 |
| COL 1324.1.1 | 53.3 | terrestrial plant | 0.45 | 360 ± 70 | 410 ± 110 |
| COL 1314.1.1 | 111.3 | terrestrial plant | 0.32 | 840 ± 70 | 790 ± 120 |
| COL 1194.1.1 | 253.0 | terrestrial plant | 1.00 | 2430 ± 30 | 2520 ± 170 |
| COL 1316.1.1 | 287.3 | terrestrial plant | 1.00 | 3080 ± 30 | 3290 ± 80 |
| COL 1317.1.1 | 309.1 | charcoal | 1.00 | 3560 ± 40 | 3850 ± 130 |
| ETH 44956.1.1 | 404.9 | carbonate | 1.01 | 6410 ± 40 | 7350 ± 80 |
| COL 1319.1.1 | 406.4 | terrestrial plant | 0.28 | 8020 ± 150 | 8960 ± 440 |
| COL 1320.1.1 | 460.9 | terrestrial plant | 0.63 | 9520 ± 160 | 10 820 ± 420 |
| ETH 44957.1.1 | 502.9 | carbonate | 1.00 | 9840 ± 40 | 11 250 ± 60 |
| COL 1321.1.1 | 521.9 | terrestrial plant | 0.90 | 9330 ± 160 | 10 660 ± 440 |
| ETH 46615.1.1 | 635.0 | bulk organic C | 1.00 | 10 220 ± 70 | 11 920 ± 310 |
| ETH 44958.1.1 | 682.0 | carbonate | 0.48 | 28 570 ± 170 | 32 830 ± 650 |

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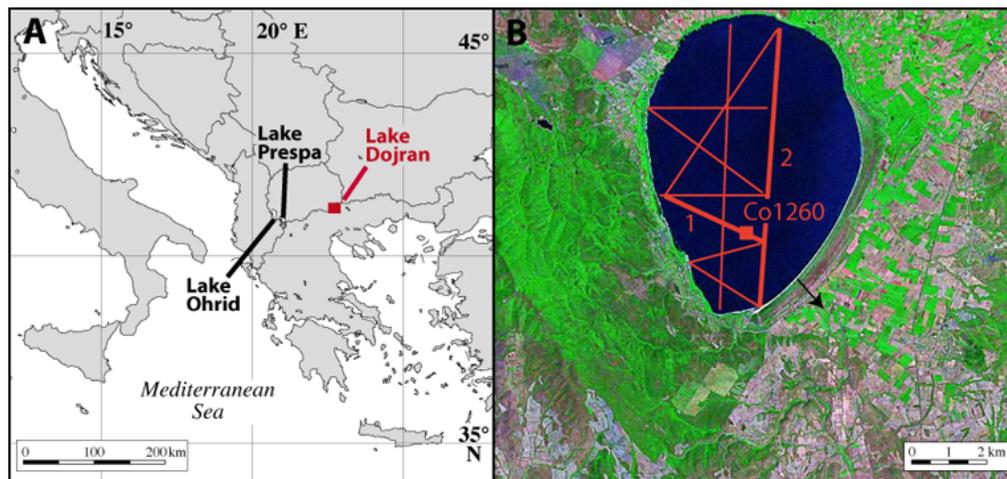


Fig. 1. (A): Locations of lakes Dojran, Ohrid and Prespa in the northeastern Mediterranean region. **(B):** Lake Dojran with the coring location Co1260 and the hydro-acoustic profiles marked. Numbers 1 and 2 mark the hydro-acoustic profiles shown in Fig. 2, the black arrow indicates the position of the former outlet River Doiranitis.

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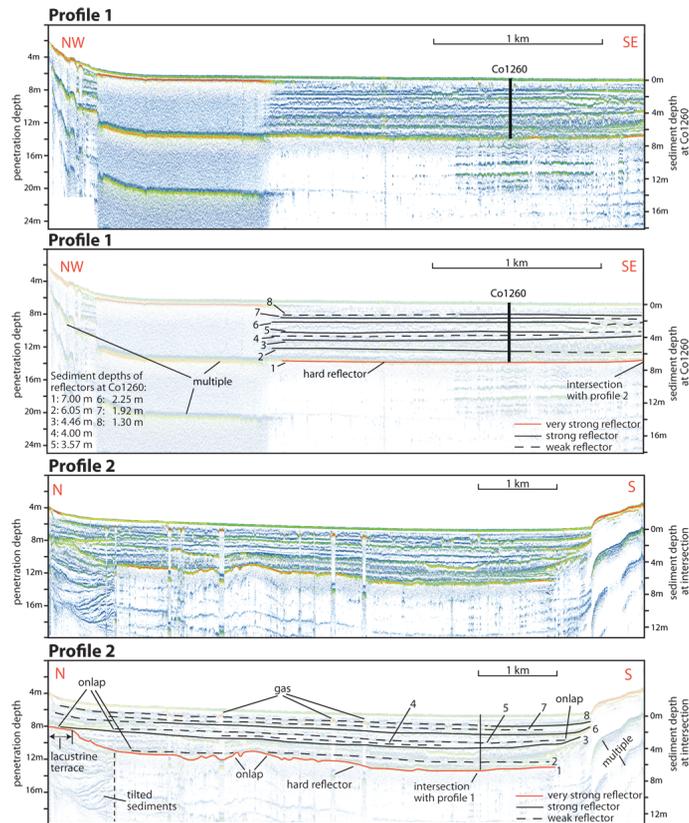


Fig. 2. Un-interpreted and interpreted hydro-acoustic profiles 1 and 2. For location see Fig. 1. The bars to the left indicates depths below lake surface, those to the right depths below sediment surface at the coring location Co1260 (profile 1) or the intersection (profile 2) between the two profiles. The length of the black bar at the coring location Co1260 corresponds to the core length.

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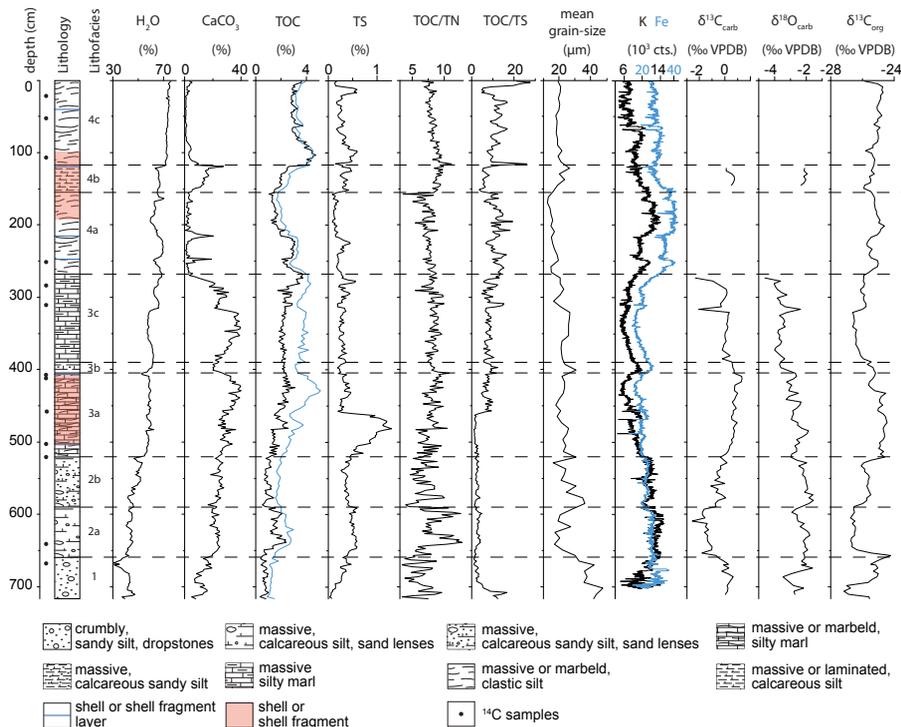


Fig. 3. Positions of ¹⁴C samples, lithology, lithofacies, water content, calcite (CaCO₃), TOC (black line) and CaCO₃ adjusted TOC (blue line), TS, TOC/N, TOC/TS, mean grain-size, Potassium (K) and Iron (Fe) counts, δ¹³C_{carb}, δ¹⁸O_{carb}, and δ¹³C_{org} of core Co1260.

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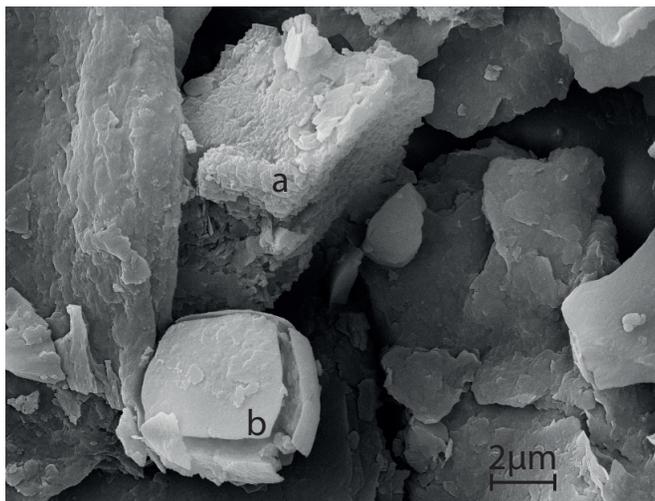


Fig. 4. SEM photos of bulk sediment from 137 cm depth in core Co1260 showing endogenic calcite (**a**, CaCO_3) and pyrite (**b**, FeS_2). The broken structure of the pyrite is probably due to sample pre-treatment and heating to 50°C .

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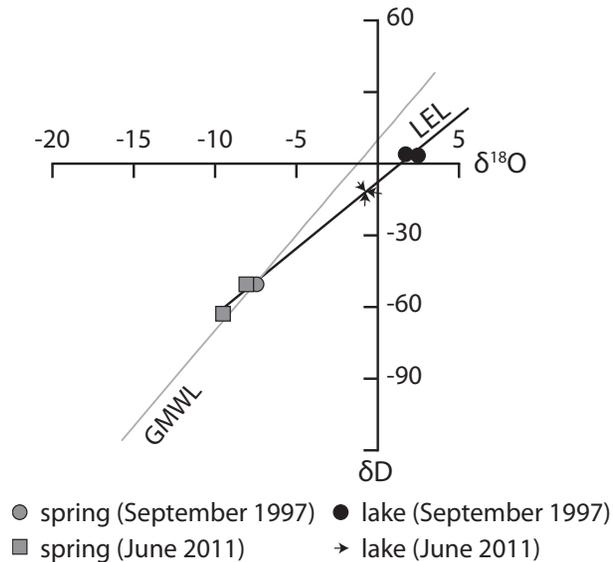


Fig. 5. The modern isotope composition ($\delta^{18}\text{O}_{\text{water}}$ and $\delta\text{D}_{\text{water}}$) from water of Lake Dojran and from marginal springs. The samples were collected in September 1997 (Griffiths et al., 2002) and in June 2011 (see also Table 1). Arrows mark the lake water samples from June 2011 because they plot very close to each other in the x-y plot. The lake water samples fall away from the Global Meteoric Water Line (GMWL) and plot on a Local Evaporation Line (LEL).

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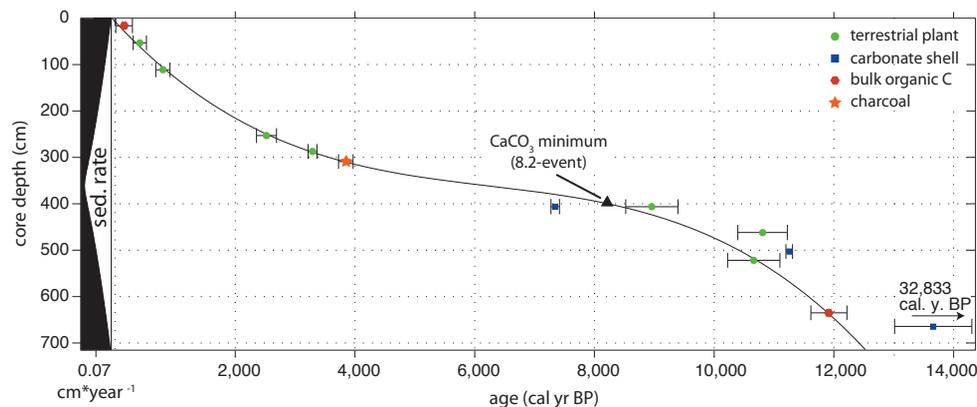


Fig. 6. Age-depth model of core Co1260 based on 13 calibrated radiocarbon ages derived from terrestrial plant material, charcoal, carbonates and bulk organic C samples. Additionally, the 8.2 ka cooling event described from lakes Ohrid and Prespa (Wagner et al., 2009, 2010; Vogel et al., 2010; Aufgebauer et al., 2012) was correlated with the minimum in CaCO₃ at 397 cm depth (see Fig. 3). Sample ETH 44958.1.1 from 663.9 cm depth, which has an age of 32 830 ± 650 cal yr BP, was most likely re-deposited. The sedimentation rate was calculated from the polynomial age-depth model.

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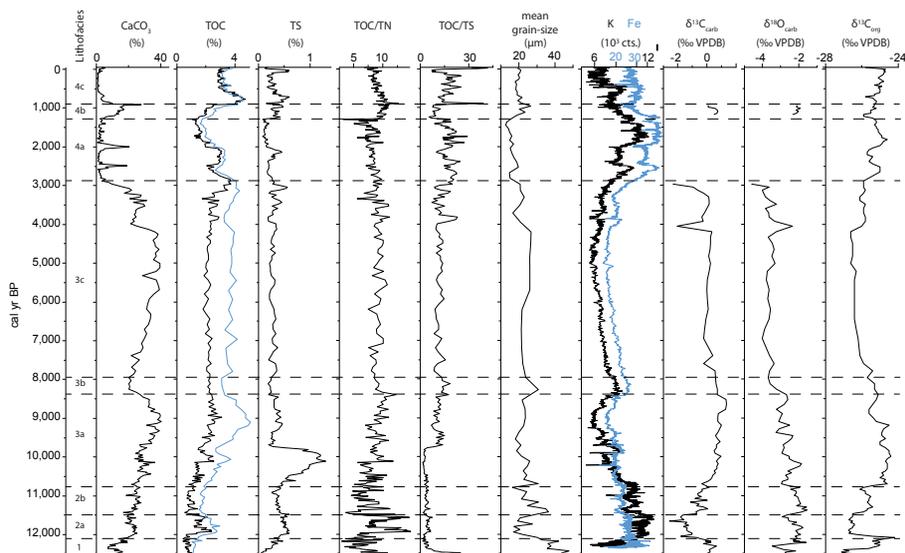


Fig. 7. Lithofacies, calcite (CaCO_3), TOC (black line) and CaCO_3 adjusted TOC (blue line), TS, TOC/N, TOC/TS, mean grain-size, Potassium (K) and Iron (Fe) counts, $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{18}\text{O}_{\text{carb}}$, and $\delta^{13}\text{C}_{\text{org}}$ of core Co1260 plotted versus age.

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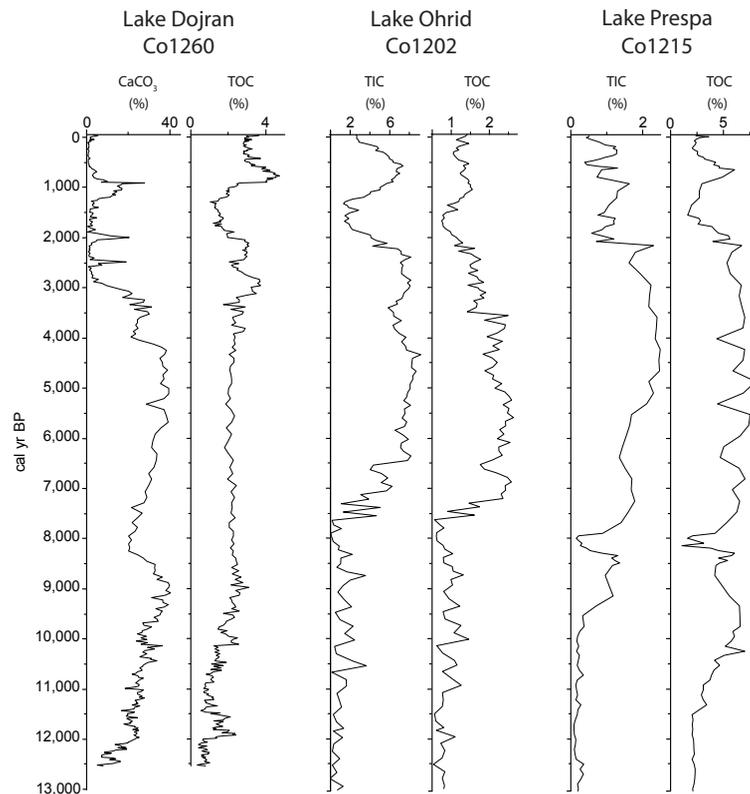


Fig. 8. CaCO₃ and TOC of core Co1260 from Lake Dojran in comparison to CaCO₃ and TOC content from lakes Ohrid (Vogel et al., 2010) and Prespa (Aufgebauer et al., 2012) during the last 13 000 cal yr BP.

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