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1	<u>Tracking the hydro-climatic signal from lake to sediment: a field study from central</u>
2	<u>Turkey</u>
3	
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25 Palaeo-hydrological interpretations of lake sediment proxies can benefit from a robust 26 understanding of the modern lake environment. In this study, we use Nar Gölü, a non-outlet, 27 monomictic maar lake in central Turkey, as a field site for a natural experiment using 28 observations and measurements over a 17-year monitoring period (1997-2014). We compare 29 lake water and sediment trap data to isotopic, chemical and biotic proxies preserved in its 30 varved sediments. Nar Gölü underwent a 3 m lake-level fall between 2000 and 2010.  $\delta^{18}$ O<sub>lakewater</sub> is correlated with this lake-level fall, responding to the change in water balance. 31 32 Endogenic carbonate is shown to precipitate in isotopic equilibrium with lake water and there is a strong relationship between  $\delta^{18}O_{lakewater}$  and  $\delta^{18}O_{carbonate}$ , which suggests the water balance 33 34 signal is accurately recorded in the sediment isotope record. Over the same period, 35 sedimentary diatom assemblages also responded, and conductivity inferred from diatoms 36 showed a rise. Shifts in carbonate mineralogy and elemental chemistry in the sediment record through this decade were also recorded. Intra-annual changes in  $\delta^{18}$ O<sub>lakewater</sub> and lake water 37 chemistry are used to demonstrate the seasonal variability of the system and the influence this 38 may have on the interpretation of  $\delta^{18}O_{carbonate}$ . We use these relationships to help interpret the 39 40 sedimentary record of changing lake hydrology over the last 1,725 years. Nar Gölü has 41 provided an opportunity to test critically the chain of connection from present to past, and its 42 sedimentary record offers an archive of decadal- to centennial-scale hydro-climatic change. 43 44 Keywords: Oxygen isotopes, Diatom analysis, Lake sediments, Monitoring, Seasonality, 45 Carbonates 46 47

# 48 Highlights

50	•	Study of non-outlet,	oligosaline,	varve-forming	lake in a	semi-arid region
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- 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

57 In order to use lake sediments to reconstruct past climate change reliably, it is vital to 58 understand the modern hydrology of the study site (e.g. Hollander and McKenzie, 1991; Leng 59 et al., 1999; Saros, 2009) and to be able to track this signal to the sediments. Lake systems 60 respond to hydro-climatic variations via a number of linked parameters, including lake volume, salinity concentrations and the oxygen isotope ( $\delta^{18}$ O) composition of waters. Non-61 62 outlet lakes respond particularly dynamically to changes in water balance (Leng and 63 Marshall, 2004 and references therein); with increased evaporation, water volume decreases, salts become concentrated and  $\delta^{18}O_{lakewater}$  becomes more positive, and vice-versa, although 64 65 parameters may be subject to hysteretic effects (Langbein, 1961) as well as other factors such 66 as saline groundwater inflows.

67 Limnological parameters such as water balance are registered by proxies preserved in 68 lake sediments, which in turn permit the reconstruction of lake hydrology for pre-69 instrumental time periods (Fritz, 2008 and references therein). Past water level fluctuations 70 can be reconstructed via dated lake marginal depositional facies, such as shoreline terraces 71 and carbonate platforms (Magny, 2006), and by changes in the species assemblages and life 72 forms of diatoms and other biological indicators (e.g. Barker et al., 1994). Salinity inferred 73 from biological indicators, such as diatom and ostracod assemblages, is sometimes quantified 74 as variability in electrical conductivity (EC) based on transfer function techniques using a 75 modern training set (e.g. Fritz et al., 2010; Reed et al., 2012). Past salinity levels can also be 76 reconstructed semi-quantitatively from elemental chemistry ratios such as Ca/Sr and Mg/Ca 77 (Ito, 2001). In many lakes, the form of carbonate precipitated from lake waters shifts from 78 low-Mg calcite in dilute lake waters to high-Mg calcite or aragonite in more saline lake 79 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  $\delta^{18}$ O is recorded in carbonates that precipitate in lake water;  $\delta^{18}$ O<sub>carbonate</sub> is also modified by temperature and potentially by disequilibrium or diagenetic effects (Leng and Marshall, 2004 and references therein).

84 Limnological sampling, monitoring and observation can provide fundamental insights 85 into all of the processes described above, and therefore strengthen the interpretation of lake 86 sediment records. Monitoring of lake levels leads to an understanding of the sensitivity of a 87 given lake to hydrological and/or climatic change. Recording biological response to measured 88 climate or hydrological change improves the interpretation of downcore species changes. 89 Monitoring data may be especially important when using stable isotopes as a hydro-climatic 90 proxy because it is not possible to apply modern analogue or transfer function techniques, 91 substituting time with space, to these records due to their dependence on multiple climatic 92 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 93 94 understanding of how the signal is transferred to carbonates in the sediment record. Such a 95 monitoring approach can provide a basis for judging which proxies provide the most reliable 96 register of environmental changes (such as hydro-climate) and why different proxies can 97 show different trends in the palaeo-limnological record, although the possibility that present 98 lake states are not good analogues for the past should also be considered.

99 There are logistical and financial barriers to collecting modern data and samples over 100 multiple years and different seasons for a length of time suitable to ensure robust proxy 101 interpretation, especially in remote regions. However, in this study, we have been able to 102 collect a substantial number of samples from Nar Gölü (göl = lake in Turkish), a small, 103 hydrologically sensitive maar lake in central Turkey, over a period of 17 years (1997-2014). 104 Although our monitoring and observational data are far from complete, they do allow an 105 assessment to be made of both seasonal variations and multi-year trends. If lake sediments 106 are sufficiently well resolved in time, it is possible to trace changes measured from lake 107 waters collected from certain years to the sediments that correspond to that year. Nar Gölü is 108 particularly useful for such an exercise because the sediment record is annually laminated 109 (varved). We have therefore been able to correlate, with high precision, monitoring and 110 instrumental climate data to palaeo-limnological information from the sediment cores over 111 the same period.

112 The study lake was subject to a progressive water level decrease between 2000 and 113 2010. We examine how this change in lake water balance was registered by different hydro-114 chemical and biological parameters over time, and how they were subsequently incorporated 115 in the contemporaneous lake sediment record. Some neo-limnological data from Nar Gölü 116 have been previously published: Jones et al. (2005) compared modelled and measured  $\delta^{18}$ O 117 results (using water isotope data from 1999-2002) and Woodbridge and Roberts (2010) 118 examined diatom assemblage data (with contemporary samples taken 2002-2007). Here we 119 present new water isotope and chemistry data to extend the record up to 2014 and new 120 sediment isotope and diatom assemblage data to bring the record up to 2010. With this longer 121 time series of monitoring data, we build on these previous studies and aim to: (1) establish 122 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 123 the system, (3) compare inter-annual variability in lake water chemistry and  $\delta^{18}O_{lakewater}$  to 124 125 physical and climate variables in order to test the drivers of the record, and (4) compare these 126 data to isotopic, biological and geochemical proxies from the sediment record. The analysis 127 of modern limnology and the tracking of signals from the lake water to sediments from the 128 last decade allow us to assess critically individual palaeo-limnological proxies at Nar Gölü,

129 ultimately to better interpret the long-term sediment record of Holocene hydro-climatic

130 change (e.g. Jones et al., 2006; Woodbridge and Roberts, 2011; Yiğitbaşıoğlu et al., in press).

131

### 132 2. Site description

133

Nar Gölü (38°20'24"N, 34°27'23"E; 1,363 m.a.s.l.) is a small (~0.7 km<sup>2</sup>) 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).

146 Although the lake watershed contains no permanent dwellings and only a few 147 agricultural fields, Nar Gölü has not entirely escaped human impact. Firstly, groundwater 148 pumping for irrigation in the valley below the lake is likely to have steepened the hydraulic 149 gradient in recent decades, possibly increasing groundwater outflows from the lake. 150 Secondly, in 1990 the Turkish Geological Survey (MTA) drilled boreholes near to the lake to 151 reach artesian geothermal groundwaters (Akbaşlı, 1992). Oral testimony indicates that one of 152 these drill holes significantly disturbed lake hydrology and ecology (potentially including a 153 breakdown in lake stratification and a decrease in the population of aquatic macrophytes),

154	probably for several years, for which there is some evidence in lake sediment cores.
155	Consequently, and given the lake residence time, we restrict our analysis of changing lake
156	conditions to the period since 1997.
157	
158	Figure 1
159	
160	3. Materials and methods
161	
162	3.1 Fieldwork
163	
164	Water samples were collected from the lake during 22 field visits between 1997 and 2014.
165	When conditions permitted, depth profiles were taken from the deepest part of the lake
166	through the water column using a Van Dorn bottle (Van Dorn, 1956) or a Glew corer (Glew
167	et al., 2001) with temperature, pH and EC measured at the time on a Myron ® meter.
168	Maximum lake depths were estimated using a Garmin Fish Finder ® and a weighted tape and
169	checked against water level stage readings at the lake edge when possible. Bathymetry was
170	measured using a Boomer system coupled with a high precision GPS, based on 53 transect
171	lines north-south and east-west (Smith, 2010), in order to identify a suitable coring site.
172	Samples were taken for isotope and major ion analysis in the UK. Surface water samples
173	were taken in bottles initially washed three times in the sample, at 0.5 m depth to remove any
174	direct effects of exchange with the atmosphere. Where it was not possible to go out on the
175	lake, surface samples were taken from the same spot on the edge of the lake. Edge samples
176	were also taken by members of the local community between February and June 2012, as
177	well as a photo diary that allowed us to establish when snowmelt occurred that year (SI
178	Figure 1). Spring waters from the catchment (Figure 1) were also regularly sampled.

179 Simple sediment traps, consisting of cylindrical plastic tubes under funnels, were 180 attached at a variety of depths onto ropes that were secured with an anchor on the lake bed 181 and a float on the surface and replaced every year. Since 2010, Tinytag ® temperature 182 loggers have been attached to the sediment trap lines at a number of depths through the water 183 column. These provide temperature measurements at 20-minute intervals throughout the year. 184 A 44 cm long sediment core, which covers all but the last few years of the period of 185 lake water monitoring, was taken in 2010 (NAR10) using a weighted stationary piston corer, 186 another having been taken with a Glew corer (36 cm) in 2006 (NAR06). Longer cores 187 spanning 1,720 years were taken in 2001/2 (NAR01/02).

188

#### 189 3.2 Laboratory analyses

190

191 Water samples were analysed for  $\delta^{18}$ O and  $\delta$ D on a VG Isoprime mass spectrometer and a 192 EuroPyrOH analyser. Isotopic ratios are given as ‰ deviations from VSMOW, and analytical 193 reproducibility was 0.05‰ for  $\delta^{18}$ O and 2‰ for  $\delta$ D. Major ion concentrations were measured 194 on water samples as soon as possible after returning from the field on a Metrohm ion 195 chromatography system. Data were converted from milligrams/litre to milliequivalents/litre 196 (meqL<sup>-1</sup>) (Hem, 1970).

197 Carbonates from sediment traps and core sediments were analysed for  $\delta^{18}$ O using an 198 offline extraction technique and a VG Optima mass spectrometer and data are given as ‰ 199 deviations from VPDB, with an analytical reproducibility of 0.1‰. Carbonate mineralogy 200 was investigated by X-ray diffraction. The scanning range used was 5-65° 20 and the scan 201 rate was 2° 20 per minute with a step size of 0.05. The TRACES program by Diffraction 202 Technology was used to identify which minerals were present. Where two or more minerals 203 were present, the proportions of each were determined by calculating the area under the peaks

204	and the percentage of aragonite compared to calcite was estimated from experimentally
205	calibrated conversion curves (Hardy and Tucker, 1988).
206	X-ray fluorescence (XRF) analysis of elemental sediment chemistry was carried out
207	on split half cores by a field portable XRF spectrometer, which produces one single
208	dispersive energy spectra for each 3 mm sampling point on the core surface, with data in
209	parts per million.
210	Diatom samples were prepared using standard methods adapted from Battarbee et al.
211	(2001), described in detail in Woodbridge and Roberts (2010).
212	
213	3.3 Numerical analyses
214	
215	To model aragonite precipitation dynamics in Nar Gölü, the palaeo-temperature equation of
216	Kim et al. (2007) is used:
217	
218	$T = (17.88*1000)/(1000*LN((1000+\delta^{18}O_{aragonite})/(1000+\delta^{18}O_{lakewater}))+30.77) - 273.15 $ (1)
219	
220	where $\delta^{18}O_{aragonite}$ and $\delta^{18}O_{lakewater}$ are expressed against VSMOW and T in °C.
221	
222	To model calcite precipitation dynamics, the palaeo-temperature equation of Hays and
223	Grossman (1991) is used:
224	
225	$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)
226	
227	where $\delta^{18}O_{\text{calcite}}$ is expressed against VPDB, $\delta^{18}O_{\text{lakewater}}$ against VSMOW and T in °C.
228	

229 Diatom data have been used to infer EC using a combined salinity training set 230 (comprising data from East Africa, North Africa and Spain) provided by the European 231 Diatom Database (EDDI) (Juggins, 2014). Training sets and models were selected based on 232 the percentage of fossil sample species represented in the modern data set, the number of sites 233 in which these species are present and the model performance (r and RMSEP), and the 234 models were run using C2 software (Juggins, 2003). The combined salinity EDDI modern 235 training set was identified as possessing the highest number of matching analogue diatom 236 species in the Nar Gölü fossil assemblage (74.4%; species not in the training set include 237 Clipeoparvus anatolicus, a species endemic to Nar Gölü; Woodbridge et al., 2010). Weighted 238 averaging with inverse deshrinking was identified as the model with highest predictive ability 239 (r=0.85) and lowest prediction errors (RMSEP = 0.47). Detrended Correspondence Analysis 240 (DCA) was also applied to the diatom percentage data because the length of the axis was >2241 units (Lepŝ and Ŝmilauer, 2003). 242 Monthly instrumental meteorological data from a nearby station at Niğde (155 m 243 altitudinal difference, 45 km from Nar Gölü) have been used to create a hydro-climatic index 244 of moisture availability (precipitation/evaporation; P/E). Because of the 8-10 year residence 245 time of the lake water (Jones et al., 2005), we calculated a cumulative weighted 8-year P/E 246 index. 247 248 4. Results 249 250 4.1 Basic limnological and sedimentological information 251

EC and major ion data show that the lake is oligosaline, with a mean conductivity value over the past 15 years of 3,270  $\mu$ Scm<sup>-1</sup> (Tables 1 and 2) and  $\delta^{18}$ O<sub>lakewater</sub> values that are higher than

254	freshwater $\delta^{18}O_{spring}$ values (Figure 2), indicating that the lake waters are evaporated relative
255	to spring waters. A former lake high-stand is evident from carbonate-encrusted rocks and
256	strandline deposits, surveyed at 5 m above the 2010 water level, or 2 m above the lake
257	elevation in 2000, and provides physical evidence of the tendency of the lake level to
258	fluctuate. The sediments of Nar Gölü comprise alternating organic and carbonate layers
259	(varves; Ojala et al., 2012), with an organic and carbonate couplet shown to represent one
260	year of sedimentation based on analysis of sediment traps, thin sections and independent
261	dating of the sediment cores by <sup>210</sup> Pb and <sup>137</sup> Cs (Jones et al., 2005; Woodbridge and Roberts,
262	2010).
263	
264	Figure 2
265	
266	Tables 1 and 2
267	
268	4.2 Intra-annual variability
269	
270	Figure 3 shows the intra-annual variability in water chemistry from samples taken
271	between June 2011 and July 2012. Within the data available, $\delta^{18}O_{lakewater}$ values peak at –
272	0.13‰ in mid-September 2011 before falling to $-1.76\%$ in mid-March 2012 and then
273	increasing to -0.39‰ in mid-July 2012. EC values also peak in mid-September 2011 at 3,540
274	$\mu$ Scm <sup>-1</sup> , before decreasing to 2,190 $\mu$ Scm <sup>-1</sup> in late February 2012 (when there was heavy
275	snowfall and partial lake icing) and increasing again to $3,500 \ \mu\text{Scm}^{-1}$ by July 2012. pH values
276	decreased from 8.1 in June 2011 to 7.3 in February 2012 before increasing to 8.0 by June
277	2012. Magnesium concentrations decreased from 9.3 meqL <sup><math>-1</math></sup> in September 2011 to a
278	minimum of 3.2 meqL <sup><math>-1</math></sup> in late February 2012 and then increased to 16.5 meqL <sup><math>-1</math></sup> by July

279 2012, whereas calcium concentrations showed the opposite trend, shifting from 2.2 meqL<sup>-1</sup> in
280 June 2011 to 4.0 meqL<sup>-1</sup> in late February 2012 to 1.2 meqL<sup>-1</sup> in July 2012.

281 Because the lake is monomictic, depth profiles, as well as surface samples, were 282 taken. In the summer, the waters of Nar Gölü are thermally and isotopically stratified, with 283 warmer and isotopically more positive waters in the epilimnion, followed by a shift at ~7 m 284 to colder and isotopically more negative values in the hypolimnion (Figure 4). The degree of 285 stratification becomes more pronounced from the spring to summer. While no depth profiles 286 were taken during the autumn or winter at Nar Gölü, temperature loggers show that the lake 287 is thermally mixed between November and March, with the same temperatures at 5 m and 21 288 m during the winter and then diverging in the spring (Figure 3 for 2011-12, but also observed 289 for other years; Eastwood et al., unpublished data).

- 290
- Figure 3
- 292
- 293 Figure 4
- 294
- 295 4.3 Inter-annual trends
- 296

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  $\pm 0.3\%$  (1 $\sigma$ , n=4) in years where both were taken, which is small

304 considering the size of the inter-annual isotopic shifts seen in the record. Therefore, edge 305 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 – 306 307 3.20% in July 2000 to -0.24% in July 2010. Over this period, the lake level fell by 308 approximately 3 m and lake water volume shrank by ~20%. Measured July surface EC values increased from 3,300 µScm<sup>-1</sup> in 2001 to 3,500 µScm<sup>-1</sup> in 2012 (Figure 5), while lake surface 309 310 pH from the same month rose from  $\sim$ 7.5 in 2001 to >8 in 2008, before declining to 7.8 by 311 2012 (Table 1).

The  $\delta^{18}O_{lakewater}$  increase for the period 2000-2010 was matched by an increase in 312 313 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 314 315 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 316 reproducibility. There are small differences between sediment trap and core  $\delta^{18}O_{carbonate}$ 317 318 values from 2003, 2004 and 2005 but the trends are the same in both data sets. Between 2006 319 and 2007 there was a start of a trend towards a reduction in the Ca/Sr ratio and a shift from 320 calcite to aragonite in lake sediment carbonates (Figure 5).

321

322 Figure 5

323

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

329	assemblages began earlier than the DI-EC increase, with C. anatolicus and Synedra acus
330	replacing Nitzschia paleacea as the dominant taxa after 2001 (Figure 6).
331	
332	Figure 6
333	
334	The closest meteorological station to Nar Gölü with a long-term data set is at Niğde.
335	Annual precipitation in this area was at or below the long-term average (339 mm) from 1997
336	to 2008, with the exception of 2001. In addition, the 1990s saw a significant (>3°C) rise in
337	average summer temperatures (Turkish State Meteorological Service, pers. comm).
338	
339	5. Discussion
340	
341	5.1 Intra-annual variability at Nar Gölü
342	
343	The seasonal variability in surface water $\delta^{18}$ O and conductivity shown in Figure 3 can be
344	explained by two main factors. Firstly, the water in the lake as a whole has lower $\delta^{18}$ O in the
345	autumn, winter and spring, as these are the main seasons for rainfall and snowfall, input of
346	which will lower $\delta^{18}O_{lakewater}$ (Dean et al., 2013). Although not quantified, observational data

show that lake levels were visibly higher in the spring than during the following summers.

 $\delta^{18}$ O<sub>lakewater</sub> 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  $\delta^{18}$ 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  $\delta^{18}$ 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  $\delta^{18}O_{lakewater}$ , we need to establish the timing of 357 358 carbonate precipitation to allow for proper interpretation of the palaeo-record. Carbonate 359 precipitation in surface waters is demonstrated by the observation that sediment traps at 5 m 360 depth are encrusted in carbonate when changed each year, whereas deeper ones are not. Variability in  $\delta^{18}O_{carbonate}$  with depth in one of the sediment traps suggests carbonate 361 precipitation under changing temperatures and/or  $\delta^{18}O_{lakewater}$  (Figure 7), i.e. that carbonate 362 precipitation occurs at different times of the year. However,  $\delta^{18}O_{carbonate}$  measured in the 363 364 sediment record from a whole-year varve will be weighted towards the time of maximum 365 precipitation. Observations suggest this occurs between May and early July. Firstly, in July, 366 calcium values at the surface are lower than at depth, suggesting draw-down of calcium 367 carbonate from the surface waters (Reimer et al., 2009), whereas in April 2013 calcium 368 concentration was still higher in surface waters than at depth, suggesting this draw-down had 369 yet to occur (Table 2). Secondly, analysis of the stratigraphy of Nar Gölü sediment traps 370 collected in July shows carbonate deposited on top of organic matter, while sediment traps 371 collected in April show organic matter on top of carbonate (Figure 8), suggesting that the 372 carbonate for that year had yet to precipitate.

- 373
- 374 Figure 7
- 375
- 376 Figure 8
- 377

Additionally, it is possible to run Eqs. 1 and 2 using various  $\delta^{18}O_{lakewater}$  and 378 379 temperature scenarios, and then to compare the calculated equilibrium  $\delta^{18}O_{carbonate}$  values from these equations to measured  $\delta^{18}O_{carbonate}$  from the sediment core. By seeing where the 380 calculated values match the measured values, it is possible to investigate better the timing of 381 382 carbonate precipitation. Before doing this, equilibrium precipitation and a lack of diagenetic 383 effects need to be demonstrated. It is not unknown for carbonate to precipitate out of 384 equilibrium with lake waters (Fronval et al., 1995; Teranes et al., 1999). During the July 2012 385 field season, carbonate in the form of aragonite was seen precipitating from the waters in a 386 'white-out' event (as seen in other lakes; Romero-Viana et al., 2008; Sondi and Juracic, 2010; 387 Viehberg et al., 2012) around the edges of the lake (SI Figure 2). Comparison of the  $\delta^{18}O_{carbonate}$  value from this aragonite precipitate (-1.3‰) to the  $\delta^{18}O_{carbonate}$  value predicted 388 using Eq. 1 (-1.8%, using the  $\delta^{18}O_{lakewater}$  (-0.39%) and temperature (+25.6°C) values 389 390 measured from a water sample taken at the same time), show that it formed in equilibrium 391 within analytical and equation error. Diagenesis may alter the carbonate isotope signal 392 between precipitation and deposition (Teranes and Bernasconi, 2000). However, at Nar Gölü, there are only small differences between the  $\delta^{18}O_{carbonate}$  values of trap and core sediments 393 394 from the same year (Figure 5) and the inter-annual trends are very similar, which suggests minimal alteration of the  $\delta^{18}$ O<sub>carbonate</sub> signal during and after deposition. 395

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 mid-June 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 403 measured July values for individual years are used. Varves from 2001-2006 were composed 404 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‰ 405 lower, the measured  $\delta^{18}O_{carbonate}$  values match the  $\delta^{18}O_{carbonate}$  predicted from the equations 406 (Figure 9). These temperature and  $\delta^{18}O_{lakewater}$  values are both representative of conditions 407 408 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. 409 410 Figure 9 411 412

- 413 5.2 Inter-annual trends at Nar Gölü
- 414

415 Nar Gölü experienced a period of falling lake levels between 2000 and 2010. It is possible 416 that this was partly caused by depletion of regional groundwater levels and steepening of the 417 hydraulic gradient north of the lake watershed. The lake may also be recovering from 418 groundwater disturbance due to the drilling of the borehole in 1990. Additionally, climate 419 changes will have had a significant control on water balance through this period. Based on 420 the climate data given in section 4.3, the combination of less precipitation and hotter 421 summers 1997-2008 would have reduced direct precipitation and shallow groundwater inflow 422 and increased water losses through evaporation from the lake surface. The cumulative 423 weighted 8-year P/E index from Niğde reached maximum values in 1997, decreasing to a 424 minimum in 2005-2008 (Figure 5) (matched by the lake level decrease of ~3 m) and then rose 425 again in 2009 and 2010 (at which time the lake level stabilised). Whatever the precise causes 426 of the observed lake-level fall (climate and/or pumping of groundwater), the results show that 427 this is reflected in the monitoring and sedimentary record. There are close parallels with

428 monitoring studies of lakes Mogan and Eymir on the edge of Ankara (Özen et al., 2010).

429 Although these two lakes have been impacted by nutrient pollution and other human actions, 430 they also showed a very clear hydrological response to the same drought conditions recorded 431 at Nar Gölü, from 2004 to 2007, demonstrating a region-wide hydrological response of lake 432 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 ~3‰ and in 433 lake surface water EC of ~600  $\mu$ Scm<sup>-1</sup> (although more EC measurements in the early 2000s 434 435 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 436 437 modification by evaporation within-lake (Leng and Marshall, 2004 and references therein).

438 Here,  $\delta^{18}O_{\text{spring}}$  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),

440 indicating that changes in  $\delta^{18}$ O<sub>precipitation</sub> could not be driving the increase in  $\delta^{18}$ O<sub>lakewater</sub>.

439

441 Rather, the strong relationship between  $\delta^{18}O_{lakewater}$  and lake depth (Figure 5) adds weight to 442 the suggestion that  $\delta^{18}O_{lakewater}$  trends are driven by changing water balance (e.g. Jones et al., 443 2005).

444 To observe how this signal has been transferred to the palaeo-limnological record, 445 isotopic, geochemical and biological proxies have been analysed for individual lake varves 446 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 447 448 effects have already been demonstrated (section 5.1). Assuming there is always equilibrium 449 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 450 effect. The very strong, positive relationship between  $\delta^{18}O_{lakewater}$  and  $\delta^{18}O_{carbonate}$  (r=+0.99, 451 452 n=8, p<0.005) and the weighting of carbonate precipitation to the summer months indicates

453 that  $\delta^{18}O_{lakewater}$  (as we have shown, itself driven by water balance) is the key driver of 454  $\delta^{18}O_{carbonate}$ .

455 There is evidence of an increase in the summer Mg/Ca ratio (Table 2), caused by 456 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 457 458 calcite precipitation 1997-2006 to mostly aragonite precipitation 2007-2010. Shifts from 459 calcite to aragonite precipitation may be associated with an increase in the Mg/Ca ratio of 460 lake water (Müller et al., 1972; Kelts and Hsü, 1978; Ito, 2001), which favours the 461 precipitation of aragonite over calcite (Berner, 1975; De Choudens-Sanchez and Gonzalez, 462 2009). At Nar Gölü, the recent switch from calcite to aragonite precipitation and the decrease 463 in the Ca/Sr ratio (Figure 5) (Tesoriero and Pankow, 1996) supports the interpretation of 464 these proxies as indicative of a negative hydrological trend. Of note, in comparison to the  $\delta^{18}$ O<sub>carbonate</sub> trends, there is a threshold response from calcite to aragonite. 465

466 Comparison of measured EC with DI-EC shows similar overall trends, but there is an 467 offset in absolute values (Figure 6). The intra-annual data provide a partial explanation as to 468 why DI-EC is lower than measured EC in Nar Gölü. Whereas the EC measurements shown 469 on Figure 6 were taken in July, much of the diatom growth is believed to occur earlier in the 470 year, when EC is substantially lower (Figure 3). The availability of measured EC data 471 unfortunately do not allow us to observe the actual nature of the inferred shift in conductivity 472 post 2006, in terms of timing and rate. Some individual diatom species change earlier than 473 the shift in the DI-EC record, albeit at a gradual rate, for example C. anatolicus. The 474 observed trends in diatom assemblages may indicate a response to controls other than 475 conductivity and/or salinity, for example changing lake habitat availability (Barker et al., 476 1994), and care must be taken when using such biological indicators as a proxy of mean 477 annual conductivity (Juggins, 2013). An increase in marginal environments as lake-levels

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

481 In summary, there is a correspondence through the 2000s between measured 482 hydrological parameters on the one hand, and lake chemistry and hydro-biology 483 reconstructed from sedimentary proxy data on the other, although parameters show different 484 responses in terms of type (threshold vs. linear) and sensitivity to change. The P/E ratio was 485 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 486 487 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 488 489 mineralogy and Ca/Sr data show threshold responses and DI-EC shows a less clear trend than  $\delta^{18}$ O<sub>carbonate</sub>, although changes are more linear when looking at the abundance of individual 490 491 diatom species.

492

493 5.3 Implications for the interpretation of palaeo-records

494

495 Monitoring work as described here is primarily carried out to improve interpretations of long-496 term palaeo-hydrological records, such as those previously published from this site (Jones et 497 al., 2006; Woodbridge and Roberts, 2011; Dean et al., 2013). In the case of Nar Gölü, the 498 magnitude of the variability in  $\delta^{18}O_{carbonate}$  and DI-EC recorded through the monitoring period 499 covers much of the variability seen in  $\delta^{18}O_{carbonate}$  and DI-EC over the last 1,720 years (shown 500 by the shaded boxes on Figure 10).

501

502 Figure 10

504 Viewing the monitored changes within the longer-term context of the palaeo-record 505 highlights a number of points of interest. There is a relative lack of response in the DI-EC record compared to  $\delta^{18}O_{carbonate}$  data (Jones et al., 2006) through most of the record. In 506 507 contrast, changes in diatom assemblages, reflected by the diatom zonation (derived by 508 stratigraphically-constrained cluster analysis; Woodbridge and Roberts, 2011), do correlate 509 well with shifts in  $\delta^{18}$ O (Figure 10), with Achnanthidium minutissimum increasing at 510 AD1400, showing the same relationship as observed through the monitoring period. This 511 shift in diatom species does not significantly alter the DI-EC reconstruction, potentially 512 because A. minutissimum and other non-planktonic species respond to habitat availability as 513 well as to EC in this system. The strength of the DI-EC reconstruction is also reduced by the 514 lack of environmental knowledge about Clipeoparvus anatolicus, a dominant species in the 515 assemblage, but a newly described species from Nar Gölü (Woodbridge et al., 2010), which 516 is not included in the modern training set. The ordination of diatom taxa via DCA provides a 517 summary representation of species changes at Nar Gölü. The DCA axis 1 score does, 518 however, show a pattern similar to the DI-EC, only showing significant changes around 519 AD500 as Cyclotella meneghiniana and Staurosira construens var venter are replaced by an 520 assemblage dominated by N. paleacea (Woodbridge and Roberts, 2011). DCA axis 2 records 521 change around AD1400 as A. minutissimum and Synedra acus become more dominant in the 522 record (Figure 10). 523 The lake monitoring described here, in conjunction with a multiproxy record of past 524 hydro-climatic change, substantially reduces the possibility of interpretive errors of the 525 palaeo-record. Our monitoring data, and the discussion of the DI-EC here and in Woodbridge

526 and Roberts (2011), suggest that care is needed when using the DI-EC reconstruction in terms

527 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.

535

536 6. Conclusions

537

538 Using the example of Nar Gölü, we have highlighted how monitoring data can be used to test 539 assumptions and to help produce more robust interpretations of the sediment record, although 540 our findings could be tested further by a larger dataset based on multiple annual 541 measurements. Due to the varved nature of the sediments, it has been possible to compare  $\delta^{18}$ O from core sediments to  $\delta^{18}$ O from trap sediments to  $\delta^{18}$ O from water samples from 542 543 specific years. While Nar Gölü is a non-outlet lake in a semi-arid region and therefore  $\delta^{18}O_{lakewater}$  is likely to reflect water balance, monitoring is still vital to test this and to assess 544 545 the response rate and magnitude of the different palaeo-hydrological proxies. The strong 546 relationship between  $\delta^{18}O_{carbonate}$ ,  $\delta^{18}O_{lakewater}$  and changes in lake depth, and the apparent equilibrium precipitation of the carbonate, indicate that  $\delta^{18}O_{carbonate}$  at Nar Gölü is likely to 547 548 provide a reliable indicator of regional hydro-climatic change over longer time periods. Based on modern response times,  $\delta^{18}$ O can offer a hydro-climatic signal of decadal-scale 549 550 resolution at this lake. Other palaeo-hydrological proxies, including DI-EC and carbonate 551 mineralogy, exhibit more complex or less easily quantified responses to changes in water 552 balance, with a less linear response between climate change and proxy records. However,

553 these proxies offer complementary data, which provide a cross-check when conducting 554 palaeo-hydrological reconstructions.

555 In the 'natural laboratory' that is offered by Nar Gölü, conditions make it possible to 556 critically test the chain of connection from present to past, and from the lake waters to the 557 palaeo-record. Our analyses link together the timescales of monitoring and observation on the 558 one hand, with those of palaeo-hydrological reconstruction on the other. The conclusions 559 drawn from this study are site-specific, and in other lakes other proxies may exhibit the 560 clearest relationship to hydro-climate. Nonetheless, our analysis does provide a critical test of 561 causal relationships that are often assumed, rather than demonstrated, to be the case.

562

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564

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# 722 Tables

723

# **Table 1** $\delta^{18}$ O from lake surface waters and the upper spring in the catchment, and EC and pH

values from surface lake waters

	δ <sup>18</sup> O <sub>lakewater</sub>	δ <sup>18</sup> O <sub>lakewater</sub>	δ <sup>18</sup> Ο	EC	рН
	surface centre	surface edge	upper spring	µScm <sup>-1</sup>	
	‰ VSMOW	<b>% VSMOW</b>	‰ 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	

	Concentration meqL <sup>-1</sup>						
	SO4 <sup>-2</sup>	CI	Na⁺	K⁺	Mg <sup>2+</sup>	Ca <sup>+2</sup>	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

**Table 2** Major ion data from surface lake water samples

**Figure 1** Nar Gölü catchment, shaded grey, with bathymetric map showing the alluvial fan in the southern part of the lake and the variability in depth. **Figure 2**  $\delta D - \delta^{18}O$  plot, with data from the Ankara GNIP station 1964-2009 (IAEA/WMO 2014) defining the meteoric water line. Spring waters plot on the meteoric water line, whereas lake waters plot on a local evaporation line. **Figure 3** Intra-annual variability in  $\delta^{18}O$ , EC, pH and magnesium and calcium concentrations

from water samples taken from the lake edge between June 2011 and July 2012, and data
from temperature loggers at 5 m and 21 m depth from the same time period (the convergence
of the lines in November signifies the thermal mixing of the lake and the divergence in March
the stratification of the lake).

**Figure 4** Depth profiles of isotope and geochemical variables from different times of the year

(although note profiles were not all taken in the same year), showing the changes in thermo-,

chemo- and iso-clines from spring to summer.

**Figure 5**  $\delta^{18}$ O<sub>lakewater</sub> (from July surface water samples), measured EC (from July surface

745 water samples),  $\delta^{18}$ O<sub>carbonate</sub> 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

changes in maximum lake depth and 8-year cumulative weighted P/E ratio from Niğde (data

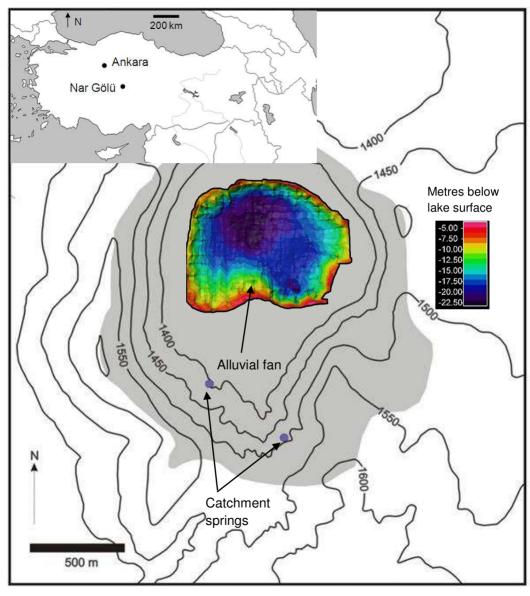
748 provided by the Turkish Meteorological Service).

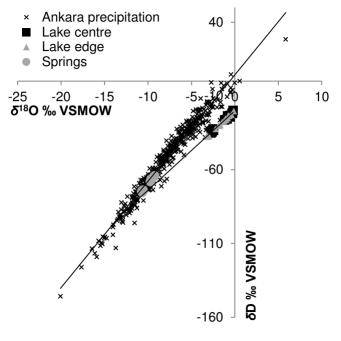
749 Figure 6 Major diatom taxa and DI-EC in NAR06 (Woodbridge and Roberts, 2010) and

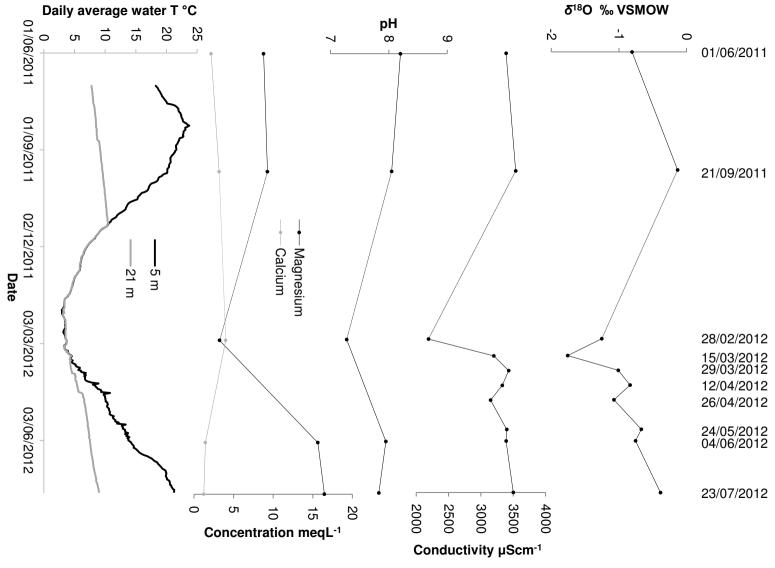
NAR10 cores (new data), and measured EC (from July surface water samples).

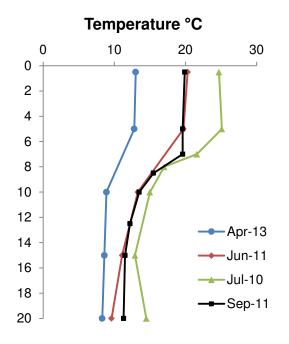
**Figure 7** Intra-annual variability in  $\delta^{18}O_{carbonate}$  as recorded in a sediment trap in the lake at 5 m depth between summer 2001 and summer 2002.

- Figure 8 Sediment trap deployed in April 2013 and collected in April 2014, showing the
  seasonality of sedimentation in Nar Gölü.
- **Figure 9** Predicted  $\delta^{18}O_{carbonate}$  values from Eqs. 1 and 2 compared to measured  $\delta^{18}O_{carbonate}$
- from NAR10 core, using a variety of lake surface temperature and  $\delta^{18}O_{lakewater}$  values that
- represent conditions in the lake from July back to May.
- **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
- boxes. Diatom zones from Woodbridge and Roberts (2011) are shown.
- 762
- 763 **SI Figure 1** Photographs of Nar Gölü between March and April 2012.
- **SI Figure 2** 'White-out' around the edges of Nar Gölü in July 2012, and inset SEM image
- identifying this as aragonite.

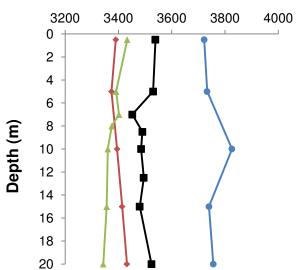




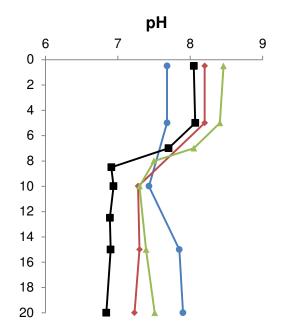


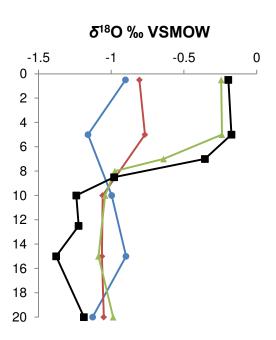


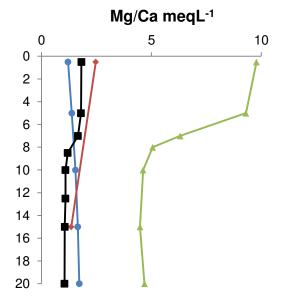


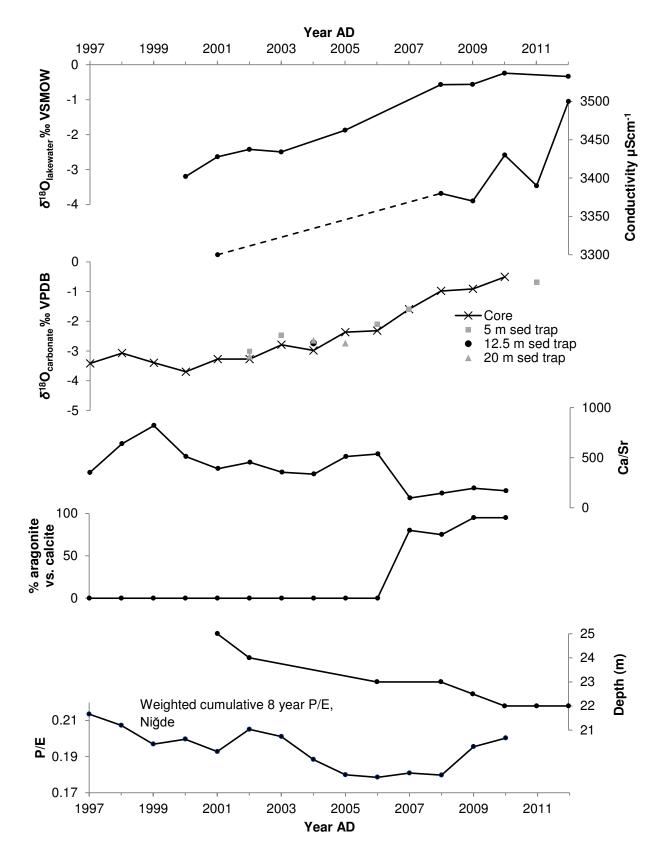


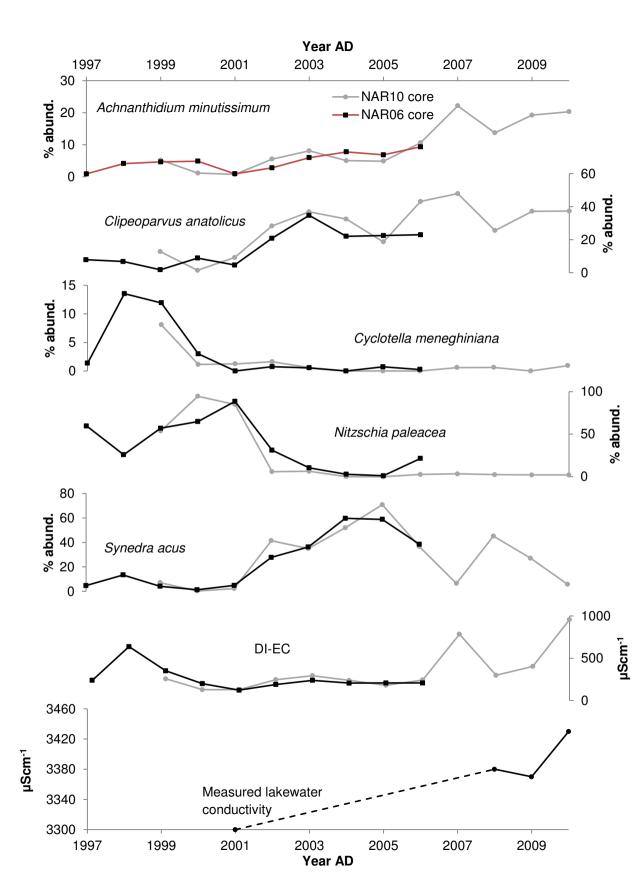
Dissolved oxygen %

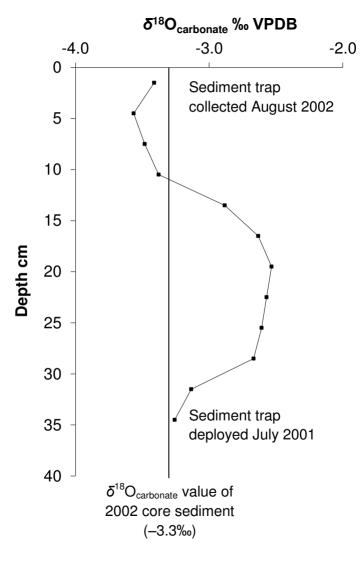












Organic material deposited prior to retrieval in April 2014

Carbonate presumed to have been deposited in summer 2013

Organic material deposited after deployment in April 2013



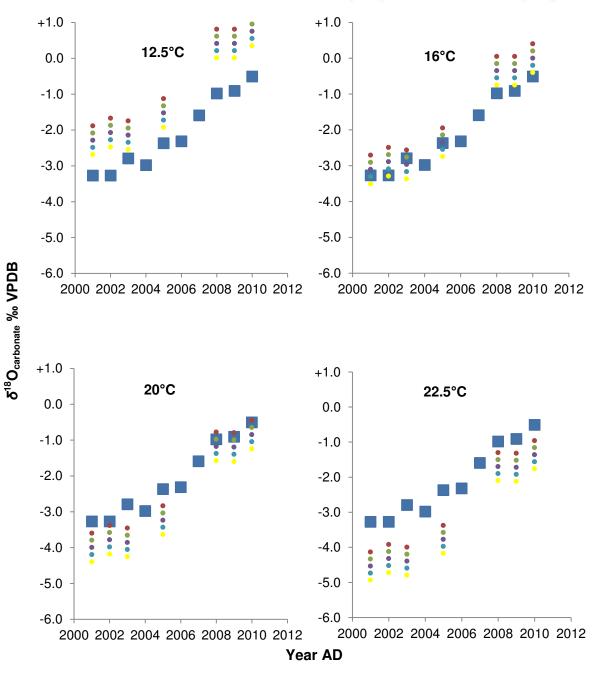
Measured

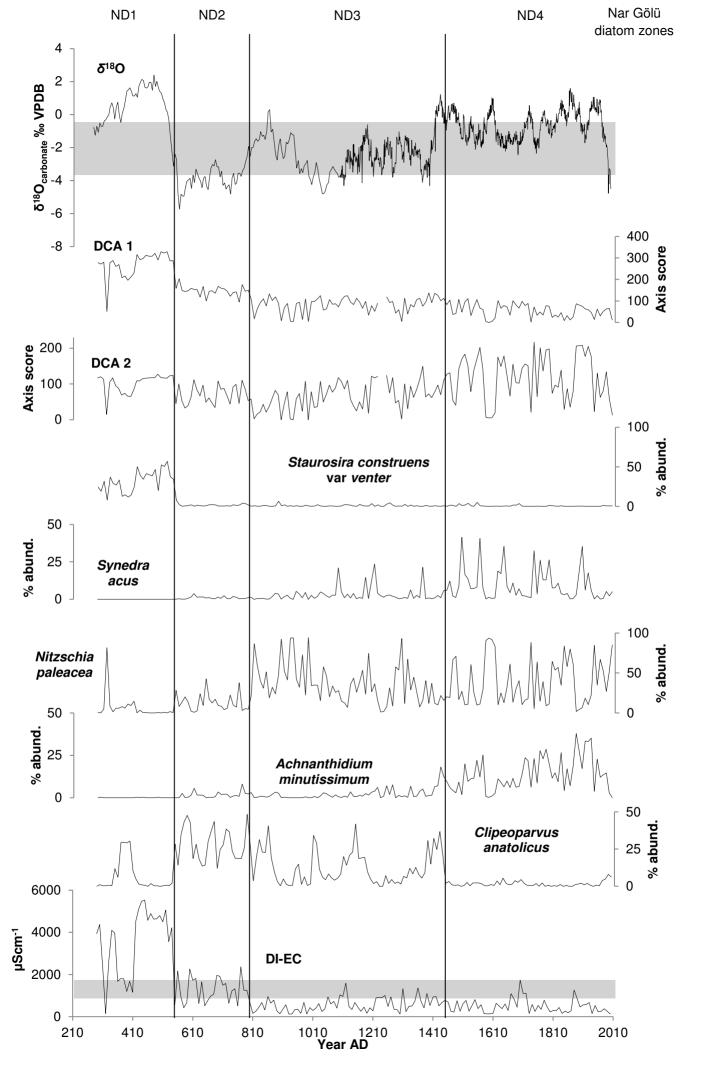
Predicted with July δ<sup>18</sup>O<sub>lw</sub> –0.2‰

Predicted with July δ<sup>18</sup>O<sub>Iw</sub> –0.6‰

Predicted with July δ<sup>18</sup>O<sub>iw</sub>

- Predicted with July δ<sup>18</sup>O<sub>lw</sub> –0.4‰
- Predicted with July δ<sup>18</sup>O<sub>1w</sub> –0.8‰





## 5 March 2012



## 19 March 2012



## 11 April 2012

