Javier Sánchez-España, *et al.,* 2019. Hydrogeochemical characteristics of the Saliencia lakes (Somiedo Natural Park, NW Spain): trophic state and relationship with anthropogenic pressures. *Boletín Geológico y Minero,* 130 (2): 251-269
ISSN: 0366-0176
DOI: 10.21701/bolgeomin.130.2.003

Hydrogeochemical characteristics of the Saliencia lakes (Somiedo Natural Park, NW Spain): trophic state and relationship with anthropogenic pressures

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RESUMEN

Los lagos de alta montaña de Saliencia (El Valle, La Cueva, Calabazosa y Cerveriz), en el Parque Natural de Somiedo (Asturias), han sufrido una notable presión antrópica en tiempos recientes (minería metálica, pastoreo de ganado vacuno, actividades de represamiento y trabajos de canalización). Este trabajo presenta los resultados y principales conclusiones de un reciente estudio realizado en estos lagos, sobre los cuales no existía información previa. En base a perfiles de temperatura, conductividad, pH y ORP, así como de concentración de oxígeno disuelto, clorofila-a, carbono orgánico, nutrientes y metales disueltos, se discute el impacto de la presión antrópica sobre estos lagos. En el periodo de estudio (Julio a Septiembre, 2014-2016), estos lagos presentaron una marcada estratificación térmica y química con notables gradientes verticales como resultado de diversos procesos físicos y biogeoquímicos. Todos los lagos mostraron un buen estado ambiental sin aparente contaminación por metales. Sin embargo, este conjunto de lagos no es homogéneo en cuanto a la disponibilidad de nutrientes, productividad primaria, o déficit de oxígeno hipolimnético, existiendo un espectro de condiciones tróficas que van desde oligotróficas (El Valle) a eutróficas (Calabazosa). Esta tendencia parece estar provocada principalmente por la variabilidad del contenido en fósforo (p.ej., 10 µg/L P en El Valle frente a 35 µg/L P en Calabazosa), aunque los procesos erosivos en la cuenca también podrían estar contribuyendo a incrementar el consumo de oxígeno mediante el aporte de materia orgánica alóctona. Las zonas con mayor presencia de ganado (ej., El Valle) parecen presentar contenidos más altos en nitratos, aunque no puede establecerse una relación directa entre ganado y eutrofización.

Palabras clave: eutrofización, explotación minera, gestión hidrológica, lagos de alta montaña, Parque Natural de Somiedo.

Características hidrogeoquímicas de los lagos de Saliencia (Parque Natural de Somiedo, NO España): estado trófico y relación con diferentes presiones antrópicas

ABSTRACT

The high-mountain lakes of Saliencia (El Valle, La Cueva, Calabazosa and Cerveriz), in the Somiedo Natural Park (Asturias, NW Spain), have been subject to different anthropogenic pressures, including metal mining, cattle grazing, damming activities and water channelling work for hydroelectric exploitation. This paper reports the results of a recent geochemical and limnological study conducted in these lakes, for which no previous study existed in the literature. Based on depth profiles of temperature, conductivity, pH and ORP, as well as dissolved oxygen, chlorophyll-a, organic carbon, nutrient and metal concentration, we discuss the impact *of anthropogenic pressure on the lakes. In the sampling period (July to September, 2014-2016), most of the lakes showed a marked stratification with vertical gradients as a result of different physical and (bio)geochemical processes. All the lakes showed a good environmental state with no apparent metal pollution. However, this set of mountain lakes is not homogeneous with regard to nutrient availability, primary productivity, or hypolimnetic oxygen deficit and a range of trophic conditions exist from oligotrophic (El Valle) to eutrophic (Calabazosa). This trend shows a good correlation with total phosphorus concentration (e.g., 10 µg/L P in El Valle vs. 35 µg/L P in Calabazosa), though erosive processes in the catchment may also have contributed to increase the oxygen consumption rate through an import of allochthonous organic matter. Higher nitrate contents seem to characterize the areas with higher grazing pressure (e.g., El Valle), though the obtained data do not allow us to establish any evident relationship between cattle activity and eutrophication.*

Keywords: eutrophication, high mountain lakes, hydrologic management, mining exploitation, Somiedo Natural Park.

VERSIÓN ABREVIADA EN CASTELLANO

Introducción y métodos

Los lagos de alta montaña de Saliencia (El Valle, La Cueva, Calabazosa y Cerveriz; Fig. 1), en el Parque Natural de Somiedo (Asturias), han sufrido una notable presión antrópica en tiempos recientes en forma de minería metálica, pastoreo de ganado vacuno, actividades de represamiento y trabajos de canalización de agua (Tabla 1). Este trabajo presenta los resultados y principales conclusiones de un reciente estudio realizado en estos lagos, sobre los cuales no existía ningún estudio de detalle previo. En base a perfiles de temperatura, conductividad, pH y ORP, así como de concentración de oxígeno disuelto, clorofila-a, carbono orgánico, nutrientes y metales disueltos, se discute el impacto de la presión antrópica sobre estos lagos. Se confeccionaron mapas batimétricos de los lagos mediante eco-sondas Humminbird y sistemas de posicionamiento geográfico de Garmin (Fig. 2). Los datos geo-espaciales fueron posteriormente tratados en ArcInfo 9.3 de ESRI para llevar a cabo cálculos volumétricos de las masas de agua y correlacionar perfiles. Las campañas de campo para levantar los perfiles físico-químicos verticales en cada uno de los lagos y tomar muestras de agua a diferentes profundidades se realizaron en diferentes periodos entre 2014 y 2016. Durante una buena parte del año (i.e., final del otoño a comienzos de la primavera), el acceso a los lagos con equipos científicos es muy complicado debido a la gran abundancia de nieve, con pistas y carreteras cerradas a vehículos durante muchos meses, y a que la superficie de los lagos se congela completamente durante los meses más fríos y a menudo hasta bien entrada la primavera. Por este motivo, tanto la monitorización como el muestreo se llevaron a cabo principalmente durante el periodo estival (julio a septiembre). Los parámetros hidroquímicos (incluyendo temperatura –T–, conductividad específica –SpC–, pH, potencial redox –ORP–, concentración y nivel de saturación de oxígeno disuelto –DO–, presión total de gases disueltos –TDG–, intensidad de la radiación fotosintéticamente activa –PAR–, y la concentración de clorofila-a –chl-a–) se midieron mediante sondas multiparamétricas Hydrolab de Hach® (MS5, DS5) o de YSI (Pro Plus). La intensidad de PAR (en µE m-2 s-1) se midió con un sensor LI-COR que mide la intensidad de luz en el intervalo de longitud de onda de 400 a 1100 nm. El sensor de chl-a mide la señal de fluorescencia y proporciona una estimación de concentración de clorofila (en µg/L). El sensor de DO mide la concentración de O_2 disuelto (en mg/L) por luminiscencia (precisión de 0.01 mg/L). Debido a las fuertes variaciones del nivel del agua en los lagos, todos los perfiles han sido referenciados a las condiciones observadas en la primera campaña de campo (Julio 2014), donde se observaron los niveles más altos de todo el periodo de estudio en todos los lagos. Las muestras más profundas son por tanto coincidentes entre las diferentes campañas, y las diferencias en la profundidad de los diferentes perfiles se evidencian por la posición relativa de la superficie del lago en cada caso. Las muestras de agua para el análisis químico (concentración de iones mayoritarios, metales traza y nutrientes) se tomaron a distintas profundidades con una botella limnológica de tipo Van Dorn® (KC Denmark). Todas las muestras de agua fueron filtradas in situ con filtros de membrana de nitrocelulosa con diámetro de poro de 0.45 µm de Millipore®, almacenadas en botes de polietileno con 125-250 mL de volumen, y refrigerados durante el transporte al laboratorio, donde se analizaron mediante diversas técnicas como cromatografía iónica (aniones), espectrometría de absorción atómica (cationes principales), espectrometría de masas con plasma acoplado por inducción (metales traza) o espectrometría UV-VIS (fósforo total). Las muestras para análisis de cationes fueron además acidificadas con HNO_3 (1 M).

Resultados y discusión

En el periodo de muestreo cubierto por el estudio (julio a septiembre, 2014-2016), la mayor parte de lagos

mostraron una marcada estratificación térmica y química con notables gradientes verticales entre el epilimnion oxigenado y el hipolimnion anóxico, como resultado de diversos procesos físicos y biogeoquímicos (Figs. 3-8). Entre estos procesos, cabe destacar los gradientes de densidad provocados por diferencias de temperatura (16-18 ºC en la zona superficial influenciada por el calentamiento solar frente a 4-6 ºC en la zona profunda), el desarrollo y sedimentación de biomasa fitoplanctónica (microalgas verdes desarrolladas en la zona fótica y sedimentadas a través de la columna de agua), la mineralización del carbono orgánico (oxidación de la materia orgánica procedente de las microalgas y transformación a dióxido de carbono por el metabolismo de bacterias heterótrofas), o los ciclos redox de metales como el Fe o el Mn (solubilizados en la zona profunda por reducción bacteriana en la interfase agua/sedimento durante la etapa de estratificación, y re-oxidados y precipitados de nuevo durante la etapa de homogenización del lago y re-oxigenación del hipolimnion). Los altos contenidos en hierro disuelto observados en el hipolimnion del lago de La Cueva (1500-4500 mg/L Fe) frente a los medidos en la zona profunda de El Valle (300-1200 mg/L Fe) parecen estar relacionados tanto con un periodo de estratificación más largo en el primero, como con la existencia de lodos mineros de naturaleza hematítica en el fondo del lago de La Cueva. Todos los lagos mostraron un estado ambiental razonablemente bueno en lo que se refiere a contaminación por metales (con todos los metales tóxicos analizados muy cerca o por debajo del límite de detección). Sin embargo, este conjunto de lagos de montaña no es homogéneo en cuanto a la disponibilidad de nutrientes (ej., concentración de fósforo), productividad primaria (espesor e intensidad de los máximos profundos de clorofila), o déficit de oxígeno hipolimnético, existiendo un espectro de condiciones tróficas que van desde aparentemente oligotróficas (El Valle) a eutróficas (Calabazosa). Esta tendencia parece estar provocada principalmente por la variabilidad del contenido en fósforo total (p.ej., 10 µg/L P en El Valle frente a 35 µg/L P en Calabazosa; Tablas 2-3) como factor limitante de la productividad primaria. Por otro lado, los procesos erosivos en la cuenca pueden estar contribuyendo en parte a incrementar el consumo de oxígeno debido a la entrada de materia orgánica alóctona, tal y como se observa en el lago La Cueva, cuyos taludes y laderas anexas están fuertemente retrabajados y modificados por la actividad minera. En este lago se observa un elevado consumo de oxígeno a pesar de su contenido relativamente bajo en fósforo, lo cual se atribuye al mencionado aporte de materia orgánica procedente de la cuenca por escorrentía. La regulación hidrológica que se produce en estos lagos, con bombeo intermitente para satisfacer la demanda de agua de la estación hidroeléctrica de La Malva, está favoreciendo los procesos erosivos, al exponer una superficie considerable de las laderas inundadas y provocar así una fuerte oscilación del nivel de los lagos y una continua re-suspensión de sedimentos en las orillas de los mismos. Las zonas con mayor presencia de ganado (ej., El Valle) parecen presentar contenidos algo más elevados en nitratos (1-2 mg/L NO_3^-), aunque aún no puede establecerse una relación directa entre ganado y eutrofización. La estrecha ventana de observación del presente estudio, que recoge sólo la época de estratificación estival, aconseja ampliar la investigación de estos lagos a otras estaciones del año para poder determinar con mayor precisión tanto el régimen de estratificación de los lagos de Somiedo como su funcionamiento hidroquímico y ecológico, incluyendo tanto la dinámica del oxígeno como su relación con la productividad primaria (actividad fotosintética del fitoplancton) y la disponibilidad de carbono orgánico y nutrientes. Por ejemplo, el estudio de los lagos en la época invernal permitiría comprobar su probable carácter dimíctico, con estratificación inversa por debajo de la capa de hielo, como ocurre en muchos lagos de alta montaña. Las futuras investigaciones deberían también centrarse en identificar fuentes y mecanismos de transporte del fósforo (ej., deposición atmosférica frente a transporte de sedimentos de la cuenca), ya que esta información tiene implicaciones de cara a la conservación de este espacio natural protegido. También sería conveniente evaluar el impacto de la minería sobre la ecología (biodiversidad, biomasa, tanto planctónica como bentónica) de los lagos, especialmente en lo que se refiere al posible efecto de metales tóxicos como As, Pb o Hg en sedimentos de los lagos o en suelos circundantes.

Introduction and objectives

Environmental framework: Anthropogenic pressures on the Somiedo lakes

The high-mountain lakes in the Somiedo Natural Park (Fig. 1) represent a stunning mountain landscape of great natural value. However, these lakes have suffered significant anthropogenic pressure in historical and modern times (Table 1), including iron mining during the period 1805-1978, damming activities for hydropower exploitation since 1920, and cattle grazing in historical and modern times.

The La Cueva Lake has been heavily contaminated by mining activity. Iron ore extraction and associated waste production took place in the adjacent Santa Rita mine (Martinez and Diaz, 1975). Although some environmental restoration was conducted in 1996, part of the mine wastes were spilled into the lake, turning the lake water a deep red colour with high turbidity that had a significant impact on the ecological equilibrium of the lake (Alonso, 1998; López and Ramos, 2007).

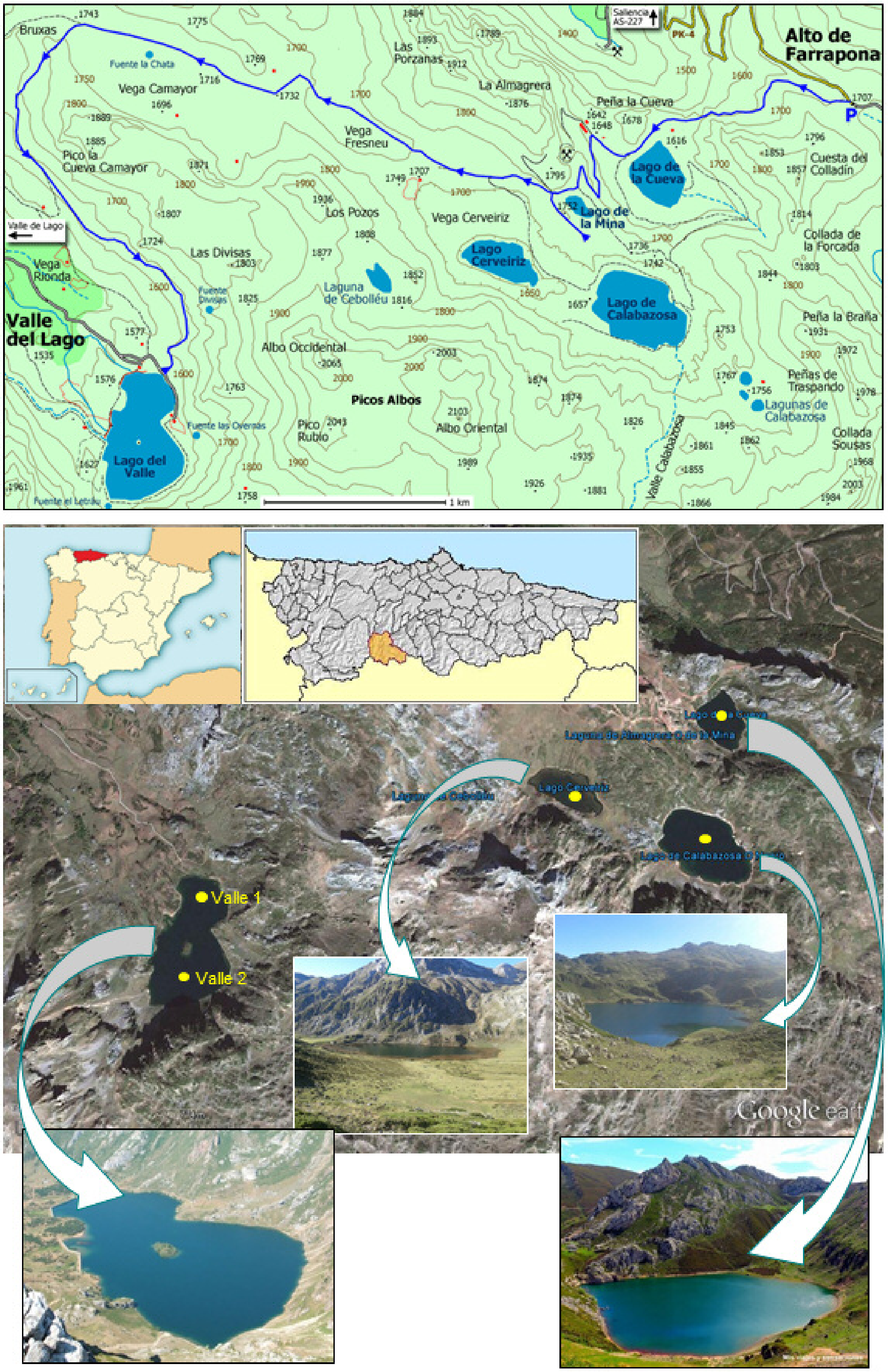

Figure 1. Geographic position, topographic map (*top*), satellite image (Google Earth, *centre*) and panoramic views of the post-glacial, high-mountain lakes of the Somiedo Natural Park (El Valle, La Cueva, Cerveriz and Calabazosa). The yellow points in the satellite image indicate the monitoring and sampling sites in all the lakes.

Figura 1. *Posición geográfica, mapa topográfico (arriba), imagen satélite (Google Earth, centro) y vistas panorámicas de los lagos post-glaciares de alta montaña del Parque Natural de Somiedo (El Valle, La Cueva, Cerveriz y Calabazosa). Los puntos amarillos en la imagen satélite indican los puntos de monitorización y muestreo en todos los lagos.*

LAKES	Altitude (m a.s.l.)	Geological substrate	Area (m^2)	Max. Depth (m)	Max. Volume (m^3)	Pressures and impacts over lake basin	Catchment: active geological processes
Calabazosa	1630	Upper Carboniferous limestones	12.5 x 10^4	50	2,9 x 10^6	Dammed	n.d.
La Cueva	1570	Lower Carboniferous limestones, Devonian sandstones and quartzarenites	7.3 x 10^4	21	0.7 x 10^6	Dammed and mining	landslides, flows, debris-flow, creeping soil
Cerveriz	1640	Upper Carboniferous limestones	6.3 x 10^4	7	0,16 x 10^6	Dammed	creeping soil
El Valle	1545	Upper Carboniferous limestones	23.7 x 10^4	29	2 x 10^6	Dammed	debris-flow creeping soils

Table 1. Hydro-geomorphological features of the Somiedo lakes.
Tabla 1. *Características hidro-geomorfológicas de los lagos de Somiedo).*

The input of these tailings has been preserved in the sedimentary record in the form of a thick layer of red mud in the uppermost 15 cm of the bottom sediments (Morellón *et al.,* 2016). Later the dismantling of mining infrastructure and geomorphological restoration in 2006 led to the remobilization of a large waste pile (100 m long with slopes up to 25%) on the western slope of the lake. An important mining-related effect on the watershed was the reactivation of erosive processes such as landslides and debris flows.

Artificial damming has produced important changes in the original morphology of these lakes of glacial origin (Vegas *et al.,* 2015). The best example is that of the El Valle lake, originally a small basin of only 15 m depth, and at present one of the largest lakes in Asturias with a maximum depth of 29 m and a surface area of 23,7 ha (López and Ramos, 2007; Rodriguez *et al.,* 2013). The four lakes are hydraulically connected by a system originally designed by a local company (*Sociedad Civil Privada de Saltos de Agua de Somiedo*, nowadays HC Energy) to supply the necessary water flow to the nearby hydroelectric power station La Malva (Fig. 2). The hydrological regulation of these lakes provokes important water level oscillations of up to several metres.

In addition, livestock grazing is widespread in the region since historical times, being especially abundant around the El Valle lake. The impact of the cattle on the lake shores is evidenced by intense trampling and direct faeces deposition.

Objectives

Despite their extraordinary environmental and landscaping value, we found no detailed study on the chemistry, limnology or ecology of these lakes. The major goal of this study was, therefore, to provide a first report on the chemistry and physical limnology of the high mountain lakes of the Somiedo Natural Park. In addition, we aimed at identifying the effects of the aforementioned anthropogenic pressures on the water quality (e.g., possible toxic metal pollution, eutrophication, anoxia) and hydrology/limnology (e.g., water level oscillations, stratification dynamics) of these lakes. Hydrological variations may potentially produce significant changes of lentic ecosystems (e.g., Camacho *et al.,* 2009), and cattle grazing is also potentially harmful (e.g., Hundey *et al.,* 2014). Understanding the hydrological and geochemical dynamics of the Somiedo lakes and their inter-relationship with distinct human impacts may help in the conservation and environmental management of these valuable ecosystems.

Regional setting

The mountain region of Somiedo was formally declared a "Natural Park" in 1988 by the regional government of Asturias (NW Spain), and was later included as Biosphere Reserve of the Man and the Biosphere Programme (UNESCO). This natural area contains four major lakes, in addition to several ephemeral ponds (Fig. 1): a) Calabazosa, Cerveriz and La Cueva in the Saliencia valley, and b) El Valle in the Valle Valley. The hydro-geomorphological characteristics of these four lakes are summarized in Table 1. The catchments of all the lakes lies on Carboniferous to Devonian karstified limestones, shales and sandstones (Marcos *et al.,* 1980). The landscape is dominated by glacier modelling with large cirques and partially eroded moraine deposits (Menéndez-Duarte & Marquínez, 1996).

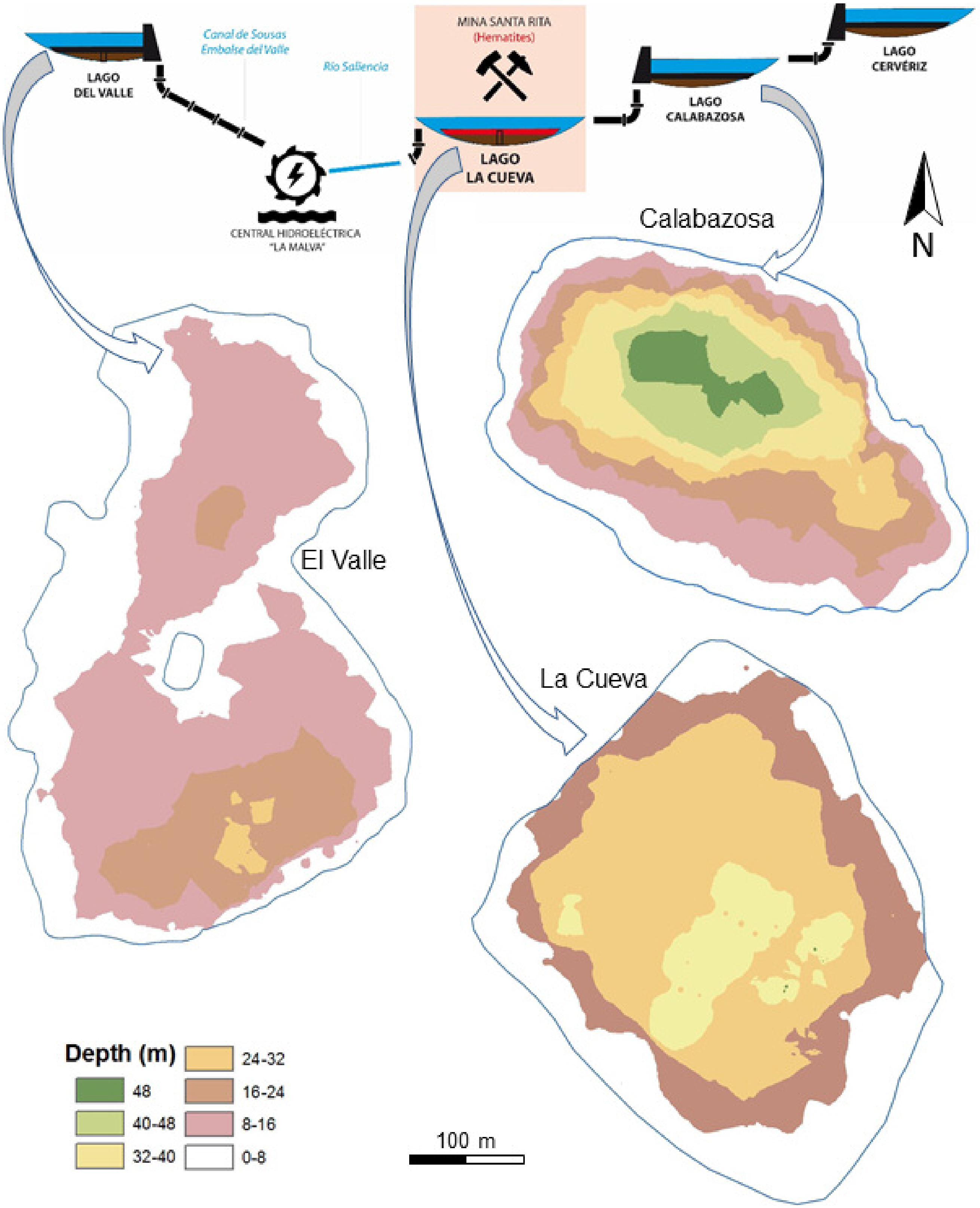

Figure 2. Schematic diagram of the hydraulic connection between the different lakes of Somiedo (*top*; modified from Morellón *et al.,* 2016), and bathymetric maps of the El Valle, La Cueva and Calabazosa lakes (*bottom*).

Figura 2. *Diagrama esquemático de la conexión hidráulica existente entre los diferentes lagos de Somiedo (arriba; modificado de Morellón et al., 2016), y mapas batimétricos de El Valle, La Cueva y Calabazosa (abajo).*

The climatic conditions are typical of high mountain environments. Data obtained from *Valle de Lago* meteorological station (situated at 1,240 m a.s.l.) reveal a mean annual precipitation of 1,376 mm (23 days of snow cover) and a mean temperature of 7.4ºC. However, the lakes are situated at an altitude of between 1,565 m a.s.l. (El Valle) to 1,645 m a.s.l. (Calabazosa), where climatic conditions are notably more severe. The abundant snow precipitation and very cold temperatures prevailing in the lakes during the winter provokes the freezing of the surface of the lakes during several months (usually, early December to late March).

Materials and methods

Morphometric and bathymetric analysis of the lake basin

Detailed bathymetric maps of the lakes (Fig. 2) were constructed with GARMIN geographic positioning systems and Humminbird eco-sounders. The spatial and bathymetric data were then analyzed with ESRI ArcInfo 9.3 to carry out volumetric calculations.

Field work: Geochemical profiling and water sampling

We carried out field campaigns for geochemical profiling and water sampling in different periods from 2014 to 2016. For an important part of year (i.e., late autumn to early spring), access to the lakes with scientific equipment and for field work are both extremely difficult, so the samplings and monitoring were concentrated in the summer time (July to September). Hydrochemical parameters (including temperature –T–, specific conductance –SpC–, pH, redox potential –ORP–, dissolved oxygen concentration –DO–, total dissolved gas pressure –TDG–, photosynthetically active radiation intensity –PAR–, and chlorophyll-a concentration –chl-a–) were taken with multi-parametric probes (Hydrolab from Hach®; Pro Plus from YSI). All the measurements were taken under manual mode at constant depth intervals of 1 m. PAR (in µE m^{-2} s^{-1}) was measured with a LI-COR sensor that measures the intensity of light in the wavelength range 400-1100 nm. The chl-a sensor measures relative fluorescence signal and provides an estimate of chl-a concentration (in µg/L). The DO sensor measures oxygen concentration (O_2 in mg/L) by luminescence (0.01 mg/L precision).

Due to strong seasonal fluctuations of the water level, all the profiles were referenced to the conditions observed in the first sampling campaign (July 2014), which was the one in which the highest water levels were observed in all the lakes. The bottom most samples are thus roughly coincident between campaigns and the differences in depth are evidenced by the varying position of the water level of the lake.

Water samples for chemical analyses of major ion and nutrient concentrations were taken from different depths with a Van Dorn® sampling bottle (KC Denmark). Samples for chemical analyses were filtered on site with 0.45 µm nitrocellulose membrane filters (Millipore®), stored in polyethylene bottles (125-250 mL), and cool-preserved during transport. Samples for metal cation analyses were acidified with HNO_3 (1 M).

Chemical analyses of waters

Chemical analyses of the water were conducted by ion chromatography and continuous flow autoanalyzer for major anions (SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, HCO_3^-, CO_3^{2-}), total organic carbon (TOC), ammonia (NH_4^+) and silica (SiO_2), and by atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) for major cations (e.g., Ca, Mg, Na, K) and trace metals (e.g., Fe, Mn, Cu, Zn, As; though only a few elements will be discussed here). Detection limits for major ions ranged between 0.08 mg/L (e.g., PO_4^{3-}) to 0.02 mg/L (e.g., NO_2^-), whereas those for trace metals were usually better than 0.05 µg/L. Total phosphorus was also measured by UV-VIS spectrophotometry using a DR2800 (Hach) and LCS 349 cuvette tests (Lange). In this case, the detection limit was 10 µg/L as P_T.

Results

Stratification and limnological dynamics

The La Cueva Lake

In the sampling period, this lake experienced strong hydrological oscillations (Fig. 3), with water level fluctuations of up to 5 m between the location of maximum depth (21 m in July 2014) to the period of minimum depth (16 m in August 2015). This drop in the water level implied the loss of 270,000 m^3 of lake water, which represented 37% of the lake volume. These sharp variations of water volume were mostly imposed by hydrological regulation (i.e., use of lake water to supply the power station situated downstream; Fig. 2). In all cases, the lake showed a marked thermal stratification typical of the summer season, with a well-defined thermocline separating a lighter and warmer epilimnion (13-17 °C) from a lower and cooler hypolimnion (7-8 °C) (Fig. 3a).

The pH ranges of the lake water were 8.3-8.7 in the epilimnion and 7.0-8.3 in the hypolimnion (Fig. 3b). The SpC profiles (Fig. 3c) showed a shift to higher values at the lake bottom during the summer (e.g., from ~200 µS/cm in July to ~270 µS/cm in September 2014). The ORP was around 200-300 mV in the O_2-saturated epilimnion and as low as -100 mV near the lake bottom at the end of the stratification period (Fig. 3e).

The profiles of dissolved oxygen concentration

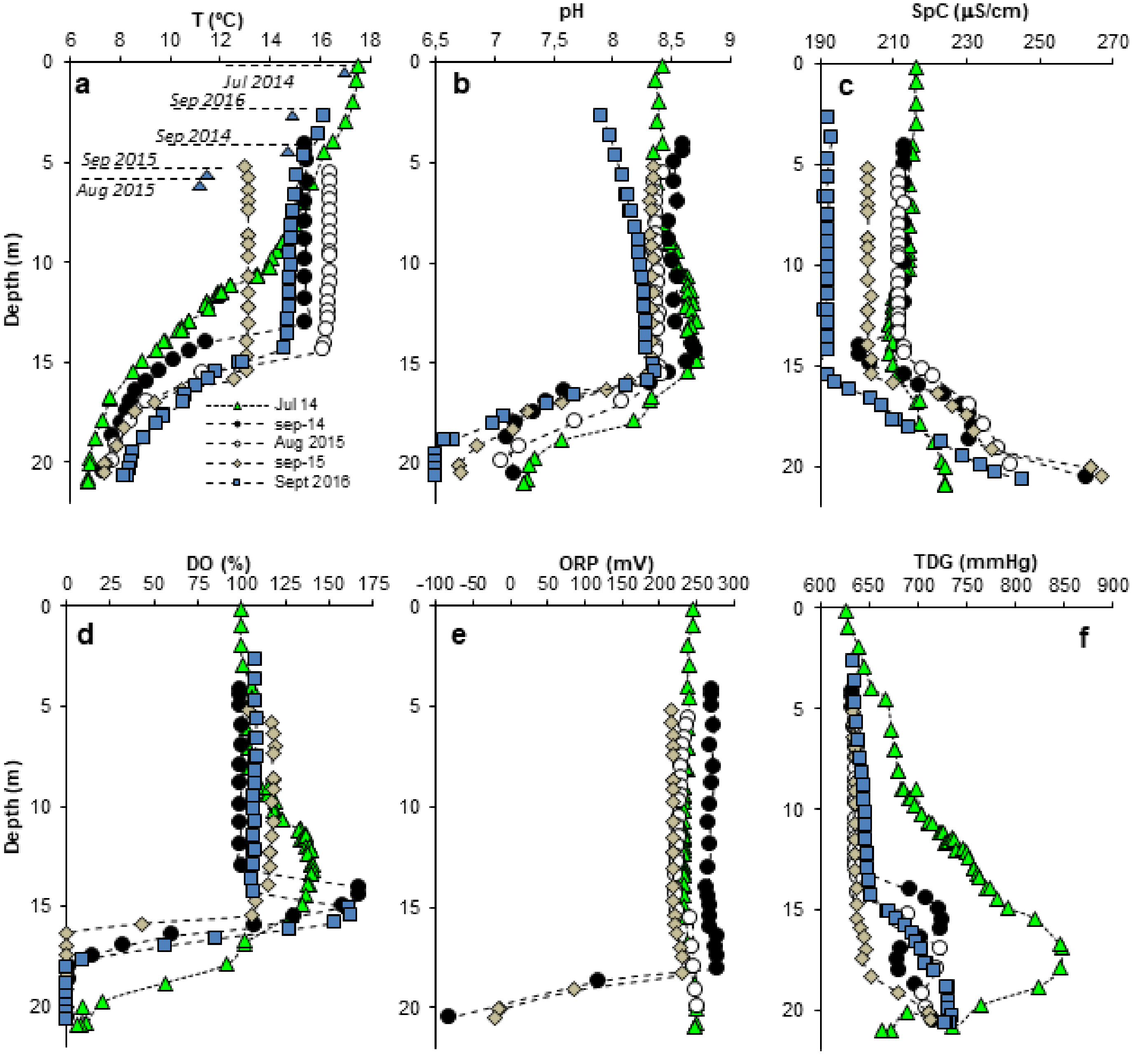

Figure 3. Vertical profiles of temperature (T), pH, specific conductance (SpC), dissolved oxygen (DO), redox potential (ORP), and total pressure of dissolved gases (TDG) in the La Cueva Lake, as measured on different dates.

Figura 3. *Perfiles verticales de temperatura (T), pH, conductividad específica (SpC), oxígeno disuelto (DO), potencial redox (ORP), y presión total de gases disueltos (TDG) obtenidos en diferentes épocas en el lago de La Cueva.*

(Fig. 3d) illustrate progressive oxygen depletion during the summer. The thickness of the anoxic hypolimnion increased from around 1 m in July to 3 m in September 2014 and up to 4 m (around 12% of the lake volume) in September 2015. This evolution suggests a strong oxygen demand by microbial respiration. Marked oxygen peaks in the thermocline (e.g., September 2014, DO~175% saturation) suggested intense photosynthetic activity by phytoplankton.

The profiles of TDG obtained in July 2014 and September 2014 (Fig. 3f) showed peaks around 740-860 mmHg which roughly matched those of dissolved oxygen in the photosynthetically active layer (Fig. 3d). However, the peak observed immediately above the sediments in September 2015 cannot be related with O_2 (which was completely absent during that period) and most likely indicates an increase in some other gases such as CO_2 resulting from either microbial respiration and/or calcite dissolution.

The profiles of PAR obtained in July and September 2014 showed two contrasting situations with regard to light penetration (Fig. 4a). In July 2014 the water transparency was extremely high (secchi depth ~12 m), and PAR could even reach the lake bottom (21 m depth) at low intensity. In September 2014, the water transparency was much lower (secchi depth ~4 m). The difference in chlorophyll-a concentration (Fig. 4b) does not account for such a contrast in transparency, so that the noted discrepancy is attributed to increased turbidity by suspended sediments in September as a result of hydrological regulation (i.e., inflowing waters pumped from Calabazosa) or by wind-driven circulation and runoff erosion of fine-grain sediments from the exposed lake shoreline.

The profiles of chl-a concentration obtained in these two periods (Fig. 4b) exhibited deep chlorophyll maxima (DCM) of 1.0-1.2 µg/L chl-a at around 16 m depth, where light intensity was around 4% of that measured at the surface. These DCM are related with corresponding oxygen maxima developed at the ther-

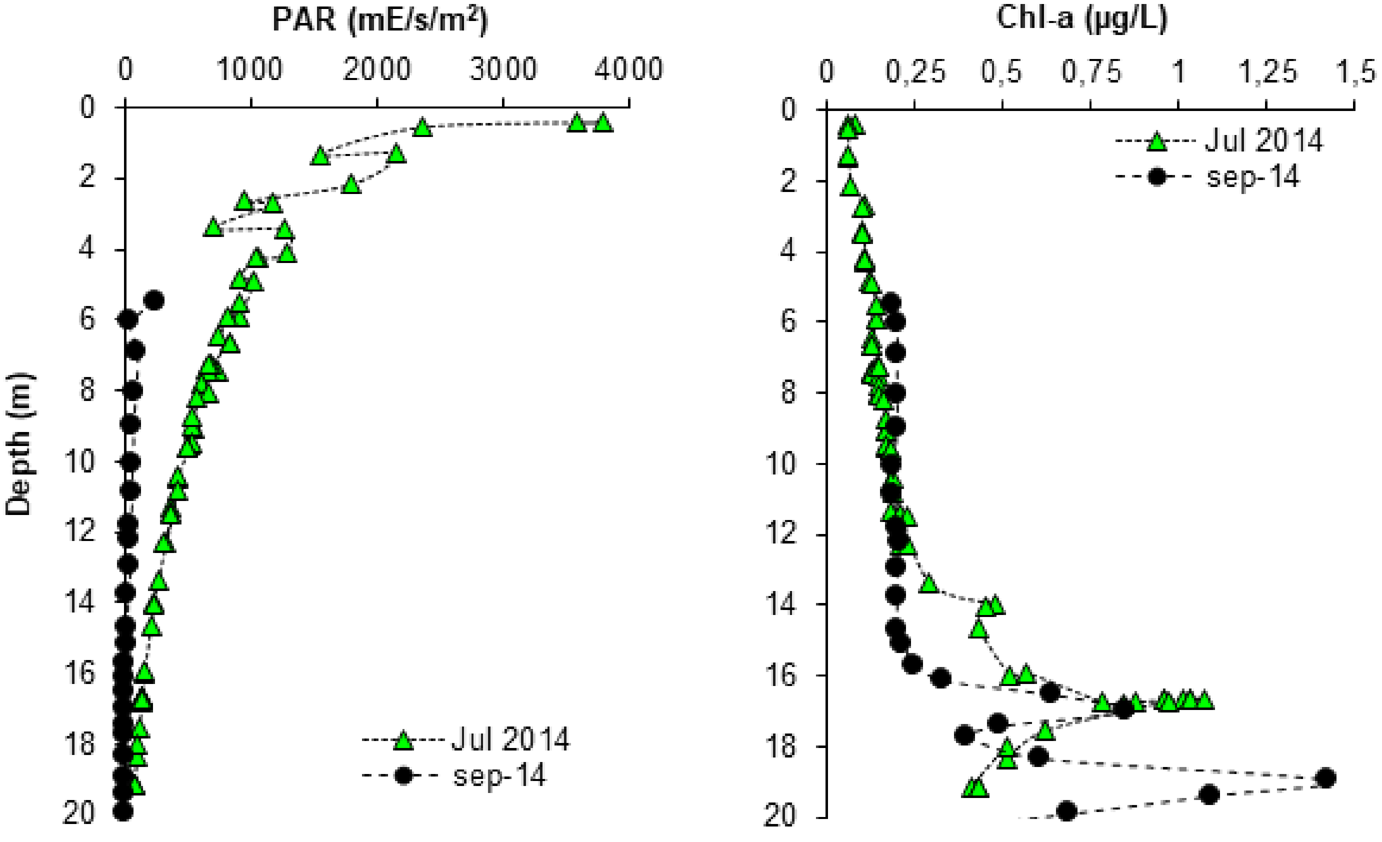

Figure 4. Vertical profiles of photosynthetically active radiation (PAR) and chlorophyll-a (Chl-a) concentrations in the La Cueva Lake, as measured on different dates.

Figura 4. *Perfiles verticales de radiación fotosintéticamente activa (PAR) y concentración de clorofila-a (Chl-a) obtenidos en diferentes épocas en el lago de La Cueva.*

mocline (Fig. 3c), and likely reflect a higher oxygen phytoplanktonic production. The chl-a concentrations measured in this layer (1.2 µg/L), however, appear too low to account for the high O_2 concentrations observed at this level. Possible explanations of this apparent contradiction could be related with either (1) metabolic strategies of the photosynthetic microalgae to cope with the low light conditions (Camacho, 2006), or alternatively, (2) the presence of bacterioplankton contributing to the photosynthetic O_2 production in the metalimnion, which would have been undetectable by our fluorescence sensor (which only measures chlorophyll-a). A second DCM was detected near the sediments in September 2014 (Fig. 4b), which could denote either resuspension of senescent algal cells from the bottom sediments or the existence of phytoplanktonic algae specialized in very low light conditions (Cullen, 1982).

The El Valle Lake

The deepest point recorded in this lake was ~26 m in its southern sub-basin (Fig. 2), though Rodriguez *et al.* (2013) reported a maximum depth of 29,2 m in 2013. The hydrological fluctuation observed in this lake during the studied period was ~2.5 m (Fig. 5a). The volume of water lost by this lake during this period was ~320,000 m^3, representing 16% of its total volume. This lake also showed a marked thermal stratification during the summer season (Fig. 5a).

The profiles shown in Figure 5 for July 2014 correspond to two different points sampled in two subbasins with notably distinct depths (Figs. 1-2). The comparison of these two profiles demonstrates that, apart from temperature (which shows lateral homogeneity), the rest of parameters show lateral gradients which probably result from the differing distances to the reactive sediment/water interface.

The pH of the lake water was slightly lower than that measured in the La Cueva lake (7.7-8.6 in the epilimnion and 6.5-7.5 in the hypolimnion; Fig. 5b). The specific conductance profiles (Fig. 5c) also showed slight increases in the hypolimnion during the summer period. The measured ORP fluctuated between 150 and 300 mV in the epilimnion and was at nearzero values near the lake bottom (Fig. 5d).

The DO profiles obtained in July 2014 and September 2016 showed slight peaks of DO concentration at depths around 8-10 m (Fig. 5e) followed by strong declines at depth due to biological consumption, but the rate of oxygen depletion in this lake is apparently less than in the La Cueva lake and probably indicates a lower productivity.

The Calabazosa (or *Lago Negro*) Lake

The Calabazosa Lake (also called *Lago Negro* due to its dark-coloured waters) is considered the deepest lake in the Cantabrian Ridge (López & Ramos, 2007), though no bathymetric study was available for this water body. Our bathymetric survey shows a subrounded basin with a maximum depth of 50 m (Fig. 2). This notable depth with respect to the rest of the lakes could have resulted from a more intense karstic dissolution favoured by tectonic structures (due to intense fracturing by folding and a fault in the southwest edge of this lake), combined by ice excavation during the glacial period.

A sharp stratification was clearly observed in September 2016 (Fig. 6a): a thermocline situated at around 10 m separated a warmer epilimnion (T=14-16 ºC) from an underlying and cooler hypolimnion (T=4-5 ºC). Important vertical variations of pH, specific conductance, ORP and DO were also observed (Fig. 6b-e). The most outstanding feature was related with the existence of a metalimnetic oxygen maximum in the thermocline, with concentrations approaching 230 %sat. (ca. 22 mg/L O_2) in a layer comprised between 9 and 14 m depth (Fig. 6d). No data on chl-a concentration could be obtained for this lake, but the water had a characteristic green colour suggesting the presence of abundant phytoplankton. Below this depth, oxygen concentration declined sharply to very low values (2 mg/L O_2 or 20%sat.) between depths of 20 and 40 m, and turned completely anoxic in the deepest layer (Fig. 6d). These data imply that 37% of the lake volume was virtually devoid of oxygen. The anoxic bottom layer exhibited low ORP typical of reducing environments and higher specific conductance denoting higher dissolved solid contents.

These geochemical profiles suggest that Lake Calabazosa is likely more productive than the rest of lakes in this Natural Park. A thicker photosynthetic layer in the photic zone is likely driving organic matter decomposition and mineralization in the deep hypolimnion. This phosynthetic activity is probably contributing to the pH increase in this zone, which reaches abnormally high values of 9.2 (Fig. 6b). The pH, SpC and TDG profiles suggest vertical cycling with calcite precipitation in the photosynthetic layer followed by calcite dissolution at depth.

The Cerveriz Lake

Due to its shallowness (max depth of 7 m, average depth around 2.5-3.0 m), this shallow lake showed a homogenous water column indicating full mixing

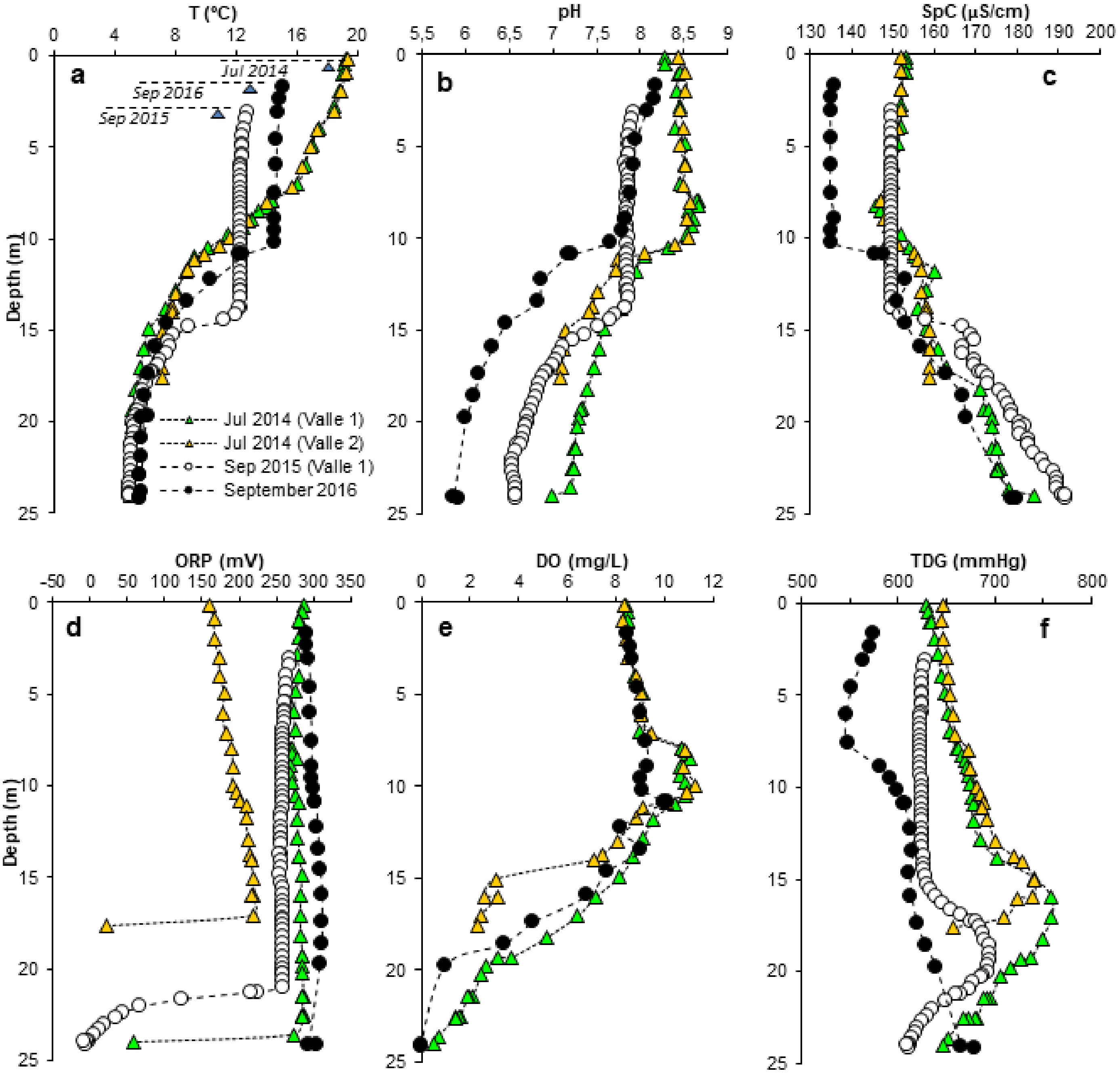

Figure 5. Vertical profiles of temperature (T), pH, specific conductance (SpC), dissolved oxygen (DO), redox potential (ORP), and total pressure of dissolved gases (TDG) in the El Valle Lake, as measured on different dates.

Figura 5*. Perfiles verticales de temperatura (T), pH, conductividad específica (SpC), oxígeno disuelto (DO), potencial redox (ORP), y presión total de gases disueltos (TDG) obtenidos en diferentes épocas en el lago de El Valle.*

(Fig. 7). With the exception of a few cm above the sediment/water interphase, no vertical gradient was observed; the water thickness is probably too low to allow thermal stratification. The shallow shores are densely colonized by *Potamogeton* and charophytes. The lake showed an important oxygen deficit at the time of sampling, with low oxygen content (4.5-6 mg/L O_2, 48-60% sat.) across the water column (Fig. 7), which indicates microbial respiration and organic matter decomposition in the sediments.

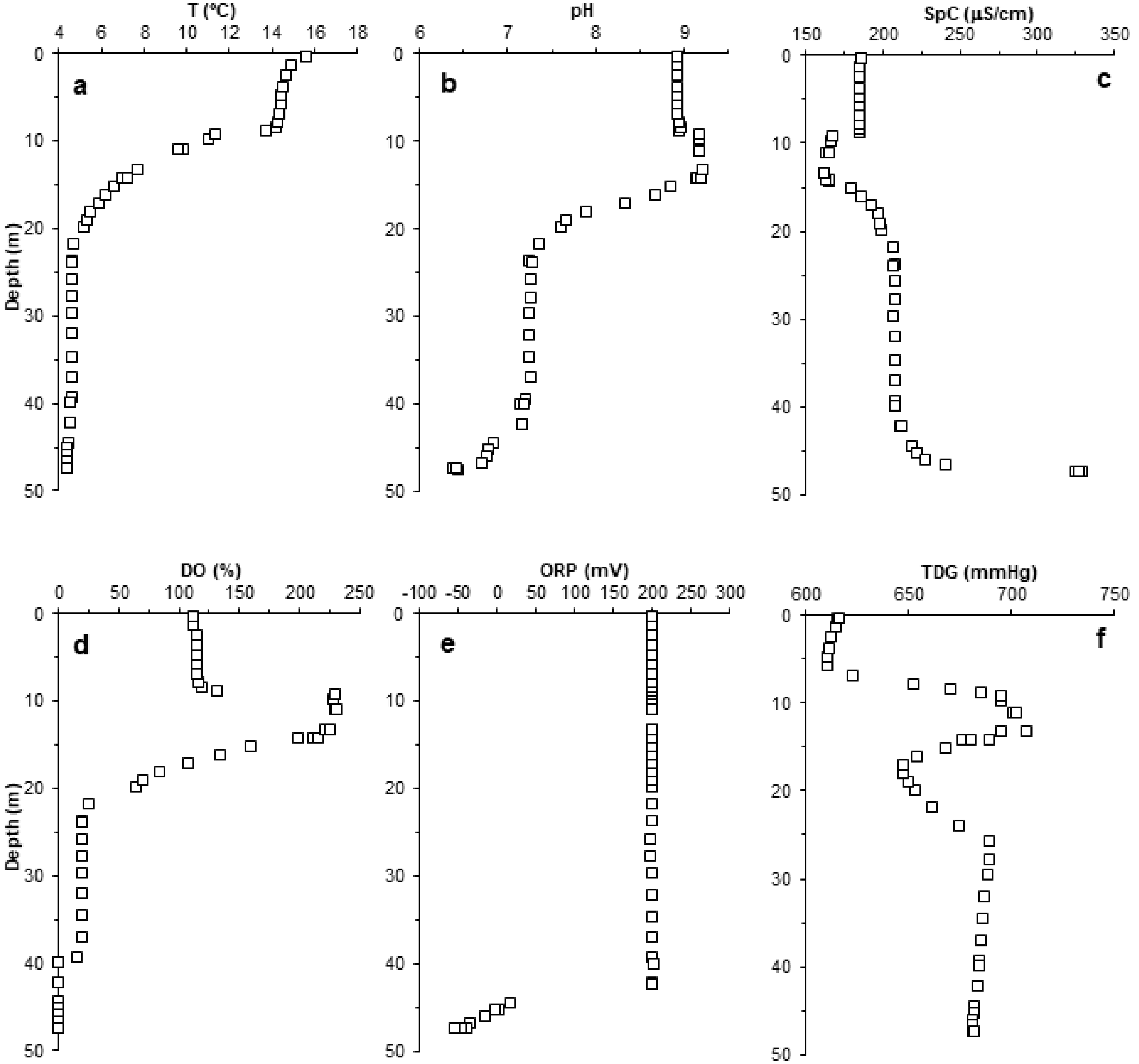

Figure 6. Vertical profiles of temperature (T), pH, specific conductance (SpC), dissolved oxygen (DO), redox potential (ORP), and total pressure of dissolved gases (TDG) in the Calabazosa Lake, as measured in September 2016.

Figura 6*. Perfiles verticales de temperatura (T), pH, conductividad específica (SpC), oxígeno disuelto (DO), potencial redox (ORP), y presión total de gases disueltos (TDG) obtenidos en septiembre de 2016 en el lago de Calabazosa.*

Water chemistry

The vertical variations of TOC, nitrate, and total iron and manganese concentration in the El Valle and La Cueva lakes (the lakes with more profiles available) are shown in Figure 8. Additional information on major cations and selected trace elements (including phosphorus) is provided in Table 2 for the four lakes. A summary with ranges of total phosphorus and nitrogen concentrations is given in Table 3.

Nutrients and major ions

Carbon, nutrient and metal concentrations varied seasonally during the studied period (Fig. 8): TOC varied

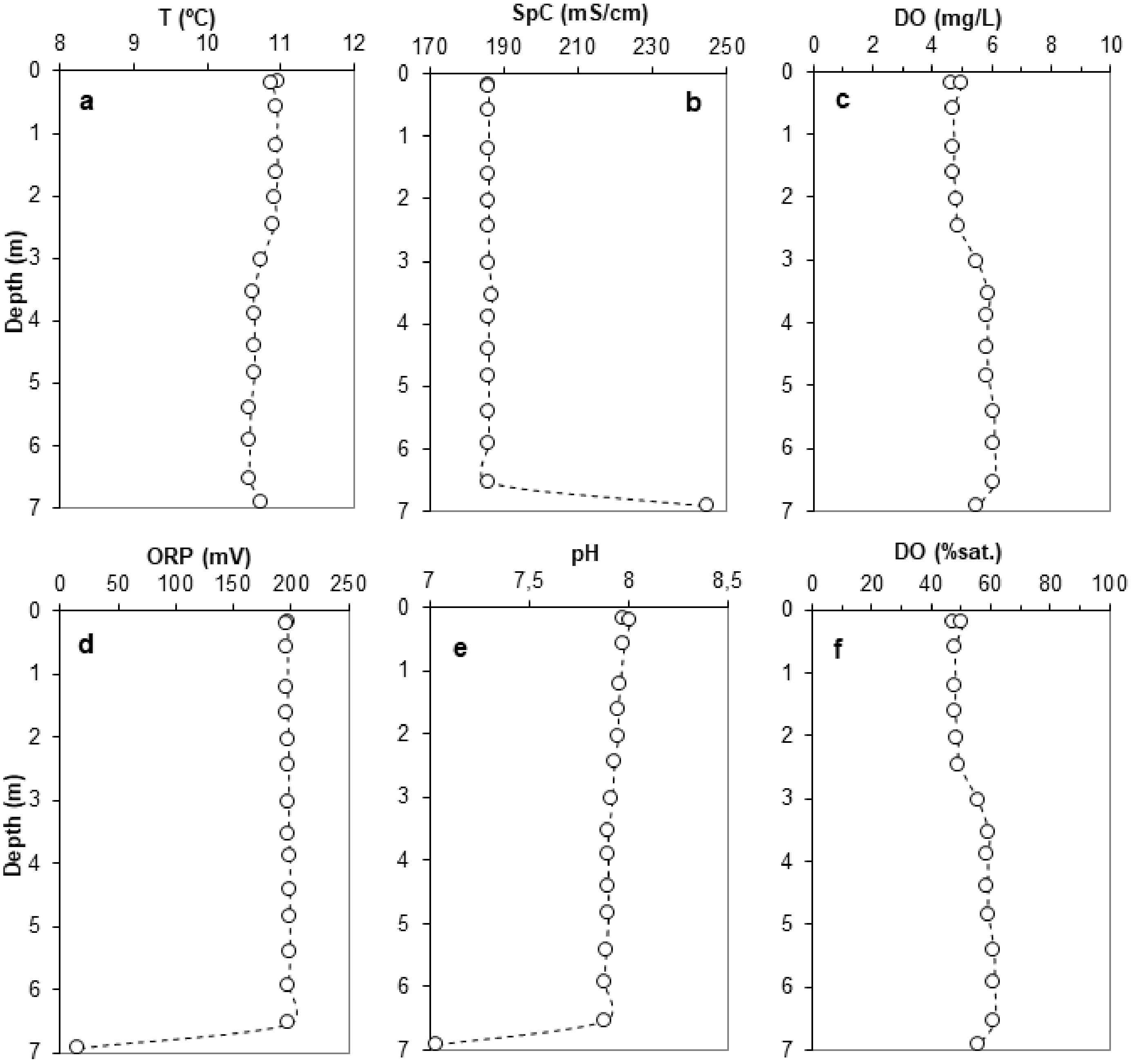

Figure 7. Vertical profiles of temperature (T), specific conductance (SpC), dissolved oxygen (DO, in mg/L and as % saturation), redox potential (ORP) and pH in the Cerveriz Lake, as measured in September 2015.

Figura 7. *Perfiles verticales de temperatura (T), conductividad específica (SpC), oxígeno disuelto (DO), potencial redox (ORP) y pH obtenidos en septiembre de 2015 en el lago de Cerveriz.*

from 0.8 to 2.2 mg/L in the La Cueva Lake, and between 0.8 and 2.8 mg/L in the El Valle Lake; nitrate was 0.2 to 1.2 mg/L in La Cueva and between 0.6 and 1.8 mg/L in El Valle; phosphate was below detection limit (<0.08 mg/L PO_4^{3-}, or <25 µg/L P-PO_4^{3-} Table 2) in both cases, and total phosphorus concentrations were in the range of 10-19 µg/L P in El Valle and 13-18 µg/L in La Cueva (Tables 2-3). The concentration of phosphorus was significantly higher in the Cerveriz Lake (28 µg/l P) and the Calabazosa Lake (35 µg/l P) (Tables 2-3). This contrast of phosphorus content amongst the lakes has allowed us to establish a clear trend in their trophic state and productivity, as discussed below.

The maximum concentration of manganese above the sediments at the end of the summer season (e.g., September 2014-2016) was around 600 µg/l Mn in

Depth	**Major ions**								**Trace elements**				
	Ca	**Mg**	**Cl**	**SO_4**	**HCO_3^-**	**CO_3^{2-}**	**PO_4^{3-}**	**SiO_2**	**P_T**	**Al**	**As**	**Cu**	**Zn**
m	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*	*µg/L*
Lake La Cueva													
0,5	23	14	2	2	138	n.d.	<0,08	0,3	16	4	0,5	0,3	9
5	23	14	2	2	139	n.d.	<0,08	0,3	17	5	0,6	0,4	6
10	23	13	1	1	137	n.d.	<0,08	0,2	18	3	0,3	0,0	4
15	24	13	1	1	138	n.d.	<0,08	0,2	17	4	0,4	0,5	14
20	26	13	1	1	146	n.d.	<0,08	0,9	18	116	1,2	1,5	90
MT	29	15	2	4	123	n.d.	<0,08	1	13	10	0,5	0,2	16
Lake El Valle													
0,5	21	6	2	1	91	n.d.	<0,08	0,3	10	7	0,5	0,8	8
5	20	7	1	1	92	n.d.	<0,08	0,3	n.a.	12	0,6	0,5	13
10	21	8	1	2	96	n.d.	<0,08	0,5	n.a.	8	0,5	0,5	15
17	22	9	1	1	106	n.d.	<0,08	1,6	19	13	0,8	0,7	25
24	24	9	2	2	111	n.d.	<0,08	2,6	18	23	0,5	0,9	30
Lake Cerveriz													
0,5	24	9	n.d.	1	123	n.d.	<0,08	1,5	n.a.	7	0,6	0,4	n.a.
4	24	9	n.d.	1	123	n.d.	<0,08	1,5	n.a.	8	0,8	0,4	n.a.
6,5	24	9	n.d.	1	122	n.d.	<0,08	1,5	28	8	0,8	0,3	n.a.
Lake Calabazosa													
0,5	15	12	2	7	116	4	<0,08	0,1	35	6	0,1	1,0	4

P_T, total phosphorus; MT, mine tunnel effluent; n.d., not detected; n.a., not analyzed.

Table 2. Chemical composition (major ions and selected trace elements) of the Somiedo lakes at different depths.
Tabla 2. *Composición química (iones mayoritarios y elementos traza seleccionados) de los lagos de Somiedo a diferentes profundidades.*

Lake	**Secchi Disk**	**Total phosphorus**	**Total nitrogen**	**Chl-a**	**RAOD**$^{(1)}$	**TSI**$^{(2)}$	**TS**$^{(3)}$
	(m)	(µg/L)	(µg/L)	(µg/L)	(mg O_2 cm^{-2} day^{-1})		
El Valle	7-8	10-19	300-680	*n.m.*	0,001	30-40	Oligotrophic
La Cueva	4-12	13-18	350-520	0,2-1,5	0,017	20-40	Oligotrophic
Cerveriz	2-3	28	*n.m.*	*n.m.*	0,033	50	Mesotrophic
Calabazosa	2-3	35	*n.m.*	*n.m.*	0,15	50-60	Meso-eutrophic

n.m., not measured; (1) Relative areal oxygen deficit (after Hutchinson, 1957); (2) trophic state index (after Carlson, 1977); (3) classical trophic classification (according to Vollenweider, 1979, and Weztel, 2001).

Table 3. Summary of selected variables associated with the trophic state for the Somiedo lakes and the trophic classification based on different criteria.
Tabla 3. *Resumen de variables seleccionadas asociadas con el estado trófico de los lagos de Somiedo y clasificación trófica provisional basada en diferentes criterios.*

both cases, but the iron concentration was much higher in the La Cueva Lake (1,500-4,500 µg/l Fe) as compared to the El Valle Lake (450-1,100 µg/l Fe). Both metals increased notably during the summer (Fig. 8b,f).

The dominant ions in all lakes are bicarbonate

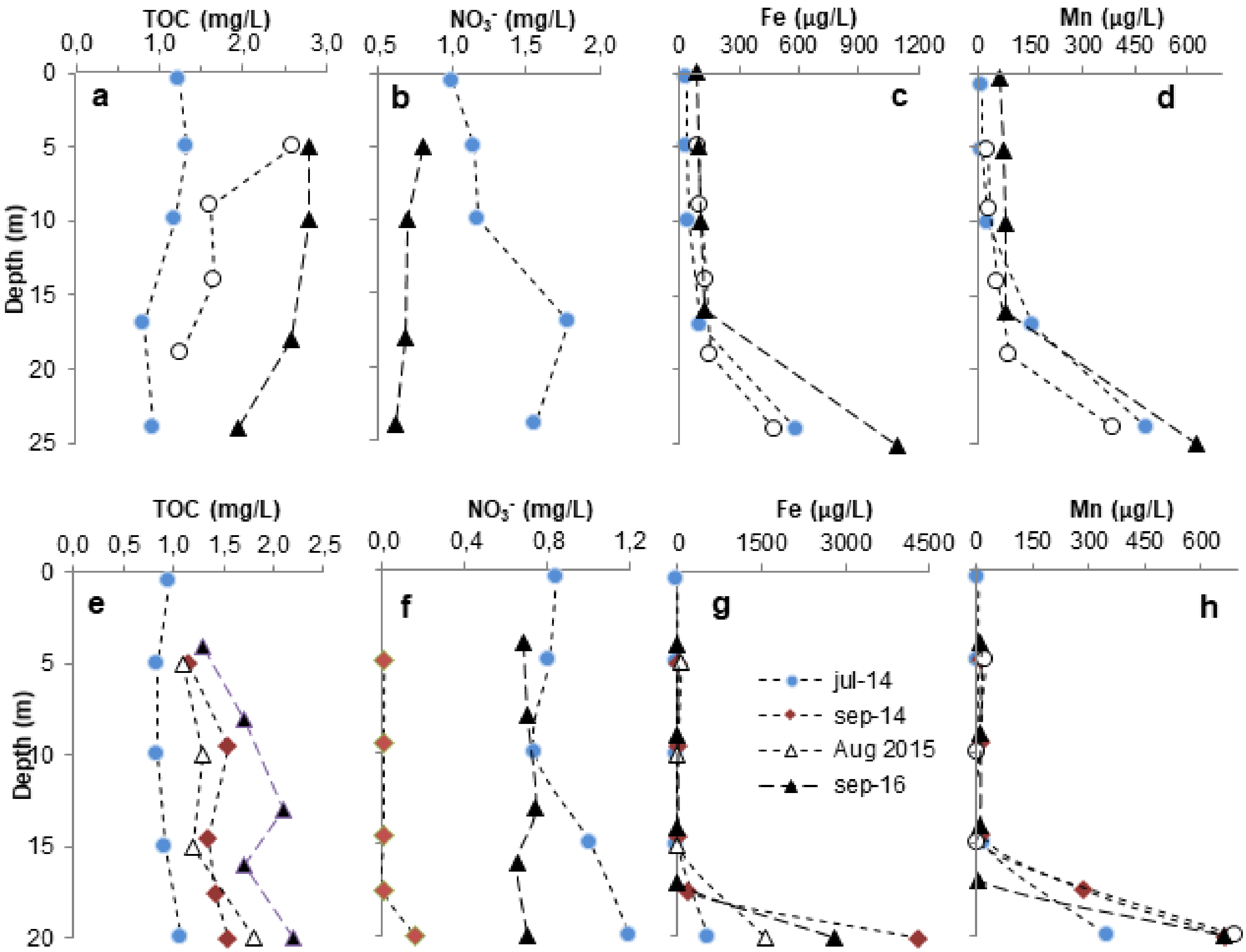

Figure 8. Vertical profiles of total organic carbon (TOC), nitrate (NO_3^-), total dissolved iron (Fe), and total dissolved manganese (Mn) in the El Valle Lake (*top*) and the La Cueva Lake (*bottom*), as measured on different dates.
Figura 8. *Perfiles verticales de carbono orgánico total (TOC), nitrato (NO_3^-), hierro disuelto total (Fe) y manganeso disuelto total (Mn) obtenidos en diferentes épocas en los lagos de El Valle (arriba) y La Cueva (abajo).*

(e.g., 138-146 mg/L and 91-111 mg/L HCO_3^- in the La Cueva and El Valle lakes, respectively; Table 2) and calcium (15-29 mg/L Ca), in accordance with the dominant carbonate lithology of the area. Calabazosa was the only lake in which some trace carbonate content (4 mg/L CO_3^{2-}) could be detected, which is in accordance with its more alkaline nature (pH 9.2; Fig. 6b). Given the limited amount of physico-chemical information available for this lake, we cannot yet ascertain if this is a permanent geochemical feature or just a temporal process favoured by a higher photosynthetic activity in the phytoplanktonic layer during the summer time.

Sulphate, chlorine and dissolved silica are present at very low concentrations in all the lakes (1-7 mg/L SO_4^{2-}, 1-2 mg/L Cl, 0.1-2.6 mg/L SiO_2; Table 2).

Trace metals

All the lakes showed a reasonably good environmental state with regard to metal pollution, with all the metals analyzed close to or below the detection limit (<0.05 µg/L; e.g., Ag, Be, Cd, Co, Cr, Hg, Mo, Ni, Pb, Sb, Se, Th, Tl, U, V; *not shown*). Aluminum and zinc (with maximum contents of 116 µg/L Al and 90 µg/L

Zn in the La Cueva Lake, and 23 µg/L Al and 30 µg/L Zn above the sediments in the El Valle Lake) were the most abundant (Table 2). Arsenic and copper were also detected at very low contents (<1 µg/L in both cases). The inflow seeping from an adjacent mine tunnel in the La Cueva Lake did not show any significant metal content (Table 2), though it exhibited a high nitrate concentration in September 2015 (24.5 mg/L NO_3^-; *not shown*), which was attributed to the presence of cattle.

Discussion

Biogeochemical cycling of carbon and metals

The chemical gradients observed in the studied lakes (especially in La Cueva and Calabazosa lakes) denote hypolimnetic decomposition and mineralization of settling phytoplankton biomass coupled to metal cycling (Wetzel, 2001). Microbial respiration leads to strong oxygen depletion and, finally, to a severe anoxia that persists for most of the summer season. Subsequent anaerobic respiration is then coupled to iron and manganese oxide reduction (Lovley and Phillips, 1988; Wetzel, 2001), which results in significant increases of Fe and Mn concentrations at depth. These biogeochemical reactions release carbon dioxide as a main product of organic matter oxidation, so the TDG increments measured above the sediments in the lakes at the end of the summer (Figs. 3f, 5f) probably reflect the release of CO_2 from the sediments. Although the presence of other gases such as methane (CH_4) or hydrogen sulphide (H_2S) cannot be totally ruled out, the moderate to high ORP values measured in the layers corresponding with the TDG peaks (200-300 mV; Figs. 3 and 5), and the lack of odour in water sampled from these depths, suggest that these other gases are probably negligible. The reductive dissolution of Fe and Mn solids is also responsible, by desorption, for parallel increases in the concentration of trace metals present in these phases, such as Al or Zn (Table 2). The higher concentration of $Fe^{(II)}$ above the sediments in the La Cueva Lake with respect to the El Valle Lake may be a consequence of a longer period of hypolminetic anoxia, but could also be related with the chemical nature of the iron-rich muds deposited on the bottom of this lake.

The re-oxidation of $Fe^{(II)}$ and Mn during re-oxygenation of the anoxic hypolimnion leads to re-precipitation as amorphous iron and manganese oxides or oxy-hydroxides. The formation of Fe and Mn precipitates (composition confirmed by SEM studies; *not shown*) was observed during filtration and sampling of anoxic hypolimnetic water in September 2015, when the oxygenation quickly produced turbidity.

Trophic state and its relationship with anthropogenic pressures

Selected variables associated with the trophic state of the lakes (e.g., secchi depth, chlorophyll-a concentration (if available), phosphorus and nitrogen content, and relative areal oxygen deficit (RAOD) –Hutchinson 1938, 1957) are given in Table 3. Although the amount of data is still limited, these variables have allowed us to provisionally classify the studied lakes based on different criteria and with the available information being taken into account. We have included the trophic state index (TSI; after Carlson, 1977), and the classical trophic classification according to Vollenweider (1979) and Wetzel (2001). In the absence of detailed biological information (e.g., productivity rates, phytoplankton biomass), the RAOD may serve as a good approximation of the productivity of the studied lakes. The RAOD considers the consumption of dissolved oxygen in the hypolimnion during the summer stratification period, and relates this oxygen amount to the surface area of sediments overlaid by anoxic water (details about RAOD definition and calculation are given in Cornett and Rigler, 1980; see also Wetzel, 2001). Taking into account the calculated volumes and respective surface areas of the hypolimnion in the studied lakes, and considering the evolution of dissolved oxygen concentration during the summer period, we have estimated the apparent RAOD and its relationship with measured concentrations of total phosphorus (Table 3; Fig. 9). The plot of Figure 9 suggests a high correlation between the apparent lake productivity (as deduced from the RAOD) and phosphorus concentration, which is coherent with the well-known dependence of algal abundance on P availability (Dillon and Rigler, 1974; Van Nieuwenhuyse and Jones, 1996). This trend suggests an apparent evolution from oligotrophic (El Valle) to mesotrophic (Cerveriz) and finally, eutrophic conditions (Calabazosa) as a natural response of these systems to increased P inputs from the catchment. This variable trophic state is also suggested by the other trophic indices provided in Table 3.

The Calabazosa Lake shows surprisingly high epilimnetic photosynthetic production and hypolimnetic consumption of DO that is uncommon amongst high mountain lakes of the Iberian Peninsula (e.g., Catalán *et al.,* 1992; Morales *et al.,* 1992; Toro *et al.,* 2006). In a large-scale study on the lakes and ponds of the Iberian Peninsula, Alonso (1998) classified this lake as

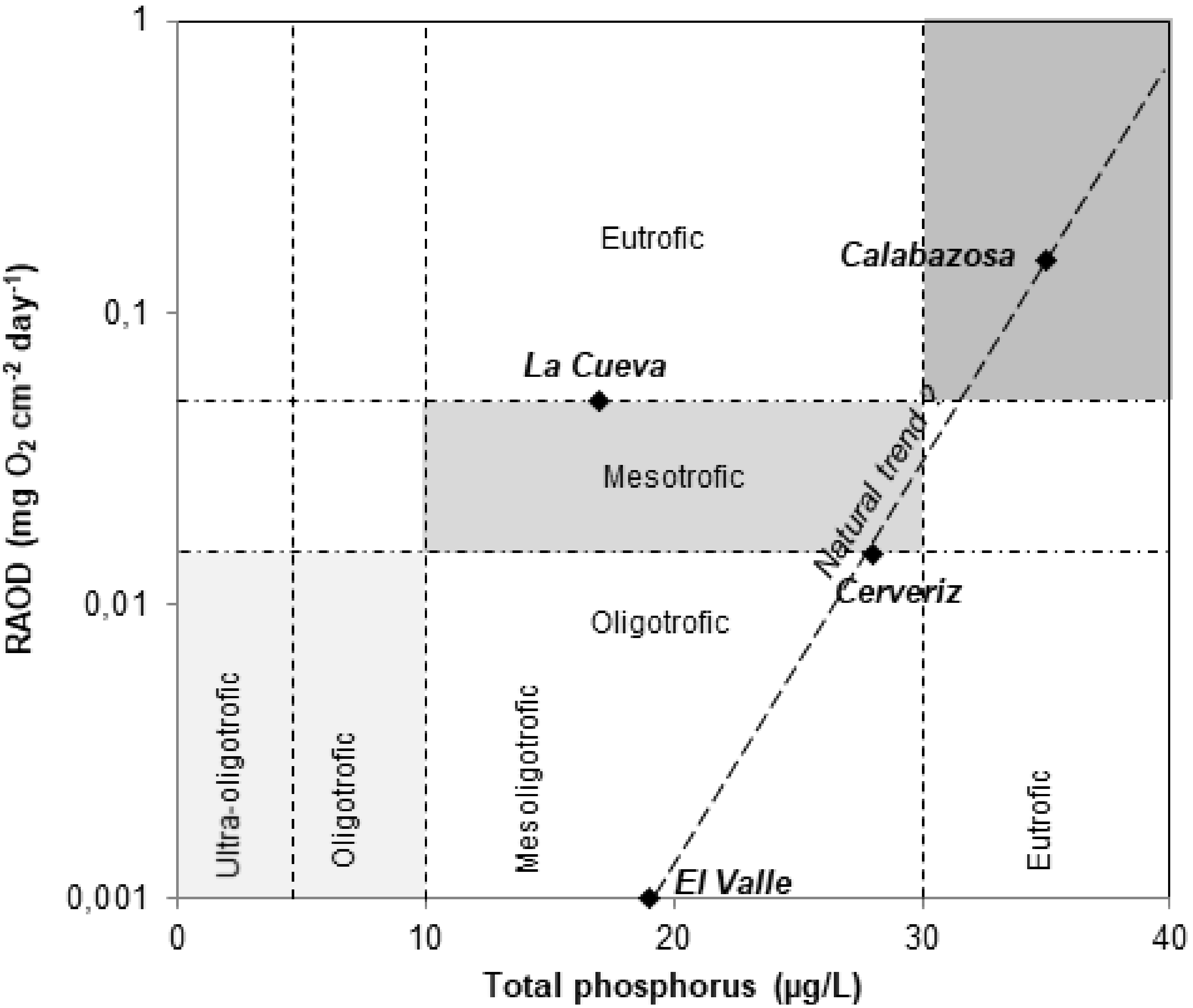

Figure 9. Binary plot of total phosphorus concentration against the relative areal oxygen deficit (RAOD) in the studied lakes. The limits for oligotrophic, mesotrophic and eutrophic conditions as defined by the RAOD value (horizontal dashed lines; from Hutchinson, 1957) and the total phosphorus content (vertical dashed lines; from Catalán *et al.,* 1992) are indicated.

Figura 9. *Diagrama binario de concentración de fósforo total frente al déficit relativo de oxígeno superficial (RAOD) en los lagos estudiados. Se indican los límites para las condiciones oligotróficas, mesotróficas y eutróficas definidas por el valor de RAOD (líneas horizontales discontinuas; tomado de Hutchinson, 1957) y el contenido en fósforo total (líneas discontinuas verticales; tomado de Catalán et al., 1992).*

oligotrophic, though this author did not provide any information on water chemistry. The data presented in this study suggest that some degree of eutrophication could have taken place in the last two decades. The reasons for the phosphorus enrichment of this lake are still unknown and should be further studied. Phosphorus fertilization is usually related with cattle grazing (e.g., Declerck *et al.,* 2006; Downs *et al.,* 2008; Hundey *et al.,* 2014), atmospheric deposition (e.g., Johannessen *et al.,* 1984; Morales *et al.,* 2006) or with combined anthropic impacts at the catchment-scale (Antoniades *et al.,* 2011). Livestock grazing around the lakes does not seem to have increased the nitrate and phosphorus contents. The El Valle Lake, where the presence of cattle is probably more significant, showed low phosphorus contents and only slightly higher nitrate concentration (Tables 2-3; Fig. 8b), and its oxygen photosynthetic production and RAOD remain low and do not suggest eutrophication.

The La Cueva Lake deviates significantly from this apparent eutrophication trend, showing a high RAOD despite a low P content (Fig. 9). The catchment area of this lake shows significant erosive processes (e.g., landslides, debris-flows, creeping soils; Table 1) due to intensive mining. A plausible explanation of this apparently anomalous behaviour is therefore that a higher erosion rate is driving a higher input of external organic matter and a higher oxygen consumption, which does not depend on lake productivity.

In addition to the impact on oxygen consumption, mining activity could have also led to other deleterious effects on the lake ecology. Although no toxic metal pollution has been detected in the water column, long periods of turbidity by deposition of large volumes of iron-rich muds from the adjacent mine and later remobilization of fine particles on the shores by strong hydrological fluctuations, could have resulted in a loss of biodiversity and/or biomass changes. This possibility deserves further study.

Conclusions

The hydrological regulation through intermittent pumping of the studied lakes imposes significant water level oscillations that favour erosion of the shorelines and sediment re-suspension. The erosion of adjacent soils and mine wastes increases sediment and organic matter input into the lakes. This is especially relevant in the La Cueva Lake since its catchment area has been greatly transformed by mining.

The obtained data on nutrients (P, N), chl-a, and DO concentration indicate a variable trophic state ranging from oligotrophic (El Valle) to eutrophic (Calabazosa). This eutrophication seems to be driven by an increased P content whose origin is still unclear. The La Cueva Lake deviates from this trend and shows a high oxygen consumption rate despite its relatively low P content, which is ascribed to the aforementioned import of sediments and organic matter from the catchment. In the Calabazosa and La Cueva lakes, biological productivity in the photic zone seems to be important and is favouring organic matter decomposition and oxygen consumption. A slightly higher nitrate content in the El Valle Lake compared to the other lakes is likely to be related with a greater presence of cattle, though this lake remains oligotrophic due to strong phosphorus limitation.

Despite the intense transformations experienced by the lakes during ancient and modern times, no evident signs of heavy metal pollution have been detected. The high content of dissolved iron found in the La Cueva Lake can be related with a longer stratification period and/or with the presence of iron-rich mine wastes. Further research should evaluate the impact of mining on the ecology of this lake (especially with regard to toxic metal contents –e.g., As, Pb, Hg– in lake sediments and surrounding soils).

The narrow observation window of this study, which has only considered the stratification period typical of the summer season, suggests that the research on these lakes should be extended to other seasons to gain knowledge of their stratification regime. This research should also include their hydrochemical and ecological functioning, including their oxygen dynamics and its relation with primary production (photosynthetic activity of phytoplanktonic communities), and with carbon and nutrient availability. For example, the study of these lakes in the winter season would allow us to demonstrate their probable dimictic nature, with inverse thermal stratification below the ice cover, which is a common feature in many high mountain lakes. Moreover, the sources and transport mechanisms of phosphorus in the Calabazosa and Cerveriz lakes (e.g., atmospheric pollution *vs*. sediment transport from the catchment) should also be investigated, as this information has clear implications for the conservation of this protected natural area.

Acknowledgements

This work has been funded by the Instituto Geológico y Minero de España (IGME) through project SINGER (Ref. number 2459). The staff of the Somiedo Natural Park is acknowledged for permission given to conduct the field work. We thank Fernando Barreiro-Lostres and Maria Leunda for field-work assistance and bathymetric data for the La Cueva Lake.

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Recibido: febrero 2018
Revisado: mayo 2018
Aceptado: septiembre 2018
Publicado: junio 2019