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1 Tracking the hydro-climatic signal from lake to sediment: a field study from central 2 Turkey 3 Jonathan R. Dean^{a*}, Warren J. Eastwood^b, Neil Roberts^c, Matthew D. Jones^d, Hakan 4 Yiğitbaşıoğlu^e, Samantha L. Allcock^f, Jessie Woodbridge^c, Sarah E. Metcalfe^d, Melanie J. 5 6 Leng^{a,g} 7 8 ^aNERC Isotope Geosciences Facilities, British Geological Survey, Nottingham NG12 5GG 9 UK jonathan.dean@bgs.ac.uk; mjl@nigl.nerc.ac.uk 10 ^bSchool of Geography, Earth and Environmental Sciences, University of Birmingham, B15 11 2TT UK w.j.eastwood@bham.ac.uk 12 ^cSchool of Geography, Earth and Environmental Sciences, University of Plymouth, PL4 8AA 13 *UK c.n.roberts@plymouth.ac.uk; jessie.woodbridge@plymouth.ac.uk* ^dSchool of Geography, University of Nottingham, NG7 2RD UK 14 15 matthew.jones@nottingham.ac.uk; sarah.metcalfe@nottingham.ac.uk 16 ^eDepartment of Geography, Ankara University, Ankara, Turkey <u>yigitbasioglu@gmail.com</u> ^fFaculty of Science and Technology, Bournemouth University, Poole BH12 5BB UK 17 18 sallcock@bournemouth.ac.uk ^g Centre for Environmental Geochemistry, School of Geography, University of Nottingham, 19 20 NG7 2RD UK 21

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Abstract

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Palaeo-hydrological interpretations of lake sediment proxies can benefit from a robust understanding of the modern lake environment. In this study, we use Nar Gölü, a non-outlet, monomictic maar lake in central Turkey, as a field site for a natural experiment using observations and measurements over a 17-year monitoring period (1997-2014). We compare lake water and sediment trap data to isotopic, chemical and biotic proxies preserved in its varved sediments. Nar Gölü underwent a 3 m lake-level fall between 2000 and 2010. δ^{18} O_{lakewater} is correlated with this lake-level fall, responding to the change in water balance. Endogenic carbonate is shown to precipitate in isotopic equilibrium with lake water and there is a strong relationship between δ^{18} O_{lakewater} and δ^{18} O_{carbonate}, which suggests the water balance signal is accurately recorded in the sediment isotope record. Over the same period, sedimentary diatom assemblages also responded, and conductivity inferred from diatoms showed a rise. Shifts in carbonate mineralogy and elemental chemistry in the sediment record through this decade were also recorded. Intra-annual changes in δ^{18} O_{lakewater} and lake water chemistry are used to demonstrate the seasonal variability of the system and the influence this may have on the interpretation of δ^{18} O_{carbonate}. We use these relationships to help interpret the sedimentary record of changing lake hydrology over the last 1,725 years. Nar Gölü has provided an opportunity to test critically the chain of connection from present to past, and its sedimentary record offers an archive of decadal- to centennial-scale hydro-climatic change.

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- Keywords: Oxygen isotopes, Diatom analysis, Lake sediments, Monitoring, Seasonality,
- 45 Carbonates

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- Study of non-outlet, oligosaline, varve-forming lake in a semi-arid region
- Water balance signal in oxygen isotopes tracked from lake waters to sediments
- Strong intra- and inter-annual relationships between isotopes and water balance
- Diatom-inferred conductivity shows a complex response to change in water balance
- Implications of monitoring data for interpretation of palaeo-records

1. Introduction

In order to use lake sediments to reconstruct past climate change reliably, it is vital to understand the modern hydrology of the study site (e.g. Hollander and McKenzie, 1991; Leng et al., 1999; Saros, 2009) and to be able to track this signal to the sediments. Lake systems respond to hydro-climatic variations via a number of linked parameters, including lake volume, salinity concentrations and the oxygen isotope (δ^{18} O) composition of waters. Nonoutlet lakes respond particularly dynamically to changes in water balance (Leng and Marshall, 2004 and references therein); with increased evaporation, water volume decreases, salts become concentrated and δ^{18} O_{lakewater} becomes more positive, and vice-versa, although parameters may be subject to hysteretic effects (Langbein, 1961) as well as other factors such as saline groundwater inflows.

Limnological parameters such as water balance are registered by proxies preserved in lake sediments, which in turn permit the reconstruction of lake hydrology for preinstrumental time periods (Fritz, 2008 and references therein). Past water level fluctuations can be reconstructed via dated lake marginal depositional facies, such as shoreline terraces and carbonate platforms (Magny, 2006), and by changes in the species assemblages and life forms of diatoms and other biological indicators (e.g. Barker et al., 1994). Salinity inferred from biological indicators, such as diatom and ostracod assemblages, is sometimes quantified as variability in electrical conductivity (EC) based on transfer function techniques using a modern training set (e.g. Fritz et al., 2010; Reed et al., 2012). Past salinity levels can also be reconstructed semi-quantitatively from elemental chemistry ratios such as Ca/Sr and Mg/Ca (Ito, 2001). In many lakes, the form of carbonate precipitated from lake waters shifts from low-Mg calcite in dilute lake waters to high-Mg calcite or aragonite in more saline lake waters (Kelts and Hsü, 1978) and the Ca/Sr ratio can decrease if there is a shift from calcite

to aragonite precipitation (Tesoriero and Pankow, 1996). Stable isotopes can also be used as a palaeo-hydrological proxy: lake water δ^{18} O is recorded in carbonates that precipitate in lake water; δ^{18} O_{carbonate} is also modified by temperature and potentially by disequilibrium or diagenetic effects (Leng and Marshall, 2004 and references therein).

Limnological sampling, monitoring and observation can provide fundamental insights into all of the processes described above, and therefore strengthen the interpretation of lake sediment records. Monitoring of lake levels leads to an understanding of the sensitivity of a given lake to hydrological and/or climatic change. Recording biological response to measured climate or hydrological change improves the interpretation of downcore species changes. Monitoring data may be especially important when using stable isotopes as a hydro-climatic proxy because it is not possible to apply modern analogue or transfer function techniques, substituting time with space, to these records due to their dependence on multiple climatic and site-specific non-climatic variables (Tian et al., 2011). Monitoring allows the establishment of the key drivers of $\delta^{18}O_{lakewater}$ in the lake being studied and a better understanding of how the signal is transferred to carbonates in the sediment record. Such a monitoring approach can provide a basis for judging which proxies provide the most reliable register of environmental changes (such as hydro-climate) and why different proxies can show different trends in the palaeo-limnological record, although the possibility that present lake states are not good analogues for the past should also be considered.

There are logistical and financial barriers to collecting modern data and samples over multiple years and different seasons for a length of time suitable to ensure robust proxy interpretation, especially in remote regions. However, in this study, we have been able to collect a substantial number of samples from Nar Gölü (göl = lake in Turkish), a small, hydrologically sensitive maar lake in central Turkey, over a period of 17 years (1997-2014). Although our monitoring and observational data are far from complete, they do allow an

assessment to be made of both seasonal variations and multi-year trends. If lake sediments are sufficiently well resolved in time, it is possible to trace changes measured from lake waters collected from certain years to the sediments that correspond to that year. Nar Gölü is particularly useful for such an exercise because the sediment record is annually laminated (varved). We have therefore been able to correlate, with high precision, monitoring and instrumental climate data to palaeo-limnological information from the sediment cores over the same period.

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The study lake was subject to a progressive water level decrease between 2000 and 2010. We examine how this change in lake water balance was registered by different hydrochemical and biological parameters over time, and how they were subsequently incorporated in the contemporaneous lake sediment record. Some neo-limnological data from Nar Gölü have been previously published: Jones et al. (2005) compared modelled and measured δ^{18} O results (using water isotope data from 1999-2002) and Woodbridge and Roberts (2010) examined diatom assemblage data (with contemporary samples taken 2002-2007). Here we present new water isotope and chemistry data to extend the record up to 2014 and new sediment isotope and diatom assemblage data to bring the record up to 2010. With this longer time series of monitoring data, we build on these previous studies and aim to: (1) establish the general physical, isotopic and geochemical characteristics of the lake, (2) scrutinise intraannual trends in lake water chemistry and $\delta^{18}O_{lakewater}$ to understand the seasonal variability of the system, (3) compare inter-annual variability in lake water chemistry and δ^{18} O_{lakewater} to physical and climate variables in order to test the drivers of the record, and (4) compare these data to isotopic, biological and geochemical proxies from the sediment record. The analysis of modern limnology and the tracking of signals from the lake water to sediments from the last decade allow us to assess critically individual palaeo-limnological proxies at Nar Gölü,

ultimately to better interpret the long-term sediment record of Holocene hydro-climatic change (e.g. Jones et al., 2006; Woodbridge and Roberts, 2011; Yiğitbaşıoğlu et al., in press).

2. Site description

Nar Gölü (38°20'24"N, 34°27'23"E; 1,363 m.a.s.l.) is a small (~0.7 km²) but relatively deep (>20 m) maar lake in Cappadocia, central Turkey (Figure 1). It is oligosaline, alkaline and predominately groundwater-fed, with a residence time of 8-11 years (Jones et al. 2005; Woodbridge and Roberts, 2010). The crater geology is predominately basalt and ignimbrite (Gevrek and Kazancı, 2000). Nar Gölü lacks any surface outflow. At its southern edge there are a series of small inflowing ephemeral stream channels forming an alluvial fan, and the bathymetric map (Figure 1) shows that this extends into the lake as a fan-delta.

The climate of the region is continental Mediterranean (Kutiel and Türkeş, 2005) with annual precipitation at Niğde, 45 km from Nar Gölü and 1,208 m.a.s.l., averaging 339 mm from 1935 to 2010. Mean monthly temperatures 1935-2010 varied from an average of +23°C in July and August to +0.7°C from December to February (see Dean et al., 2013 for more detailed regional climate data).

Although the lake watershed contains no permanent dwellings and only a few agricultural fields, Nar Gölü has not entirely escaped human impact. Firstly, groundwater pumping for irrigation in the valley below the lake is likely to have steepened the hydraulic gradient in recent decades, possibly increasing groundwater outflows from the lake.

Secondly, in 1990 the Turkish Geological Survey (MTA) drilled boreholes near to the lake to reach artesian geothermal groundwaters (Akbaşlı, 1992). Oral testimony indicates that one of these drill holes significantly disturbed lake hydrology and ecology (potentially including a breakdown in lake stratification and a decrease in the population of aquatic macrophytes),

probably for several years, for which there is some evidence in lake sediment cores.

Consequently, and given the lake residence time, we restrict our analysis of changing lake

conditions to the period since 1997.

158 Figure 1

3. Materials and methods

3.1 Fieldwork

Water samples were collected from the lake during 22 field visits between 1997 and 2014. When conditions permitted, depth profiles were taken from the deepest part of the lake through the water column using a Van Dorn bottle (Van Dorn, 1956) or a Glew corer (Glew et al., 2001) with temperature, pH and EC measured at the time on a Myron ® meter.

Maximum lake depths were estimated using a Garmin Fish Finder ® and a weighted tape and checked against water level stage readings at the lake edge when possible. Bathymetry was measured using a Boomer system coupled with a high precision GPS, based on 53 transect lines north-south and east-west (Smith, 2010), in order to identify a suitable coring site.

Samples were taken for isotope and major ion analysis in the UK. Surface water samples were taken in bottles initially washed three times in the sample, at 0.5 m depth to remove any direct effects of exchange with the atmosphere. Where it was not possible to go out on the lake, surface samples were taken from the same spot on the edge of the lake. Edge samples were also taken by members of the local community between February and June 2012, as well as a photo diary that allowed us to establish when snowmelt occurred that year (SI

Figure 1). Spring waters from the catchment (Figure 1) were also regularly sampled.

Simple sediment traps, consisting of cylindrical plastic tubes under funnels, were attached at a variety of depths onto ropes that were secured with an anchor on the lake bed and a float on the surface and replaced every year. Since 2010, Tinytag ® temperature loggers have been attached to the sediment trap lines at a number of depths through the water column. These provide temperature measurements at 20-minute intervals throughout the year.

A 44 cm long sediment core, which covers all but the last few years of the period of lake water monitoring, was taken in 2010 (NAR10) using a weighted stationary piston corer, another having been taken with a Glew corer (36 cm) in 2006 (NAR06). Longer cores spanning 1,720 years were taken in 2001/2 (NAR01/02).

3.2 Laboratory analyses

Water samples were analysed for δ^{18} O and δD on a VG Isoprime mass spectrometer and a EuroPyrOH analyser. Isotopic ratios are given as ‰ deviations from VSMOW, and analytical reproducibility was 0.05‰ for δ^{18} O and 2‰ for δD . Major ion concentrations were measured on water samples as soon as possible after returning from the field on a Metrohm ion chromatography system. Data were converted from milligrams/litre to milliequivalents/litre (meqL⁻¹) (Hem, 1970).

Carbonates from sediment traps and core sediments were analysed for δ^{18} O using an offline extraction technique and a VG Optima mass spectrometer and data are given as ‰ deviations from VPDB, with an analytical reproducibility of 0.1‰. Carbonate mineralogy was investigated by X-ray diffraction. The scanning range used was 5-65° 2 θ and the scan rate was 2° 2 θ per minute with a step size of 0.05. The TRACES program by Diffraction Technology was used to identify which minerals were present. Where two or more minerals were present, the proportions of each were determined by calculating the area under the peaks

and the percentage of aragonite compared to calcite was estimated from experimentally calibrated conversion curves (Hardy and Tucker, 1988).

X-ray fluorescence (XRF) analysis of elemental sediment chemistry was carried out on split half cores by a field portable XRF spectrometer, which produces one single dispersive energy spectra for each 3 mm sampling point on the core surface, with data in parts per million.

Diatom samples were prepared using standard methods adapted from Battarbee et al. (2001), described in detail in Woodbridge and Roberts (2010).

213 3.3 Numerical analyses

To model aragonite precipitation dynamics in Nar Gölü, the palaeo-temperature equation of Kim et al. (2007) is used:

 $218 \qquad T = (17.88*1000)/(1000*LN((1000+\delta^{18}O_{aragonite})/(1000+\delta^{18}O_{lakewater})) + 30.77) - 273.15 \quad (1)$

220 where $\delta^{18}O_{aragonite}$ and $\delta^{18}O_{lakewater}$ are expressed against VSMOW and T in ${}^{\circ}C$.

To model calcite precipitation dynamics, the palaeo-temperature equation of Hays and Grossman (1991) is used:

 $T = 15.7 - 4.36 * (\delta^{18}O_{calcite} - \delta^{18}O_{lakewater}) + 0.12 * (\delta^{18}O_{calcite} - \delta^{18}O_{lakewater})^{2}$ (2)

where $\delta^{18}O_{calcite}$ is expressed against VPDB, $\delta^{18}O_{lakewater}$ against VSMOW and T in °C.

Diatom data have been used to infer EC using a combined salinity training set (comprising data from East Africa, North Africa and Spain) provided by the European Diatom Database (EDDI) (Juggins, 2014). Training sets and models were selected based on the percentage of fossil sample species represented in the modern data set, the number of sites in which these species are present and the model performance (r and RMSEP), and the models were run using C2 software (Juggins, 2003). The combined salinity EDDI modern training set was identified as possessing the highest number of matching analogue diatom species in the Nar Gölü fossil assemblage (74.4%; species not in the training set include *Clipeoparvus anatolicus*, a species endemic to Nar Gölü; Woodbridge et al., 2010). Weighted averaging with inverse deshrinking was identified as the model with highest predictive ability (r=0.85) and lowest prediction errors (RMSEP = 0.47). Detrended Correspondence Analysis (DCA) was also applied to the diatom percentage data because the length of the axis was >2 units (Lepŝ and Ŝmilauer, 2003).

Monthly instrumental meteorological data from a nearby station at Niğde (155 m altitudinal difference, 45 km from Nar Gölü) have been used to create a hydro-climatic index of moisture availability (precipitation/evaporation; P/E). Because of the 8-10 year residence time of the lake water (Jones et al., 2005), we calculated a cumulative weighted 8-year P/E index.

4. Results

4.1 Basic limnological and sedimentological information

EC and major ion data show that the lake is oligosaline, with a mean conductivity value over the past 15 years of 3,270 μ Scm⁻¹ (Tables 1 and 2) and $\delta^{18}O_{lakewater}$ values that are higher than

freshwater $\delta^{18}O_{spring}$ values (Figure 2), indicating that the lake waters are evaporated relative to spring waters. A former lake high-stand is evident from carbonate-encrusted rocks and strandline deposits, surveyed at 5 m above the 2010 water level, or 2 m above the lake elevation in 2000, and provides physical evidence of the tendency of the lake level to fluctuate. The sediments of Nar Gölü comprise alternating organic and carbonate layers (varves; Ojala et al., 2012), with an organic and carbonate couplet shown to represent one year of sedimentation based on analysis of sediment traps, thin sections and independent dating of the sediment cores by ^{210}Pb and ^{137}Cs (Jones et al., 2005; Woodbridge and Roberts, 2010).

264 Figure 2

266 Tables 1 and 2

4.2 Intra-annual variability

Figure 3 shows the intra-annual variability in water chemistry from samples taken between June 2011 and July 2012. Within the data available, $\delta^{18}O_{lakewater}$ values peak at -0.13% in mid-September 2011 before falling to -1.76% in mid-March 2012 and then increasing to -0.39% in mid-July 2012. EC values also peak in mid-September 2011 at 3,540 μ Scm⁻¹, before decreasing to 2,190 μ Scm⁻¹ in late February 2012 (when there was heavy snowfall and partial lake icing) and increasing again to 3,500 μ Scm⁻¹ by July 2012. pH values decreased from 8.1 in June 2011 to 7.3 in February 2012 before increasing to 8.0 by June 2012. Magnesium concentrations decreased from 9.3 meqL⁻¹ in September 2011 to a minimum of 3.2 meqL⁻¹ in late February 2012 and then increased to 16.5 meqL⁻¹ by July

2012, whereas calcium concentrations showed the opposite trend, shifting from 2.2 meqL⁻¹ in June 2011 to 4.0 meqL⁻¹ in late February 2012 to 1.2 meqL⁻¹ in July 2012.

Because the lake is monomictic, depth profiles, as well as surface samples, were taken. In the summer, the waters of Nar Gölü are thermally and isotopically stratified, with warmer and isotopically more positive waters in the epilimnion, followed by a shift at ~7 m to colder and isotopically more negative values in the hypolimnion (Figure 4). The degree of stratification becomes more pronounced from the spring to summer. While no depth profiles were taken during the autumn or winter at Nar Gölü, temperature loggers show that the lake is thermally mixed between November and March, with the same temperatures at 5 m and 21 m during the winter and then diverging in the spring (Figure 3 for 2011-12, but also observed for other years; Eastwood et al., unpublished data).

291 Figure 3

293 Figure 4

4.3 Inter-annual trends

When considering inter-annual trends, samples collected from the same time of year over multiple years are used to remove possible issues caused by the significant intra-annual variability in the system presented in section 4.2. July is the month for which most data are available. Samples from the lake centre are considered most representative of overall lake conditions, because shallow water edge samples may be more affected by evaporation, particularly in summer months. Nonetheless, the difference between centre and edge $\delta^{18}O_{lakewater}$ samples is only $\pm 0.3\%$ (1σ , n=4) in years where both were taken, which is small

considering the size of the inter-annual isotopic shifts seen in the record. Therefore, edge samples from 2000 and 2005 have been combined with centre samples from other years to provide a more complete record. As Figure 5 shows, $\delta^{18}O_{lakewater}$ values increased from – 3.20% in July 2000 to –0.24% in July 2010. Over this period, the lake level fell by approximately 3 m and lake water volume shrank by ~20%. Measured July surface EC values increased from 3,300 μ Scm⁻¹ in 2001 to 3,500 μ Scm⁻¹ in 2012 (Figure 5), while lake surface pH from the same month rose from ~7.5 in 2001 to >8 in 2008, before declining to 7.8 by 2012 (Table 1).

The $\delta^{18}O_{lakewater}$ increase for the period 2000-2010 was matched by an increase in sediment core $\delta^{18}O_{carbonate}$ values from -3.7% to -0.5%. There is a close relationship between sediment trap and core $\delta^{18}O_{carbonate}$ values from the same years, with both showing an increase over the period of study (Figure 5). Sediment trap samples collected from different depths in the same years (2002 and 2004) have $\delta^{18}O_{carbonate}$ values that are the same within analytical reproducibility. There are small differences between sediment trap and core $\delta^{18}O_{carbonate}$ values from 2003, 2004 and 2005 but the trends are the same in both data sets. Between 2006 and 2007 there was a start of a trend towards a reduction in the Ca/Sr ratio and a shift from calcite to aragonite in lake sediment carbonates (Figure 5).

Figure 5

EC inferred from sedimentary diatom assemblages (diatom-inferred electrical conductivity; DI-EC) underestimates modern measured lake EC (Figure 6) (reasons for this will be proposed in sections 5.2 and 5.3, partly related to the fact *C. anatolicus* is not included in the modern training set), but DI-EC trends do broadly match those from measurements taken during the monitoring period. A change in sedimentary diatom

assemblages began earlier than the DI-EC increase, with *C. anatolicus* and *Synedra acus* replacing *Nitzschia paleacea* as the dominant taxa after 2001 (Figure 6).

Figure 6

The closest meteorological station to Nar Gölü with a long-term data set is at Niğde. Annual precipitation in this area was at or below the long-term average (339 mm) from 1997 to 2008, with the exception of 2001. In addition, the 1990s saw a significant (>3°C) rise in average summer temperatures (Turkish State Meteorological Service, pers. comm).

5. Discussion

5.1 Intra-annual variability at Nar Gölü

The seasonal variability in surface water δ^{18} O and conductivity shown in Figure 3 can be explained by two main factors. Firstly, the water in the lake as a whole has lower δ^{18} O in the autumn, winter and spring, as these are the main seasons for rainfall and snowfall, input of which will lower δ^{18} O_{lakewater} (Dean et al., 2013). Although not quantified, observational data show that lake levels were visibly higher in the spring than during the following summers. δ^{18} O_{lakewater} in 2012 was lowest in mid-March and the photo diary (SI Figure 1) shows this was the time in that year of snowmelt from the catchment. Rainfall is also greatest in the spring (Kutiel and Türkeş, 2005). Secondly, stratification of lake waters in the summer leads to more positive δ^{18} O values in surface waters than at depth because the hypolimnion is unaffected by evaporative processes. Comparison of the depth profiles from April, June, July and September (Figure 4) show that the isocline becomes more enhanced as the year

progresses, with a 1.00% difference between surface and bottom water δ^{18} O values in September 2011 compared to a 0.75% difference in July 2010, 0.24% in June 2011 and 0.23% in April 2013.

Given the seasonal variability in δ^{18} O_{lakewater}, we need to establish the timing of carbonate precipitation to allow for proper interpretation of the palaeo-record. Carbonate precipitation in surface waters is demonstrated by the observation that sediment traps at 5 m depth are encrusted in carbonate when changed each year, whereas deeper ones are not. Variability in δ^{18} O_{carbonate} with depth in one of the sediment traps suggests carbonate precipitation under changing temperatures and/or δ^{18} O_{lakewater} (Figure 7), i.e. that carbonate precipitation occurs at different times of the year. However, $\delta^{18}O_{carbonate}$ measured in the sediment record from a whole-year varve will be weighted towards the time of maximum precipitation. Observations suggest this occurs between May and early July. Firstly, in July, calcium values at the surface are lower than at depth, suggesting draw-down of calcium carbonate from the surface waters (Reimer et al., 2009), whereas in April 2013 calcium concentration was still higher in surface waters than at depth, suggesting this draw-down had yet to occur (Table 2). Secondly, analysis of the stratigraphy of Nar Gölü sediment traps collected in July shows carbonate deposited on top of organic matter, while sediment traps collected in April show organic matter on top of carbonate (Figure 8), suggesting that the carbonate for that year had yet to precipitate.

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Figure 7

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376 Figure 8

Additionally, it is possible to run Eqs. 1 and 2 using various $\delta^{18}O_{lakewater}$ and temperature scenarios, and then to compare the calculated equilibrium δ^{18} O_{carbonate} values from these equations to measured δ^{18} O_{carbonate} from the sediment core. By seeing where the calculated values match the measured values, it is possible to investigate better the timing of carbonate precipitation. Before doing this, equilibrium precipitation and a lack of diagenetic effects need to be demonstrated. It is not unknown for carbonate to precipitate out of equilibrium with lake waters (Fronval et al., 1995; Teranes et al., 1999). During the July 2012 field season, carbonate in the form of aragonite was seen precipitating from the waters in a 'white-out' event (as seen in other lakes; Romero-Viana et al., 2008; Sondi and Juracic, 2010; Viehberg et al., 2012) around the edges of the lake (SI Figure 2). Comparison of the δ^{18} O_{carbonate} value from this aragonite precipitate (-1.3%) to the δ^{18} O_{carbonate} value predicted using Eq. 1 (-1.8%, using the δ^{18} O_{lakewater} (-0.39%) and temperature (+25.6°C) values measured from a water sample taken at the same time), show that it formed in equilibrium within analytical and equation error. Diagenesis may alter the carbonate isotope signal between precipitation and deposition (Teranes and Bernasconi, 2000). However, at Nar Gölü, there are only small differences between the δ^{18} O_{carbonate} values of trap and core sediments from the same year (Figure 5) and the inter-annual trends are very similar, which suggests minimal alteration of the δ^{18} O_{carbonate} signal during and after deposition.

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Based on the observations already outlined, we assume that most carbonate is precipitated sometime after April but before the end of July and in surface waters. Therefore, we use likely surface water temperature and $\delta^{18}O_{lakewater}$ values from May to July to calculate potential $\delta^{18}O_{carbonate}$ values. Temperatures vary from year to year, but temperature loggers suggest temperatures change from ~+12.5°C in the beginning of May to ~+17.5°C in midJune to ~+20.0°C in the beginning of July to ~+22.5°C in mid-July (Figure 3). Consequently, temperatures ranging from +12.5°C to +22.5°C and $\delta^{18}O_{lakewater}$ at 0.2% intervals from the

measured July values for individual years are used. Varves from 2001-2006 were composed of calcite, whereas varves from 2007-2010 were >75% aragonite, so Eqs. 2 and 1 were used respectively. In the majority of years, at ~+20°C and a $\delta^{18}O_{lakewater}$ value from July, or 0.2‰ lower, the measured $\delta^{18}O_{carbonate}$ values match the $\delta^{18}O_{carbonate}$ predicted from the equations (Figure 9). These temperature and $\delta^{18}O_{lakewater}$ values are both representative of conditions around the end of June and the beginning of July, suggesting carbonate precipitation peaks at this time and that $\delta^{18}O_{carbonate}$ in the sediment record should reflect $\delta^{18}O_{lakewater}$ at these times.

Figure 9

5.2 Inter-annual trends at Nar Gölü

Nar Gölü experienced a period of falling lake levels between 2000 and 2010. It is possible that this was partly caused by depletion of regional groundwater levels and steepening of the hydraulic gradient north of the lake watershed. The lake may also be recovering from groundwater disturbance due to the drilling of the borehole in 1990. Additionally, climate changes will have had a significant control on water balance through this period. Based on the climate data given in section 4.3, the combination of less precipitation and hotter summers 1997-2008 would have reduced direct precipitation and shallow groundwater inflow and increased water losses through evaporation from the lake surface. The cumulative weighted 8-year P/E index from Niğde reached maximum values in 1997, decreasing to a minimum in 2005-2008 (Figure 5) (matched by the lake level decrease of ~3 m) and then rose again in 2009 and 2010 (at which time the lake level stabilised). Whatever the precise causes of the observed lake-level fall (climate and/or pumping of groundwater), the results show that this is reflected in the monitoring and sedimentary record. There are close parallels with

monitoring studies of lakes Mogan and Eymir on the edge of Ankara (Özen et al., 2010). Although these two lakes have been impacted by nutrient pollution and other human actions, they also showed a very clear hydrological response to the same drought conditions recorded at Nar Gölü, from 2004 to 2007, demonstrating a region-wide hydrological response of lake ecosystems to climatic forcing. Our monitoring shows that decreasing water levels of Nar Gölü between 2000 and 2010 were associated with an increase in $\delta^{18}O_{lakewater}$ of $\sim 3\%$ and in lake surface water EC of $\sim 600~\mu Scm^{-1}$ (although more EC measurements in the early 2000s would have been required to clarify that there was indeed a period of low EC at this time).

Changes in $\delta^{18}O_{lakewater}$ are generally driven by changes in $\delta^{18}O_{precipitation}$ and/or modification by evaporation within-lake (Leng and Marshall, 2004 and references therein). Here, $\delta^{18}O_{spring}$ values are seen to represent local precipitation since they plot on the meteoric water line (Figure 2) and have remained more or less stable over the study period (Table 1), indicating that changes in $\delta^{18}O_{precipitation}$ could not be driving the increase in $\delta^{18}O_{lakewater}$. Rather, the strong relationship between $\delta^{18}O_{lakewater}$ and lake depth (Figure 5) adds weight to the suggestion that $\delta^{18}O_{lakewater}$ trends are driven by changing water balance (e.g. Jones et al., 2005).

To observe how this signal has been transferred to the palaeo-limnological record, isotopic, geochemical and biological proxies have been analysed for individual lake varves from short sediment cores. There is a good match between changes in hydro-climate, lake depth and the $\delta^{18}O_{carbonate}$ record (Figure 5). Equilibrium precipitation and a lack of diagenetic effects have already been demonstrated (section 5.1). Assuming there is always equilibrium precipitation and diagenesis never significantly alters the isotope signal, two factors should control $\delta^{18}O_{carbonate}$: $\delta^{18}O_{lakewater}$ and the temperature-dependent carbonate-water fractionation effect. The very strong, positive relationship between $\delta^{18}O_{lakewater}$ and $\delta^{18}O_{carbonate}$ (r=+0.99, n=8, p<0.005) and the weighting of carbonate precipitation to the summer months indicates

that $\delta^{18}O_{lakewater}$ (as we have shown, itself driven by water balance) is the key driver of $\delta^{18}O_{carbonate}$.

There is evidence of an increase in the summer Mg/Ca ratio (Table 2), caused by concentration of magnesium due to evaporation and loss of calcium by precipitation of calcium carbonate (Kelts and Talbot, 1990). There was also a shift in the sediment core from calcite precipitation 1997-2006 to mostly aragonite precipitation 2007-2010. Shifts from calcite to aragonite precipitation may be associated with an increase in the Mg/Ca ratio of lake water (Müller et al., 1972; Kelts and Hsü, 1978; Ito, 2001), which favours the precipitation of aragonite over calcite (Berner, 1975; De Choudens-Sanchez and Gonzalez, 2009). At Nar Gölü, the recent switch from calcite to aragonite precipitation and the decrease in the Ca/Sr ratio (Figure 5) (Tesoriero and Pankow, 1996) supports the interpretation of these proxies as indicative of a negative hydrological trend. Of note, in comparison to the δ¹⁸O_{carbonate} trends, there is a threshold response from calcite to aragonite.

Comparison of measured EC with DI-EC shows similar overall trends, but there is an offset in absolute values (Figure 6). The intra-annual data provide a partial explanation as to why DI-EC is lower than measured EC in Nar Gölü. Whereas the EC measurements shown on Figure 6 were taken in July, much of the diatom growth is believed to occur earlier in the year, when EC is substantially lower (Figure 3). The availability of measured EC data unfortunately do not allow us to observe the actual nature of the inferred shift in conductivity post 2006, in terms of timing and rate. Some individual diatom species change earlier than the shift in the DI-EC record, albeit at a gradual rate, for example *C. anatolicus*. The observed trends in diatom assemblages may indicate a response to controls other than conductivity and/or salinity, for example changing lake habitat availability (Barker et al., 1994), and care must be taken when using such biological indicators as a proxy of mean annual conductivity (Juggins, 2013). An increase in marginal environments as lake-levels

fall, for example, may explain increases in periphytic taxa such as *A. minutissimum* (Woodbridge and Roberts, 2011) and/or a change in seasonal mixing regime during the period of lake-level decrease.

In summary, there is a correspondence through the 2000s between measured hydrological parameters on the one hand, and lake chemistry and hydro-biology reconstructed from sedimentary proxy data on the other, although parameters show different responses in terms of type (threshold vs. linear) and sensitivity to change. The P/E ratio was highest (most positive water balance) in 1997, with a marked decline after 2003, ending in 2008. The lake-level decline ended in 2010. $\delta^{18}O_{lakewater}$ and EC show a rise through the 2000s with the former stabilising after 2008 in a similar way to the P/E trend (Figure 5). The shift to higher $\delta^{18}O_{carbonate}$ from 2000 also starts to slow after 2008. In contrast, carbonate mineralogy and Ca/Sr data show threshold responses and DI-EC shows a less clear trend than $\delta^{18}O_{carbonate}$, although changes are more linear when looking at the abundance of individual diatom species.

5.3 Implications for the interpretation of palaeo-records

Monitoring work as described here is primarily carried out to improve interpretations of long-term palaeo-hydrological records, such as those previously published from this site (Jones et al., 2006; Woodbridge and Roberts, 2011; Dean et al., 2013). In the case of Nar Gölü, the magnitude of the variability in $\delta^{18}O_{carbonate}$ and DI-EC recorded through the monitoring period covers much of the variability seen in $\delta^{18}O_{carbonate}$ and DI-EC over the last 1,720 years (shown by the shaded boxes on Figure 10).

Figure 10

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Viewing the monitored changes within the longer-term context of the palaeo-record highlights a number of points of interest. There is a relative lack of response in the DI-EC record compared to δ^{18} O_{carbonate} data (Jones et al., 2006) through most of the record. In contrast, changes in diatom assemblages, reflected by the diatom zonation (derived by stratigraphically-constrained cluster analysis; Woodbridge and Roberts, 2011), do correlate well with shifts in δ^{18} O (Figure 10), with Achnanthidium minutissimum increasing at AD1400, showing the same relationship as observed through the monitoring period. This shift in diatom species does not significantly alter the DI-EC reconstruction, potentially because A. minutissimum and other non-planktonic species respond to habitat availability as well as to EC in this system. The strength of the DI-EC reconstruction is also reduced by the lack of environmental knowledge about Clipeoparvus anatolicus, a dominant species in the assemblage, but a newly described species from Nar Gölü (Woodbridge et al., 2010), which is not included in the modern training set. The ordination of diatom taxa via DCA provides a summary representation of species changes at Nar Gölü. The DCA axis 1 score does, however, show a pattern similar to the DI-EC, only showing significant changes around AD500 as Cyclotella meneghiniana and Staurosira construens var venter are replaced by an assemblage dominated by N. paleacea (Woodbridge and Roberts, 2011). DCA axis 2 records change around AD1400 as A. minutissimum and Synedra acus become more dominant in the record (Figure 10). The lake monitoring described here, in conjunction with a multiproxy record of past

The lake monitoring described here, in conjunction with a multiproxy record of past hydro-climatic change, substantially reduces the possibility of interpretive errors of the palaeo-record. Our monitoring data, and the discussion of the DI-EC here and in Woodbridge and Roberts (2011), suggest that care is needed when using the DI-EC reconstruction in terms of absolute values of conductivity change. By superimposing the range of variability in

different proxies during the period of lake monitoring with that shown in the palaeo-record, it is also possible to identify which periods in the past potentially lack a modern analogue. The similarity between the shifts in the monitoring period and at AD1400 now allows partial quantification of this change. Although there is no direct analogue of the changes at AD500, the record points to a lake-level increase, associated with a shift in the diatom assemblage, with a magnitude that was larger than changes in the reverse direction ~AD1400 (Figure 10) and that observed in recent times.

6. Conclusions

Using the example of Nar Gölü, we have highlighted how monitoring data can be used to test assumptions and to help produce more robust interpretations of the sediment record, although our findings could be tested further by a larger dataset based on multiple annual measurements. Due to the varved nature of the sediments, it has been possible to compare δ^{18} O from core sediments to δ^{18} O from trap sediments to δ^{18} O from water samples from specific years. While Nar Gölü is a non-outlet lake in a semi-arid region and therefore δ^{18} O_{lakewater} is likely to reflect water balance, monitoring is still vital to test this and to assess the response rate and magnitude of the different palaeo-hydrological proxies. The strong relationship between δ^{18} O_{carbonate}, δ^{18} O_{lakewater} and changes in lake depth, and the apparent equilibrium precipitation of the carbonate, indicate that δ^{18} O_{carbonate} at Nar Gölü is likely to provide a reliable indicator of regional hydro-climatic change over longer time periods. Based on modern response times, δ^{18} O can offer a hydro-climatic signal of decadal-scale resolution at this lake. Other palaeo-hydrological proxies, including DI-EC and carbonate mineralogy, exhibit more complex or less easily quantified responses to changes in water balance, with a less linear response between climate change and proxy records. However,

these proxies offer complementary data, which provide a cross-check when conducting palaeo-hydrological reconstructions.

In the 'natural laboratory' that is offered by Nar Gölü, conditions make it possible to critically test the chain of connection from present to past, and from the lake waters to the palaeo-record. Our analyses link together the timescales of monitoring and observation on the one hand, with those of palaeo-hydrological reconstruction on the other. The conclusions drawn from this study are site-specific, and in other lakes other proxies may exhibit the clearest relationship to hydro-climate. Nonetheless, our analysis does provide a critical test of causal relationships that are often assumed, rather than demonstrated, to be the case.

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722 Tables

Table 1 δ^{18} O from lake surface waters and the upper spring in the catchment, and EC and pH values from surface lake waters

	δ ¹⁸ O _{lakewater}	δ ¹⁸ O _{lakewater}	δ ¹⁸ Ο	EC	рН
	surface centre	surface edge	upper spring	µScm ⁻¹	
	% VSMOW	% VSMOW	% VSMOW		
Mar. 1997		-3.20			
Aug. 1999		-2.95		2500	7.4
July 2000		-3.22			
July 2001	-2.64		-10.55	3300	7.9
Mar. 2002		-3.14	-10.63		
July 2002	-2.42		-10.70		
July 2003	-2.50		-10.59		
May 2004	-2.73				
July 2005		-1.88			
Sep. 2006	-0.87	-1.67	-10.56	3390	7.8
July 2008	-0.57		-10.60	3380	8.3
May 2009	-1.17	-1.46		3430	8.5
July 2009	-0.56		-10.63	3370	8.2
July 2010	-0.24		-10.65	3430	8.5
June 2011	-0.81		-10.55	3390	8.2
Sep. 2011	-0.19	-0.13	-10.63	3540	8.1
Feb. 2012		-1.25		2190	7.3
June 2012		-0.75			
July 2012	-0.34	-0.39	-10.74	3500	7.8
April 2013	-0.90		-10.57	3720	7.7
April 2014	-1.10		-10.61	3333	

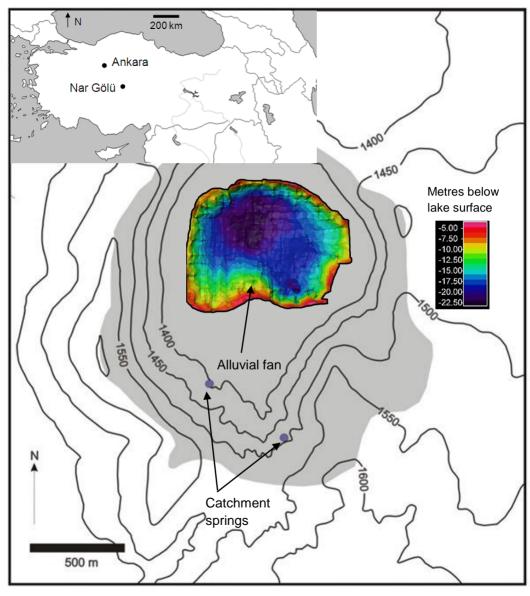
Table 2 Major ion data from surface lake water samples

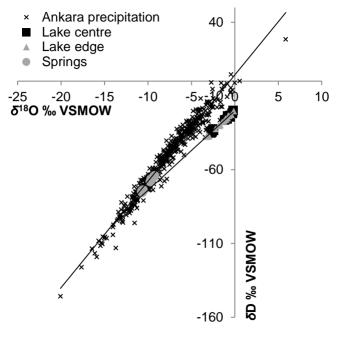
	Conce	entratio	n med	L ⁻¹			
	SO ₄ ⁻²	Cl	Na⁺	K⁺	Mg ²⁺	Ca ⁺²	Mg/Ca
Aug. 1999	3.2	27.4	16.5	3.7	8.5	3.0	2.8
July 2009	3.6	20.1	14.6	3.8	10.1	2.1	4.8
July 2010	3.8	22.7	16.2	3.6	15.4	1.0	15.4
June 2011	2.9	20.2	13.7	4.0	8.8	2.2	4.0
Sep. 2011	4.4	22.4	19.0	3.8	9.4	3.2	2.9
Feb. 2012	3.0	20.2	4.1	0.0	3.2	4.0	0.8
July 2012	4.1	23.9	16.9	3.8	16.5	1.2	13.8
April 2013	3.6	20.2	19.8	3.6	7.1	3.6	2.0

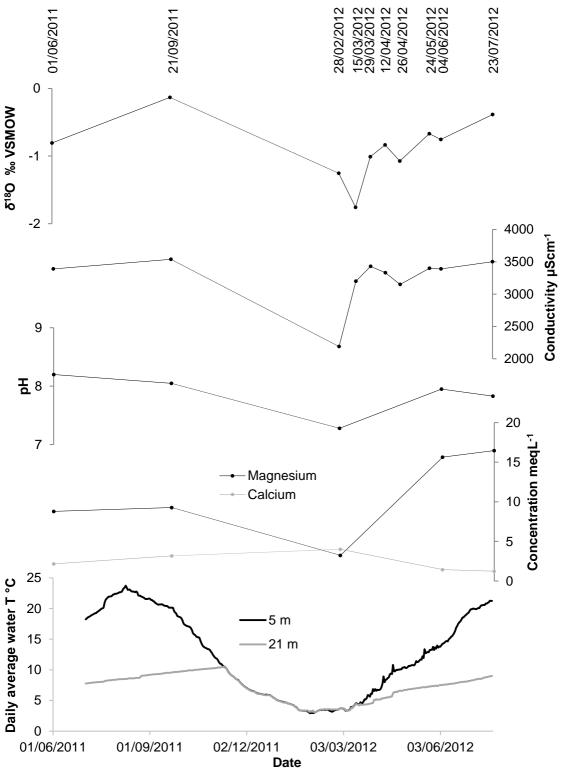
729	Figure captions
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731	Figure 1 Nar Gölü catchment, shaded grey, with bathymetric map showing the alluvial fan in
732	the southern part of the lake and the variability in depth. Figure 2 δ D- δ^{18} O plot, with data
733	from the Ankara GNIP station 1964-2009 (IAEA/WMO 2014) defining the meteoric water
734	line. Spring waters plot on the meteoric water line, whereas lake waters plot on a local
735	evaporation line.
736	Figure 3 Intra-annual variability in δ^{18} O, EC, pH and magnesium and calcium concentrations
737	from water samples taken from the lake edge between June 2011 and July 2012, and data
738	from temperature loggers at 5 m and 21 m depth from the same time period (the convergence
739	of the lines in November signifies the thermal mixing of the lake and the divergence in March
740	the stratification of the lake).
741	Figure 4 Depth profiles of isotope and geochemical variables from different times of the year
742	(although note profiles were not all taken in the same year), showing the changes in thermo-,
743	chemo- and iso-clines from spring to summer.
744	Figure 5 δ^{18} O _{lakewater} (from July surface water samples), measured EC (from July surface
745	water samples), $\delta^{18} O_{carbonate}$ from NAR10 core and sediment traps, XRF-derived Ca/Sr ratio
746	(see section 3.2 for details) and % aragonite vs. calcite from NAR10 core, plotted with
747	changes in maximum lake depth and 8-year cumulative weighted P/E ratio from Niğde (data
748	provided by the Turkish Meteorological Service).
749	Figure 6 Major diatom taxa and DI-EC in NAR06 (Woodbridge and Roberts, 2010) and
750	NAR10 cores (new data), and measured EC (from July surface water samples).
751	Figure 7 Intra-annual variability in δ^{18} O _{carbonate} as recorded in a sediment trap in the lake at 5

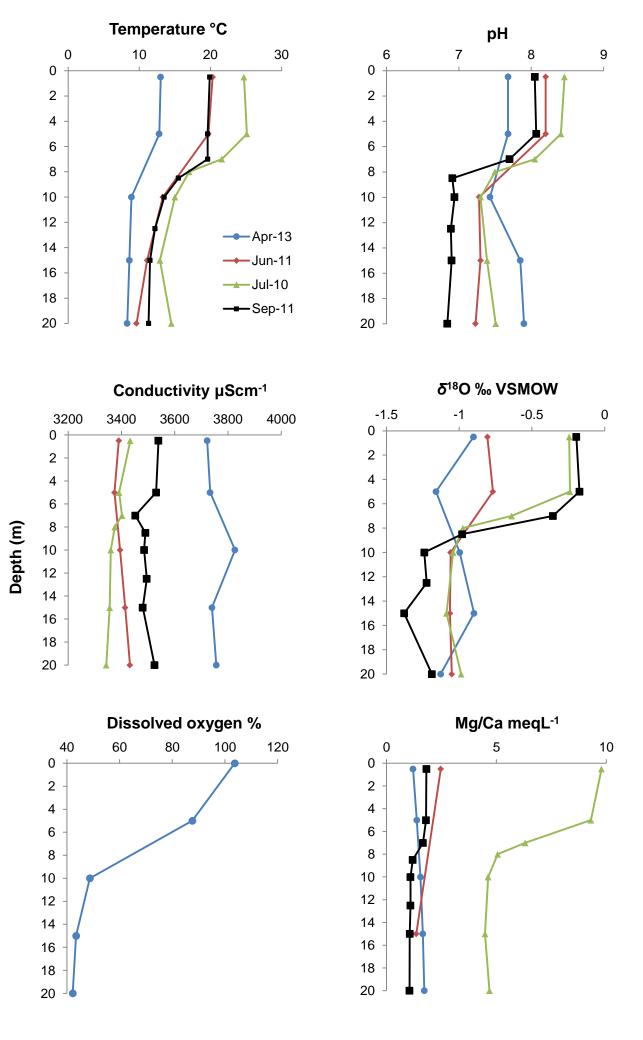
m depth between summer 2001 and summer 2002.

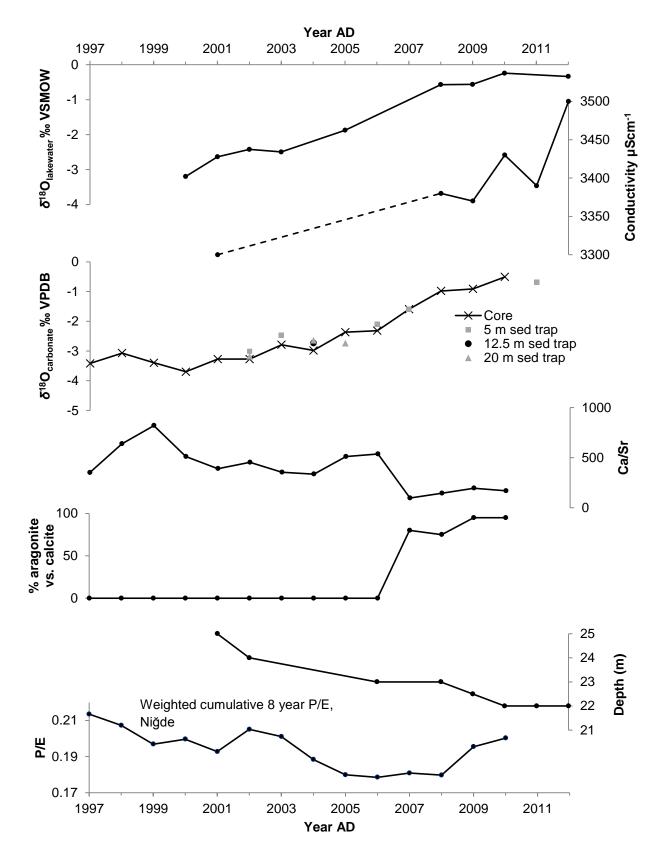
753	Figure 8 Sediment trap deployed in April 2013 and collected in April 2014, showing the
754	seasonality of sedimentation in Nar Gölü.
755	Figure 9 Predicted $\delta^{18}O_{carbonate}$ values from Eqs. 1 and 2 compared to measured $\delta^{18}O_{carbonate}$
756	from NAR10 core, using a variety of lake surface temperature and $\delta^{18} O_{lakewater}$ values that
757	represent conditions in the lake from July back to May.
758	Figure 10 1,720-year records of diatom species (Woodbridge and Roberts, 2011) and
759	$\delta^{18} O_{carbonate}$ (Jones et al., 2006) from the NAR01/02 cores. The variability in DI-EC and
760	$\delta^{18} O_{carbonate}$ seen during the monitoring period from the NAR10 core are shown by the shaded
761	boxes. Diatom zones from Woodbridge and Roberts (2011) are shown.
762	
763	SI Figure 1 Photographs of Nar Gölü between March and April 2012.
764	SI Figure 2 'White-out' around the edges of Nar Gölü in July 2012, and inset SEM image
765	identifying this as aragonite.

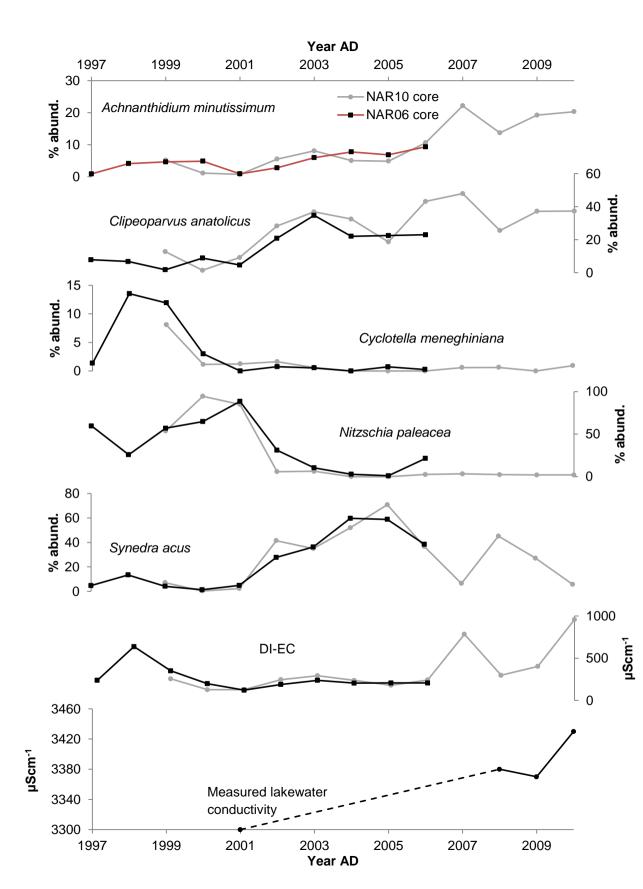


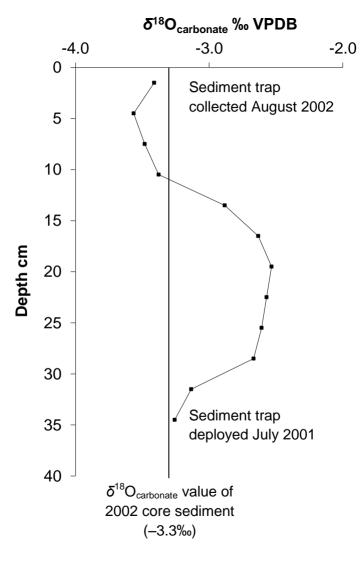












Organic material deposited prior to retrieval in April 2014

Carbonate presumed to have been deposited in summer 2013

Organic material deposited after deployment in April 2013



