**Modern sedimentary analogues and integrated monitoring to understand varve
formation in the Mediterranean Lake Montcortès (Central Pyrenees, Spain).**

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35 **Abstract**

36 Varved sediments provide unique opportunities to carry out high-resolution
37 paleoclimatic and paleoenvironmental reconstructions with accurate time control. To
38 better interpret the sediment record it is necessary to understand the physical,
39 chemical and biological factors that influence varve formation and preservation. We
40 explored the link between the annual limnological cycle and current varve deposition in
41 the oligotrophic hard-water Lake Montcortès (Central Pyrenees). The varves of this
42 lake consist of couplets of dark organic and light calcareous laminae. A two-year
43 limnological monitoring (10/2013-10/2015) combined with a sediment trap study were
44 conducted at monthly resolution. Limnological and sedimentological measurements
45 were compared with meteorological data. Although the lake was considered meromictic
46 in the first limnological studies, we documented total mixing of the water column both
47 winters. In spite of this, long periods of stratification and hypolimnetic anoxia create
48 suitable conditions for varve formation and preservation. Sediment deposition followed
49 a clear seasonal pattern related to biological processes in the euphotic zone. During
50 summer and fall, calcite precipitation was favored by high calcite saturation indices and
51 enhanced primary production that promoted relatively high pH values as a result of
52 CO₂ uptake. There was considerable variability in the amount of calcite deposition
53 between years, which was linked to seasonal temperature differences. In addition,
54 calcite crystal sizes and diatom fluxes showed seasonal patterns related to calcite
55 saturation index and changes in water stratification, which in turn were also related to
56 temperature variability. Seasonal sedimentation patterns were strongly linked to
57 primary producers and especially sensitive to temperature shifts. It results in a clear
58 seasonal signal and varve formation. We compared our results with previous
59 sedimentological interpretations of the varved record of this lake. This study improves
60 the interpretation of Lake Montcortès sediment record extending back several
61 millennia.

Key words: Biogenic varves, Seasonal resolution, Calcite precipitation, Sediment traps, Modern analogs, Mediterranean region.

1. Introduction

Lake sediments are one of the most valuable environmental archives used for paleoenvironmental reconstructions. The sediments store past environmental changes by recording the influences of a variety of processes in the lake water body as well as in the catchment area. Among the different types, varved sediments are especially suitable for this purpose because they allow the performance of high resolution (annual, sub-decadal) paleoenvironmental and paleoclimatic reconstructions with accurate time control (Saarnisto 1986; Ojala et al., 2013). Formation and preservation of varves require specific conditions. Annually laminated sediment formation is favored in places with strong seasonal contrast and requires a variable flux of components from multiple autochthonous and allochthonous sources to the sediment (Zolitschka et al., 2015). These sediments are preserved only in the absence of post-depositional reworking and sediment mixing. This condition is more common to happen in deeper lakes because they tend to be stratified and favor oxygen consumption in bottom waters. Then, prolonged (meromictic) or seasonal (monomictic/dimictic) suboxic to anoxic conditions in the hypolimnion are needed to prevent bioturbation, the most important mechanism of sediment mixing in lakes (Zolitschka et al., 2015).

Based on their composition and genesis, three main varve types (and their mixtures) can be distinguished: clastic, endogenic, and biogenic (Zolitschka et al., 2015). Deposition of clastic and endogenic varves depends mainly on seasonal runoff from the catchment and chemical precipitation of minerals from the water column (Zolitschka et al., 2015). However the mechanisms involved in biogenic varve formation

are much more complex because they include bio-geochemical processes. Processes responsible of varve formation are highly variable and site-specific. Therefore, a good understanding of the local processes that promote particle flux dynamics and seasonal changes in sediment fluxes in each individual site and for a particular record is crucial to better interpret the sediment signal (Leeman and Niessen 1994; Brauer, 2004).

The understanding of depositional conditions must be recognized as a prerequisite for a reliable varve chronology and appropriate interpretation of multi-proxy records to fully exploit the potential of varved sediments. For this reason, modern analogue studies are highly valuable and needed. Sediment trap studies in combination with limnological and meteorological monitoring are the best way to obtain feasible modern analogs. This approach not only allows identification of the distinct pathways involved in varve formation but also determination of the period of varve deposition to assess the seasonal signal (Rodrigo et al., 1993; Miracle et al., 2000; Tylmann et al., 2012; Bonk et al., 2015).

While most published varved records are from northern and central Europe (Ojala et al., 2012), varved sequences have also been found in southern Europe and in the Mediterranean region, e.g. in the Iberian Peninsula (IP). This region is particularly attractive due to its sensitivity and vulnerability to climate change. In fact, during the last decades, temperatures have risen faster than the global average in the Mediterranean regions (Lionello et al., 2014). Also, model projections agree that future warming and drying in this area will be higher than during last century (Mariotti et al., 2015).

To date, six lakes with varved sediments have been studied in the IP, including a pliocene paleolake (Muñoz et al., 2002), and 5 extant karstic lakes: La Cruz (Romero-Viana et al., 2008), Zofar (Martín-Puertas et al., 2009), Banyoles (Morellón et al., 2015), Arreo (Corella et al., 2011a) and Montcortès. This latter lake is the subject of our study and shows the longest continuous varved record retrieved thus encompassing

three millennia of well established varve chronology (Corella et al., 2011b; 2016). Montcortès varves appear as couplets of light calcite and brownish organic layers that are believed to have deposited in spring/summer and fall/winter, respectively, as it occurs in biogenic varves typical of lakes located in carbonate bedrock (Corella et al., 2012). Due to the absence of modern analogue studies, these authors suggested potential mechanisms to explain varve formation based on the available literature for other similar hard-water lakes (Brauer, 2004).

Actually, among the five prevailing varved lakes in the IP mentioned above, only Lake La Cruz has been studied and monitored to obtain modern analogues to suitably interpret the sediment record (Miracle et al., 2000; Romero et al., 2006, Romero-Viana et al., 2010). In spite of the growing research interest that varved sediments have recently attracted (Ojala et al., 2012) and although some modern analogue studies are already available -mainly from north-central Europe (Tylman et al., 2012; Ojala et al., 2013; Bonk et al., 2015)- more monitoring data is needed to properly interpret the sediment signal, especially for Mediterranean lakes.

With this study, we aim to better understand the link between varve formation and the annual limnological cycle at Lake Montcortès and provide modern analogues to better explore the potential for high resolution paleoecological and paleoclimatic reconstruction of its sedimentary record. We carried out i) *in situ* measurements of physicochemical parameters in the water column and ii) measurements of sedimented material using sediment traps at monthly resolution. Special attention was paid to processes related to calcite precipitation and to understand how sediment composition varies seasonally and inter-annually related to environmental variables. It is expected that these results help to test previous hypotheses regarding varve formation in Lake Montcortès (Corella et al., 2011b; 2012).

2. Study site

Lake Montcortès is a relatively small and deep karstic lake located in the Pre-Pyrenean Range (NE Spain) in the Pallars Sobirà region (42° 19' N; 0° 59' E) at 1,029 m a.s.l. (Fig. 1). The lake's catchment area is small (watershed surface area ~1.39 km²). It lies on Oligocene conglomerates and Triassic rocks mainly comprising carbonates, evaporites, claystones and shales. The lake is mainly fed by groundwater and runoff (Corella et al., 2011b). It has no permanent inlet and only two ephemeral streams located on the southern area of the watershed drain the lake. Water losses are due to evaporation and drainage from an outlet located on the northern shore that controls maximum lake levels (Corella et al., 2014). The lake is roughly circular, with a surface area of 0.14 km² and a maximum water depth of 30 m. Although Lake Montcortès has been considered meromictic (Camps et al., 1976), there is evidence of a holomictic event that occurred during the winter of 1978–79 (Modamio et al., 1988). Available data indicate that the lake water is alkaline and oligotrophic (Camps et al., 1976; Modamio et al., 1988; URS 2010). According to the nearest meteorological station, la Pobla de Segur (Fig. 1A), total annual mean precipitation is 668.5 mm, with February being the driest month and May being the wettest. Annual average air temperature is 12.8°C, with maximum and minimum mean temperatures of 23.3 (July) and 2.9°C (January), respectively. The lake is situated in a transitional climatic area between the Mediterranean lowlands and the Middle Montane Belt within the sub-Mediterranean bioclimatic domain (Vigo and Ninot 1987). Therefore, the lake is very sensitive to climate changes. The surrounding vegetation is basically forest formations of evergreen and deciduous oak trees (*Quercus rotundifolia* and *Q. pubescens*) and conifer forests of *Pinus nigra* subsp. *salzmannii* (Mercadé et al., 2013). The lake's nearest surroundings are dominated by herbaceous vegetation types represented by pastures (for cattle and horses), hay meadows and crops of cereal and alfalfa (Rull et

al., 2011; Mercadé et al., 2013). The lake's shoreline presents a steep talus and a littoral vegetation belt dominated by hygrophite communities of *Phragmites australis* accompanied by *Juncus sp.*, *Scirpus sp.*, *Typha sp.* and *Sparganium sp.* (Mercadé et al., 2013).

Lake Montcortès is located at the *Baix Pallars* municipality which has a total population of 350 habitants, with only 26 belonging to the town of Montcortès itself (Idescat 2015) Land use is limited to cereal crops and livestock pastures (Fig. 1B). The lake has historically been an important water resource for numerous surrounding villages and farmhouses with a long history of human occupation (Scussolini et al., 2011; Rull et al., 2011).

Fig. 1. Study site: A. Geographical location within the Iberian Peninsula and regional map showing Lake Montcortès (square and arrow) and the meteorological station (black point) (source: Courtesy of U.S. Geological Survey). B. Aerial photograph of Lake Montcortès (white arrow) and surrounding area. C. Bathymetric map of Lake

Montcortès and location of sampling point (black point). D. Field arrangement of sedimentary traps.

3. Methods

3.1. Limnological monitoring

Physical and chemical variables were monitored in the water column, and samples were collected monthly from October 2013 to October 2015. Profiles at 1 m depth intervals were obtained from the surface to the bottom of the water column for temperature (T), dissolved oxygen (DO), electric conductivity (EC) and pH using a multi-parameter water quality probe (Hydrolab DS5). Water transparency was determined using a Secchi disc. Light penetration was measured using a Photosynthetic Active Radiation (PAR) sensor. Water samples for chemical analyses and phytoplankton identification and counting were collected at three different depths coinciding with the epilimnion (~0.5 m), metalimnion (thermocline; from ~ 5 to 17m) and hypolimnion (~20 m). Phytoplankton samples were stored in amber glass bottles and fixed with concentrated Lugol's iodine solution. Identification and counting was carried out under inverted microscope at 400x magnification following the Uthermöhl method (Uthermöhl, 1931). Cellular biovolume determinations were carried out according to Wetzel and Likens (1991).

Total alkalinity was analyzed using standard titration methods for freshwater samples. Total nitrogen (TN) and total phosphorus (TP) were analyzed using alkaline persulfate oxidation, whilst soluble reactive phosphorous (SRP) was analyzed by the molybdate ascorbic method following Grasshoff et al. (1983). Cation concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{2+}) and potassium (K^{+}) were determined at the Scientific and Technological Center of the University of Barcelona (CCiTUB) using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) with a Perkin Elmer Optima 8300 spectrometer under standard conditions. The calcite saturation index (Ω) was calculated according to equation 1:

$$\Omega = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{\text{cal}} \quad (1)$$

where $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the molar concentrations of calcium and carbonate ions, and K_{cal} is the solubility product of calcite. Here, we use $\log_{10}(\Omega)$ to express the calcite saturation index (SI).

Values of $[\text{CO}_3^{2-}]$ were computed from alkalinity and pH with the CO2SYS_XLS v 2.1 program (Pierrot et al., 2006).

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218 3.2. Sampling and analyses of sediment trap material

219 Particulate matter settling through the water column was collected using
 220 sediment traps. Two cylindrical opaque PVC traps, 8.5 cm in diameter and with a 9:1
 221 aspect ratio (Bloesh and Burns 1980) were used. They were fastened to a floating
 222 platform (Fig. 1D) and placed at 20 m water depth at 5 m above the sediment surface.
 223 One trap was emptied quarterly at the end of each season for seasonal diatom and
 224 calcite crystal analysis. Trapped material for diatom analysis was preserved in
 225 formaldehyde (4%). The second trap was emptied every month for trapped material
 226 characterization and quantification. The collected material was transferred into a plastic
 227 container and stored at 4 °C prior to subsampling. To determine sediment weight and
 228 composition, sample aliquots were filtered through pre-ashed (500 °C) and pre-
 229 weighed GF/F filters until filter saturation and then oven-dried for 48 h at 60 °C. Filters
 230 for total suspended solids (TSS; g L^{-1}) analysis were weighed, and total mass fluxes
 231 (TMF) were calculated from equation (2):

$$\text{TMF (g m}^{-2} \text{ d}^{-1}) = \text{dry net weight (g) / active area (m}^2\text{) time (d)} \quad (2)$$

233 To analyze carbon and nitrogen content of TSS, filters were weighed and
 234 analyzed for total particulate carbon (TPC), total particulate organic carbon (POC) and
 235 total nitrogen (TN). Samples for POC analysis were acidified to remove inorganic

carbon. TPC, POC and TN were analyzed at the CCiTUB using an elemental organic analyzer, Thermo EA 1108, working under standard conditions. Total inorganic particulate carbon (PIC) was calculated as the difference between TPC and POC. Calcite contents was calculated from PIC concentrations by multiplying by 8.33, a factor referring to the molar weight of CaCO_3 . To estimate organic matter (OM) from POC content in the trapped material, we applied a widely used conversion factor for soils and sediments by multiplying POC by 1.7 (Nelson and Somers 1996; Bluszc et al., 2008). We also used the theoretical relationship defined by pure organic matter in its simplest form (CH_2O) and multiplied POC by a factor of 2.5 (Leipe et al., 2010). With this approach, we obtained a range of estimated OM that covers possible variations depending upon the type of OM present in the sample.

To confirm the presence of calcite crystals and to assess seasonal variations of their size and shape trapped material from quarterly traps was analyzed by SEM. For this purpose, samples were oxidized with H_2O_2 at 200 °C, washed and then filtered using a Whatman polycarbonate filter of 0.4 μm pore size. Calcite crystals were then identified by means of spectrograms obtained in the microanalysis and characterized for size and morphology under the scanning electron microscope (SEM) with an Energy Dispersive X-ray Spectroscope and the help of the *Inca250* software. A minimum of 170 and a maximum of 358 calcite crystals were counted per sample, and the maximum (l_{max}) and minimum lengths (l_{min}) were measured.

For diatom analysis, an aliquot of trapped material from the quarterly traps was cleaned and prepared using standard methods (Abrantes et al., 2005). At least 300 valves per sample were counted, and microspheres were added to calculate valve influx (Battarbee et al., 2001). Samples were mounted in Naphrax® and analyzed using a Polyvar light microscope at 1000x magnification. Diatom species were identified using Krammer and Lange-Bertalot (1986-2004).

Meteorological data were obtained from the meteorological station of La Pobla de Segur (Catalonian Meteorological Service) located 19 km of Lake Montcortès (Fig. 1A). We used these data to assess inter-annual climatic variability covering the monitoring period by calculating the deviation or anomaly of monthly precipitation and temperature values from the mean long-term reference period 1961–1990. The selected variables were mean monthly air temperature (TM), mean monthly precipitation (PPT) and wind speed (W) (reference period 1961–1990) and the calculated TM and PPT anomalies as Anom TM and Anom PPTM, respectively.

4. Results

4.1. Modern limnology and water column properties

Water column temperature profiles of Lake Montcortès showed thermal stratification during most of the year, with mean surface and bottom temperatures of 14.6 °C and 5.2 °C, respectively. During winter, the surface water cooled until it reached 4–5 °C, and the increase in water density promoted thermic homogenization of the entire water column and all physical properties (Fig. 2). During spring and summer warming (April to September), surface temperature rose quickly, and thermal stratification developed. The mixing zone moved to shallower depths (5–7 m); a well-defined thermocline developed between 5 and 15 m and lasted until early winter (December) (Fig. 2A). Maximum epilimnetic temperatures of 24.7 °C were recorded during summer 2015, while the maximum during 2014 was 22.2 °C.

Dissolved oxygen showed maximum concentrations (14–17 mg L⁻¹) between 7 to 10 m in the euphotic metalimnion from May to September around the thermocline (Fig. 2B) and then decreased with depth. Secchi disc ranged from ~4 to ~9 m, and the limit of the euphotic zone was always deeper than 7 m and below the oxygen peak

(Fig. 2B). Winter water column mixing events took place in January 2014 and 2015. When stratification began from March onward, oxygen depletion occurred, and anoxic conditions started to develop in the hypolimnion. Hypoxia ($\leq 2 \text{ mg L}^{-1}$) began in April, and anoxia (0 mg L^{-1}) was reached in June and remained until December (Fig. 2B). The maximum thickness of the anoxic layer was observed at the end of summer (September–October) and reached up to 15 m lake depth in 2014 and close to 17 m lake depth in 2015. This represents an anoxic layer thickness close to 10 m.

Values of pH were highest coinciding with oxygen maxima in the metalimnion. During stratification, pH values ranged from 7.1 close to the bottom to 8.7 in the epilimnion (Fig. 2C), coinciding with increasing phytoplankton biovolumes, and were near 7.8 during winter mixing. Total alkalinity was roughly constant through time and depth, with mean values ranging from 3 to 3.5 meq L^{-1} , indicating well-buffered waters even in the hypolimnion, where pH was lower (Fig. 2C). Electric conductivity (EC) did not experience significant seasonal changes along the water column, except for subtle EC minima that occurred during stratification in both years coinciding with oxygen maxima. EC anomalies, calculated as the difference between depth average and the corresponding value for each depth, were plotted to document these minima (Fig. 2E).

Fig. 2. Depth profiles of A. water temperature; B. oxygen concentration with euphotic zone (solid line); C. pH; D. electric conductivity (EC) anomalies and E. four discrete electric conductivity profiles corresponding to mixing periods (February 2014 and 2015) and stratification period (October 2013 and August 2015) note the EC decreases in metalimnetic waters during stratification .

Ca^{2+} was the most abundant dissolved cation followed by Mg^{2+} (Table 1). Values of SRP and TP were very low. TN was relatively more abundant and increased notably in the hypolimnion during the stratification period, while it was depleted in epi and metalimnion (Table 1).

The succession of main phytoplankton groups followed a seasonal pattern during the entire sampling period (Table 1). Central diatoms belonging mainly to the genus *Cyclotella* peaked in early spring, taking advantage of turbulence after overturn. During summer and early fall Chlorophytes were the most abundant group, except in summer 2015 when diatoms remained dominant in the metalimnion, while in the epilimnion Cryptophytes dominated. Cryptophytes were dominant mainly during winters when all other groups decreased in abundance. Interestingly, a significant part of the planktonic diatoms and Chlorophytes was extremely small, exhibiting sizes of only ~5 μm .

Table 1. Seasonal average concentration of cations and nutrients and main phytoplankton groups.

	2013		2014			2015		
Ca (mg L^{-1})	Fall	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Epi ^a .	128.09	127.50	102.5	145.00	107	83.57	83.57	82.78
Meta ^b .	112.99	127.95	122.67	138.36	101.21	82.97	81.71	81.56
Hypo ^c .	125.03	144.21	130.18	118.25	103.44	82.96	81.76	84.38
Mg (mg L^{-1})								
Epi.	15.65	18.26	13.92	19.21	17.93	17.89	18.12	17.32
Meta.	17.04	18.29	16.02	19.16	18.82	17.76	17.8	17.18
Hypo.	17.38	19.23	16.2	19.19	18.56	17.76	17.61	17.50
K (mg L^{-1})								
Epi.	2.34	2.78	2.20	2.79	2.45	2.53	2.73	2.63

Meta.	2.52	2.81	2.40	2.81	2.69	2.54	2.53	2.68
Hypo.	2.60	2.88	2.60	2.78	2.69	2.54	2.53	2.63
Na (mg L ⁻¹)								
Epi.	3.04	3.66	2.26	3.63	3.31	3.24	3.60	3.63
Meta.	3.50	3.71	2.91	3.29	3.17	3.08	3.31	3.58
Hypo.	3.34	3.36	2.87	3.32	3.23	3.28	3.32	3.50
SRP (μM)								
Epi.	0.050	0.042	0.037	0.051	0.049	0.040	0.010	0.034
Meta.	0.019	0.012	0.053	0.047	0.042	0.050	0.010	0.036
Hypo.	0.071	0.036	0.047	0.047	0.049	0.057	0.011	0.050
TP (μM)								
Epi.	0.190	0.200	0.170	0.350	0.650	0.045*	0.180	0.050
Meta.	0.191	0.200	0.212	0.853	0.624	0.547*	0.511	0.130
Hypo.	0.198	0.201	0.264	0.697	0.900	0.512*	0.402	0.396
TN (μM)								
Epi.	30.28	50.63	34.37	24.19	28.06	45.35	36.84	28.65
Meta.	43.21	50.73	37.25	27.36	34.55	45.63	39.54	28.84
Hypo.	71.47	53.81	61.68	69.81	59.55	44.84	53.45	59.45
Phytoplankton succession								
Epi.	Chlorophyta	Cryptophyta	Bacillariophyta	Chlorophyta	Chlorophyta	Cryptophyta	Bacillariophyta	Cryptophyta
Meta.	Chlorophyta	Cryptophyta	Bacillariophyta	Chlorophyta	Chlorophyta	Cryptophyta	Bacillariophyta	Bacillariophyta

(*) Missing sample of January; ^a Epilimnion; ^b Metalimnion; ^c Hypolimnion.

4.2. Fluxes of trapped material

Total mass fluxes (TMF), calcite and POC fluxes are displayed in Figure 3. The collected material from sediment traps reveals important changes during the two years of sampling. TMF followed a clear seasonal pattern in which low values occurred mainly during winter and early spring and the highest values during summer and fall (Fig. 3A). Progressive flux increases started in early spring (April–May), coinciding with oxygen increase together with increasing fluxes of POC (Fig. 3B). After that, both TMF and POC started to decrease during fall with oxygen depletion. Increases in POC fluxes were roughly followed by increases in calcite deposition (Fig. 3B and C). Calcite is mainly deposited during summer and fall, with higher values recorded in fall 2013 and summer 2015 (Fig. 3C). Periods with more intense calcite deposition also coincided with higher values of calcite saturation in the epilimnion and metalimnion.

The Mg-to-Ca molar ratio did not exceed 0.37 (Fig. 3C), and epi- and metalimnion remained permanently calcite-saturated throughout the study period (Fig. 3E). The highest values of calcite saturation were recorded during spring and summer (Fig. 3E), coinciding with rising temperature and primary production. The hypolimnion also endured saturation during most of the year but presented lower saturation values than epi- and metalimnetic waters. Overall, calcite saturation values declined in late summer and fall. During the late fall of 2014, the hypolimnion was near undersaturation for calcite, and it was only during the fall of 2015 when values fell below zero recording undersaturation values (Fig. 3E).

TMF, POC and calcite fluxes showed a similar behavior and are moderately correlated (TMF vs POC $r = +0.80$, $p(a) < 0.05$, $n = 25$; TMF vs PIC $r = +0.86$, $p(a) < 0.05$, $n = 25$ and PIC vs POC $r = +0.76$, $p(a) < 0.1$, $n = 25$). Total amounts of calcite deposition varied broadly between years, a fact that is evident by comparison with the data from 2014 to 2015 (Fig. 3C). During 2014, calcite fluxes remained below OM fluxes, while during 2013 and 2015 calcite values clearly exceeded OM during fall and from early summer to fall (Fig. 3D).

358

359 **Fig. 3.** Monthly fluxes of major sediment components deposited in sediment traps
360 during monitoring period 10/2013-10/2015: A. Total mass fluxes (TMF) with changes in
361 phytoplankton biovolume for the epilimnion and the metalimnion; B. POC fluxes and
362 corresponding POC/TN ratios; C. calcite fluxes with epi-, meta and hypolimnion Mg/Ca;
363 D. calcite fluxes versus estimated range of organic matter fluxes (OM); E. Calcite
364 saturation index (SI) for epi-, meta- and hypolimnion.

365

366 4.3. Calcite crystal characterization

367 Presence of calcite crystals was confirmed in all trapped samples. A clear seasonal
368 pattern in calcite sizes was observed (Fig. 4A). Larger crystals with higher $I_{\max}$ and $I_{\min}$
369 correspond to fall and winter in traps and tend to decrease progressively from fall to
370 summer through the two years of the study. Most of the crystals have blocky and
371 polyhedral habits (Fig. 4B to 4G). Some crystals appeared attached to central diatom
372 frustules of the genus *Cyclotella* (Fig. 4H).

373

Fig. 4 Calcite crystals found in quarterly sediment traps in Lake Montcortès: A. Mean values of $I_{\max}$ and $I_{\min}$ (μm) corresponding to Fall (Fl), winter (Wn), spring (Sp) and summer (Sm) and bars indicate standard deviation; B-H. SEM images of calcite crystals: B. $I_{\max}$ and $I_{\min}$ measurements; C. calcite spectogram; D-G. images of calcite crystals. Thin section microscopic image showing one of the varve structures found in Lake Montcortès sediment: I. calcite layer with fine-grained calcite crystals followed by coarse-grained calcite crystals and the organic layer; I') more magnified detail of varve structure.

4.4. Trapped diatoms

We analyzed diatoms from quarterly trapped sediment samples to estimate their timing and contribution to the deposited material. Higher diatom fluxes were recorded during spring and summer (Fig. 5A). This pattern roughly matches with the total diatom cells counted in the water column (Fig. 5B). Central diatoms accounted for more than 50% of the diatom composition during most of the year and reached abundances above 75% during spring and summer. Seasonal changes in relative abundances of the main species of central diatoms *Cyclotella cyclopuncta*, *C. ocellata*, *C. radiosa* and *Stephanodiscus hantzschii* are shown in Figure 5C. *C. cyclopuncta* generally dominated the assemblage, while *C. ocellata* was less abundant with constant proportions. *C. radiosa* showed small proportions, except during spring for both years, when it increased. The differences between the diatom content of the traps and the water column during the spring of 2015 can be explained by poor preservation of the material deposited in the corresponding trap, which was considerably damaged, diluted and hardly able to be counted.

Fig. 5. Diatom dynamics: A. fluxes of diatoms in quarterly traps; B. Diatom cell abundances in the epilimnion and metalimnion; C. relative abundances of centric diatoms

4.5. Meteorological conditions

Monthly mean air temperatures decreased from August–September to December–January, when temperatures remained above 4 °C. Maximum temperatures were reached during July of both years: 22 °C for July 2014 and 26.5 °C for July 2015 (Fig. 6A). Temperature anomalies corresponding to 2015 were generally positive and higher than anomalies in 2014, indicating a warmer year (Fig. 6A). Precipitation was high in late summer and fall for both years (Fig. 6B). During 2015, negative precipitation anomalies were persistent from December 2014 to June 2015 and positive from July to October. Comparing the same periods for 2014, December 2013 to June 2014 was wetter than in 2015 with more positive anomalies, while July to October 2015 was similar to 2014.

Monthly mean wind speeds during the studied period reached maximum values during spring and the minimum values during winter of both years and did not exceed 1.5 m s⁻¹ during the studied period (Fig. 6B).

Fig. 6 Meteorological data: A. Monthly mean air temperature (TM); B. mean precipitation (PPT) and their anomalies (black bars) along with wind speed (W) (line).

5. Discussion

5.1. Varve formation: sediment fluxes and composition during the annual cycle.

The annual pattern of particle flux dynamics and composition in Lake Montcortès was closely related to biogeochemical processes in the euphotic zone and changing meteorological conditions throughout the year. Fluxes of sediment reached maximum values in summer and fall that matched with maxima of phytoplanktonic growth, pH, and calcite and POC deposition in traps values. POC values were higher during summer and fall when calcite was mainly deposited, suggesting that the main origin of calcite crystals are autochthonous. Other sources of calcite input, such as detrital carbonates from the catchment, seem to be not significant during the studied period. Well-formed blocky and rhombohedral calcite crystals and the presence of diatom frustules attached to these crystals support the autochthonous origin of calcite (Pere Anadón pers. com.). Moreover, low values of the POC-to-TN ratio indicate the prevalence of cellulose-poor autochthonous algal organic matter over lignin and cellulose-rich allochthonous organic matter derived from vascular plants (Meyers and Teranes 2001), suggesting low input to the lake from the catchment area. Additionally, there are no discontinuities in TMF that could be attributed to external inputs, i.e., there are no TMF increases that coincide with months of higher precipitation anomalies (Fig. 3 and 6). These observations are consistent with the fact that biologically induced calcite precipitation took place in Lake Montcortès.

Calcite precipitation can be triggered by CO₂ uptake during algal photosynthesis. Primary productivity affects the carbonic-carbonate system in epilimnetic and metalimnetic waters by decreasing CO₂, increasing pH, and shifting the equilibria toward the CO₃²⁻ species (Kelts and Hsü 1978, Dittrich and Obst 2004). This

biochemical mechanism leads to calcite supersaturation in the limnetic zone (Hodell et al., 1998). In addition, when photosynthesis occurs, precipitation would be enhanced by phytoplankton providing particulate surface areas for calcite-crystal growth (Dittrich et al., 2004). In fact, the epi- and metalimnetic waters of Lake Montcortès were already supersaturated with calcite when precipitation occurred at $\log \Omega \geq 1$ and with a rather low Mg/Ca molar ratio that indicates favorable environmental conditions for the formation of pure calcite or low Mg-calcite crystals (Müller et al., 1972). Calcite supersaturation values for calcite precipitation need to be $\log \Omega \geq 2$ under experimental conditions (Dittrich and Obst 2004), but it has been shown that precipitation in lakes can happen far below that threshold. Some examples are Lake Constance, where calcite precipitates at $\log \Omega \leq 1$ (Stabel et al., 1986), and the oligotrophic Lake Lucerne, where precipitation occurred when $\log \Omega$ was near 0.4 (Dittrich et al., 2004). A likely explanation for this discrepancy is the presence of nuclei provided by phytoplankton cells, which are necessary for crystal growth (Dittrich and Obst 2004). Nucleation of calcite crystals triggered by phytoplankton and small particles of picoplankton (0.2-2 μm), such as cyanobacteria or sulfur-reducing bacteria, have been shown and documented by several studies (Dittrich and Obst 2004; Baumgartner et al., 2006). This explanation likely applies in our case, since small Chlorophyta (such as *Tetraedron minimum* and *Oocystis spp.*) and small centric diatoms (~5 μm) are dominant during periods of calcite precipitation, and persistent populations of sulfur bacteria (Chromatiaceae and Chlorobiaceae) are known to thrive at the hypolimnion-metalimnion boundary of Lake Montcortès (Cristina et al., 2000). Additionally, during stratification period, the filters we used to trap deposited material were intensely stained with the unmistakable color of purple bacteria (Supplementary Fig.1), and their presence was confirmed by okenone and isorenieratene pigment analysis (Vegas-Villarúbia et al., 2018). Moreover, high calcite fluxes happened at the same time that negative EC anomalies were recorded. This slight decrease in EC could be a consequence of ion depletion caused by nutrient uptake and precipitation of calcite, but

any simultaneous decrease in alkalinity and Ca concentration that could support the link between EC and calcite precipitation went unnoticed. This outcome may be a consequence of sampling resolution; in fact, variations in Ca and alkalinity might have happened between sampling data and thus remained unnoticed in our records. Nonetheless, decreases in EC in epilimnetic and metalimnetic water related to calcite precipitation have been observed in other hard-water lakes (Miracle et al., 2000; Bluszcz et al., 2008).

The spring and the summer of 2015 were anomalously warm, and the calcite flux was more than twice compared to the preceding year for the same seasons (Fig. 3C). These warmer conditions were perfectly recorded in epi- and metalimnetic water temperatures that coincided with higher values of DO as a result of enhanced primary production. Thus, the influence of atmospheric temperature increase on processes involved in calcite precipitation is evidenced by the differences in the magnitudes of deposited material between both years.

Actually, 2015 was the warmest year on the record registered in Europe (NOAA 2015) recording the second warmest summer on the record. Also, 2015, was the warmest year in Spain tied with 2011 that recorded 0.96 °C temperature anomaly (1981-2010 reference period) (AEMET 2015). Since the late 1990ies until nowadays, increases of mean lake-water temperature between 0.5 and 0.6 °C per decade have been recorded in the majority of studied European lakes (Dokulil, 2013). Besides, the average thickness of calcite sublayers of the Montcortès record has nearly doubled since the 19th century (Corella et al., 2011b, 2012). These results suggest that variations of biogenic calcite in the sedimentary record might indicate temperature changes, at least partially. The thickness of calcareous layer in Lake Montcortès seems to be a reliable paleotemperature proxy.

5.2. Varve preservation: Limnological conditions

Previous studies of Lake Montcortès found persistent anoxic conditions and sulfide production on bottom waters year-round in 1975/1976 and 1997/1998 respectively (Camps et al., 1976; Cristina et al., 2000). Based on these studies and in the laminated nature of the sediment record, Lake Montcortès was considered to be meromictic (Corella et al., 2012; Valero-Garcés et al., 2014). However, Modamio et al., (1988) reported a complete oxygenation of the water column associated with a winter mixing event (1978/1979). During the two-year period of monitoring, we observed that Lake Montcortès mixed during both winters. Nevertheless, during 2016 the lake did not mix completely (unpublished data). The observed mixing events in Lake Montcortès were tightly related with a mean air-temperature decrease below the lake's surface water-temperature that caused denser surface water layers to sink, promoting the mixing of the water column and thus, homogenization of oxygen concentration throughout the water column. Meteorological forcing at the air-water interface is known to be the main determinant of the heat balance of many lakes (Edinger et al., 1968; Sweers, 1976). All this evidence suggests that Lake Montcortès has an interannually changing mixing regime and cannot be considered meromictic *sensu stricto* (Hakala 2014). This is supported by a recent study documenting a 45.3% mixing recurrence during the last 500 years (Vegas-Vilarrúbia et al., 2018). With present global warming, an expected strengthening might significantly affect nutrient and oxygen regeneration within the water column.

Although meromictic conditions are especially suitable for varve preservation, short periods of mixing and seasonally suboxic to anoxic conditions during stratification seem to be enough to prevent bioturbation and allow varve preservation, even in dimictic lakes (Ojala 2000; Hakala 2004; Zolitschka et al., 2015). In Lake Montcortès this is supported by the continuous presence of varves shown by the sediment record of the last three millennia. Other factors that may affect varve preservation are

resuspension of bottom sediments through wind or density-driven water circulation and bottom currents that interrupt continuous sedimentation and cause erosional hiatuses. The latter two processes can be excluded if the lake basin is deep with a small surface area and geomorphologically protected (O'Sullivan 1983), this is the case for Lake Montcortès (Corella et al., 2012). Furthermore, lake mixing took place when minimum wind speeds were recorder both years studied (Fig.6.B)

5.3. Comparison with previous varve interpretations

The seasonal sedimentation pattern obtained from the sediment trap study is consistent with the alternating structure of light (calcite) and dark (organic) laminae observed in the sediment record of Lake Montcortès supporting the seasonal nature of the sediment laminane. According to our study, calcium calcite layer would form mostly in summer/fall and dark organic laminae mostly during winter/spring. This is more clearly evidenced in Figure 3D where OM and calcite fluxes are compared. Thus, our results do not totally agree with former studies that situated the formation of the calcite layer in spring/summer, and the formation of the organic layer in fall/winter (Corella et al., 2012). We did not observe conspicuous pulses of calcite precipitation, as occurs in lakes with the presence of whiting events (Miracle et al., 2000). Nonetheless, there was a clear differentiation between calcite and OM deposition in fall 2013 and summer/fall 2015, while this was not the case during 2014. In the latter case, the depositional pattern might result in a lack of sublayer differentiation and consequently of a varve or sub-layer absence for that particular year. In fact, this is coherent with Corella et al.(2011b), as they found laminated intervals with scarce light calcite layers in the Montcortès record of the last 6,000 years. Knowing when and why such events happened is crucial when it comes to building varve chronologies to minimize the counting error. Varve fading or absence can lead to mistakes in the recognition of annual cycles in the sediments.

Calcite precipitation began to increase in late spring with higher deposition rates during summer lasting until fall. Consequently, the light laminae would represent the merged effect of temperature and primary production. Dark laminae (OM) would represent the productivity of the lake through the year. Calcite laminae differentiation would depend of the amount of calcite precipitated during summer/fall. Such correspondence should be demonstrated by analyzing the individual sediment layers covering the studied period but presently this cannot be accomplished as it is necessary to wait for diagenesis to consolidate the sedimentary deposits. So far, our results give further information about seasonal composition of sediment material and highlight the importance of modern analogue studies to properly interpret the sediment signal at a seasonal and sub-annual scale.

Calcite crystal-sizes from quarterly traps found in this study showed a seasonal pattern likely related to water temperature, being smaller when formed during spring and summer. Additionally, deposition of smaller crystals was concurrent with higher fluxes of diatoms and high SI. It is known that when calcite saturation is high, e.g. in spring and summer, crystals were formed rapidly and do not have time to grow. However, in fall and winter, water is not very supersaturated in calcite, and crystals can increase their sizes while travelling to the bottom (Kelts and Hsü 1978). Thus, smaller calcite crystals in Lake Montcortès would be interpreted as occurring during periods with elevated SI related to higher temperatures and primary production. This pattern bears some relationship with the internal calcite sub-layering present in the sediment record of Lake Montcortès (fining upward with coarser calcite crystals in the lower part of the calcite layer; coarsening upward, the converse of fining upward; and a homogeneous layer of coarse crystals (Corella et al., 2012)). The seasonal calcite-crystal distribution observed in quarterly traps would likely result in a coarsening upward calcite sub-layering, with fine grained calcite crystals deposited in summer and coarse-grained calcite crystals in fall (Fig. 4I and I'). This texture is frequently observed in the sedimentary sequence from AD ~1350 to 1850 AD and less frequently from then

until present day (Corella et al., 2012). Future micro-facies analysis of the sediment record retrieved after 2015 might show the corresponding varves and sub-layering patterns of the studied period (2013-2015).

Three *Cyclotella* species coexisted over the studied period: *C. cyclopuncta*, the dominant taxon, together with *C. ocellata*, while *C. radiosa*, which is bigger than the two other species, increased in spring, being competitive during periods of high turbulence promoted by winter mixing. The growth of highly silicified species as a response to turbulence, as well as increases in small centric diatoms during stratification (e.g., *C. cyclopuncta*), have been observed in other lakes as a consequence of changes in water stratification (Rühland et al., 2015). Changes in relative abundances of *C. cyclopuncta* and *C. radiosa* in Lake Montcortès are chiefly a response to shifts in stratification of the water column. Therefore, increasing temperature would favor small *C. cyclopuncta* during intensified stratification periods. These findings provide new insights at seasonal time resolution to refine inferences made from the diatomological record in former studies working at coarser resolution. For instance, based on available information on diatom autoecology, the presence of *Cyclotella compta* (a synonym for *C. radiosa*) and *C. cyclopuncta* in the sediment record was attributed to warmer and cooler periods, respectively (Corella et al., 2012). Another study found frequencies of *C. cyclopuncta* and *C. radiosa* to vary inversely and only appeared together in a single sample over the last 1500 years and suggested that these shifts may be a response to nutrient availability (Scussolini et al., 2011). However, present-day data reveals an alternative scenario where both taxa coexist together and differences in relative abundances respond to seasonal changes in water stability with warmer conditions favoring *C. cyclopuncta*.

Both changes in diatom species abundances as well as in shapes and sizes of calcite crystals are related indirectly to temperature by means of changes in SI and water column stratification. Additionally, the occurrence of calcite precipitation and

differences in calcite amounts between the years are related with temperature variability. Consequently, varve succession in Lake Montcortès is a direct product of seasonally changing environmental conditions and is especially sensitive to alterations in temperature.

The importance of modern analogue studies lies in the need of understanding the specific processes taking place in a specific place within specific features (hydrology, geomorphology, limnology, climate and anthropogenic influence) that shape the resulting sedimentary sequence and the resulting environmental signal. Then, general validity processes could not apply properly to successfully interpret the paleorecord. For example, Bonk et al. (2015) demonstrated that multiple calcite precipitation events took place in a single year related with changes in the mixing regime of lake Żabińskie (Poland) depending of climate conditions. These results were coherent with the sedimentary structure of the last 20 years where a maximum of four calcite layers were observed within a single year. The modern analogue study in this case provided a basis to establish a reliable varve chronology. Based on three years of monitoring data on seasonal particle pulses in Lake Van (Turkey), Stockhecke et al. (2012) found that the temporal and lateral variations of lake basin changes on particle accumulation and composition (lithology) were linked to atmospheric circulation patterns that controlled hydrological and meteorological conditions. Thus, they provide a basis for the reconstruction of past seasonal climate patterns. All of these monitoring studies successfully gave sense to modern processes to be compared with the fossil record for these specific places setting a baseline to reduce sources of error for future sediment studies. Anyhow, although monitoring studies are highly time consuming and costly, long-term water column and particle-flux monitoring should continue to better assess inter-annual variability and to improve future interpretations of the past.

6. Conclusions

Two years of sediment trap and limnological monitoring in the Lake Montcortès enabled us, for the first time for this lake, to link the limnological cycle to seasonal particle fluxes and provide modern sedimentary analogues potentially useful for improving the quality and quantity of paleoenvironmental and paleoecological information.

Varve deposition in Lake Montcortès is a direct result of seasonal limnological changes occurring in the water column and its seasonality is consistent with the annually laminated nature of the sediment record. Sedimentary patterns are closely related to biological processes occurring in the euphotic zone. There is a clear seasonal signal, useful for paleolimnological interpretation, expressed in the alternation of calcite precipitation during summer and fall and organic matter precipitation during winter and spring. Summer/fall calcite precipitation is favored by high calcite saturation indices and high pH values, in connection with enhanced primary production and the eventual capacity of phytoplankton cells to act as condensation nuclei. Inter-annual differences were expressed in terms of the amount of precipitated calcite, which is related to temperature variability. Thus, the thickness of calcite layers in the sediment could be considered as a potential paleoclimatic temperature proxy. A hypothesis that should be tested in the future. In addition, changes in calcite-crystal size and in the composition of diatom assemblages would give additional information about changes in SI and thermal stratification.

According to our results, the varves that formed during the two studied years would likely match one of the varve types previously identified in the sedimentary record of the last millennium. Microstratigraphic investigations from sediment cores retrieved after 2015 is needed to confirm the resulting sedimentary pattern corresponding to the two studied years. Relationships between environmental and meteorological conditions and characteristics of individual varves need to be tested against longer time series of environmental and meteorological data.

Although it has been demonstrated that Lake Montcortès is not strictly meromictic but with alternating holomictic and meromictic periods, the long duration of thermal stratification and hypolimnetic anoxia create suitable conditions for varve formation and preservation. Nonetheless, the limnological monitoring and the sediment trap survey should continue to account for potential inter-annual variability, which is especially meaningful in the Mediterranean area and in the context of global warming

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861 **Supplementary material:**

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864 **S1.** Pink colored filter resulting after filtering hypolimnetic water. This color is due to
865 purple sulphur bacteria living at the hypo-metalimnetic boundary of Lake Montcortès.

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