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Short-term nutrient fluxes of a groundwater-fed, flow-through lake

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ABSTRACT

Short-term nutrient fluxes of a groundwater-fed, flow-through lake

Nutrient fluxes take place in lakes through different flow paths, and the importance of their nutrient flux changes depend on the biogeochemical processes involved. In flow-through lakes, the hydrological control of these flux processes appears to be very important, but the significance of other processes is poorly understood. To test this significance, we analyzed C, N and P fluxes on a weekly scale during mid-stratification in a Spanish calcareous lake fed by agriculturally-drained streams and groundwater. As expected, hydrologic flow paths were more important than those of biogenic fluxes for the nutrient budgets. The organic C (OC hereafter), total N and total P surface inflows and outflows differed. While C and N surface hydrological fluxes covaried, P input or output fluxes were unrelated with those of other nutrients. Net groundwater C and P fluxes covaried, but they were not related with those of N. The accumulations of OC, N and P were also related with each other.

All of the biogenic fluxes were highly variable. Primary production by emergent plants (*Cladium*) were higher than water column photosynthesis, the latter being net autotrophic most of the time. Particulate nutrient settling rates were within the range of those in oligotrophic lakes. Denitrification was not as high as expected in the nitrate-rich water of this lake, which was limited by low levels of soluble reactive phosphorus and dissolved organic carbon. CO_2 degassing from the surface to the atmosphere was always positive, suggesting net heterotrophy, but this was the opposite of previous results. These conflicting results could be reconciled by the high hydrological inputs of inorganic carbon, which yielded more carbon dioxide to be outgassed. Albeit low, the CO_2 production from $CaCO_3$ formation could sometimes be a source of CO_2.

However, the biogenic fluxes were higher than expected in flow-through lakes, mostly arising from the role of littoral emergent plants in nutrient fluxes, which was often neglected in biogeochemical budget studies. Furthermore, no relationship was found between water renewal time and accumulation, thus emphasizing the significance of biogenic fluxes on nutrient retention. At the ecosystem level, our study highlighted both the importance of the hydrogeological setting of the basin on nutrient fluxes and the importance of emergent vegetation on lake nutrient budgets.

Key words: Nutrient accumulation, lake metabolism, water renewal, emergent plants, basin geology.

RESUMEN

Flujos de nutrientes a corto plazo en un lago fluvial alimentado por aguas subterráneas

Los flujos de nutrientes tienen lugar en los lagos siguiendo líneas de flujo diferentes, cuya importancia depende de los procesos biogeoquímicos implicados en ellos. En los lagos fluviales el control hidrológico de estos flujos es muy notable, pero la importancia de otros procesos sobre dicho control aún se conoce mal. Con objeto de mejorar el conocimiento de estos aspectos limnológicos, analizamos aquí los flujos de C, N y P a escala semanal durante el periodo central de la estratificación en un lago calcáreo español (laguna Conceja, Centro de España), alimentado por ríos y agua subterránea que han drenado zonas agrícolas. El transporte hidrológico fue más importante que los flujos biogénicos en los balances de nutrientes. Las entradas de carbono orgánico, nitrógeno y fósforo totales fueron diferentes de las salidas. Aunque los flujos hidrológicos superficiales de C y N covariaron, las entradas y salidas de P no lo hicieron. Los flujos subterráneos de C y P covariaron, pero no se relacionaron con los de N. Las acumulaciones de C orgánico, N y P estuvieron relacionadas entre sí.

*Todos los flujos biogénicos de nutrientes fueron muy variables. La producción primaria debida a las plantas emergentes (*Cladium*) fue mayor que la fotosíntesis en la columna de agua, la cual experimentó una autotrofia neta durante la mayor parte del periodo de estudio. La sedimentación de los nutrients particulados estuvo dentro del rango de la observada en otros lagos oligotróficos. La desnitrificación no fue tan alta como la esperada a juzgar por el elevado contenido en nitrato del lago, lo cual se debió a la limitación por las escasas concentraciones de fósforo reactivo soluble y carbono orgánico disuelto. El* *lago perdió CO_2 hacia la atmósfera, lo cual sugiere heterotrofia neta, cosa que contradice el resultado referido más arriba, estos datos contradictorios se explican teniendo en cuenta las elevadas entradas de carbono inorgánico por vía hidrológica, que aportaron más carbono gaseoso para su expulsión por el lago hacia la atmósfera. Aunque baja, la producción de CO_2 a partir de la formación de $CaCO_3$ en este lago kárstico pudo ser en ocasiones una fuente significativa de CO_2.*

Sin embargo, los flujos biogénicos fueron mayores de lo esperado en ambientes como los lagos fluviales, y se debieron sobre todo al papel que tienen las plantas emergentes en los flujos nutritivos, el cual se suele pasar por alto en los estudios de balances biogeoquímicos. No encontramos relación entre el tiempo de renovación del agua y la acumulación de nutrientes en el lago, lo cual recalca el peso de los flujos biogénicos en la retención de nutrientes. A nivel del ecosistema, nuestro estudio revela la importancia que tiene el contexto hidrogeológico del agua sobre los flujos de nutrientes y la de la vegetación emergente sobre el balance de nutrientes en el lago.

Palabras clave: *Acumulación de nutrientes, metabolismo del lago, renovación del agua, plantas emergentes, geología de la cubeta.*

INTRODUCTION

There are many processes that affect nutrient fluxes in lakes. Nutrients can enter lakes through streams, groundwater and atmospheric deposition (Winter, 2004) and can be exported downstream and to groundwater. Carbon net exchanges are also derived from submerged and emergent plants, phytoplankton and benthic microalgae through plant metabolic processes, such as photosynthesis and respiration, and by bacterial respiration (Wetzel, 2001). The carbon flux is also important at the lake-air interface because of CO_2 degassing (Cole & Caraco, 1998). Particulate carbon losses resulting from sedimentation can be important if the lake is productive (Downing *et al.,* 2008). In carbonate-rich lakes, the formation of $CaCO_3$ results in CO_2 production that is added to the C budget (Stets *et al.,* 2009). The nitrogen flux is clearly dependent on N transformation in the water column and sediments, as well as on N inputs. If the ecosystem is supplied with high nitrate inputs, denitrification is expected to occur at significant rates, providing that anoxic sites are abundant (Groffman *et al.,* 2009). On the contrary, phosphorus is assumed to be the main limiting factor of primary productivity, particularly in oligo-mesotrophic freshwater environments (Vollenweider, 1968).

The study of multiple nutrient (Carbon, Nitrogen and Phosphorus) fluxes simultaneously in lakes is not often undertaken (Burford *et al.*, 2012; Cook *et al.,* 2010). In these studies, the lake is considered as a sort of black-box reservoir, without paying closer attention to the processes occurring within the lake. This is especially true in flow-through lakes experiencing fast water renewal. Given that the hydrological control is often of paramount importance to nutrient fluxes (Buso *et al.*, 2009), the importance of the hydrological control of nutrient fluxes when compared to other environmental processes is a logical subject for investigation.

The study was undertaken during mid-stratification, a period when the significance of biogenic processes is usually higher in this lake (Alvarez Cobelas *et al.,* 2006). However, this also coincided with a period of high hydrological inputs, which were negligible in this lake previously, but were very important during the study period, due to the lagged enhanced discharge of groundwater upstream of the lake. Therefore, this unique situation of coincidental peaks of hydrological inputs and organismal metabolism enabled us to compare the relative contributions of different abiotic and biotic fluxes to the overall lake metabolism in a flow-through lake; a lake type for which very little is known in terms of nutrient fluxes and transformations. Hence, the short-term nature of this study was mandatory because of the sudden hydrological inputs, which were slowly declining after our study was over. This study provided clues to understand the role of biogenic nutrient fluxes in apparently hydrologically-controlled lake systems.

MATERIALS AND METHODS

Study Site

Conceja Lake is located in central Spain (38°55′N, 2°49′W; Fig. 1) and belongs to a chain of 18 barrage tufa lakes that encompass the main section of a protected environmental area (Ruidera Lakes Natural Park). This lake is supplied by water from surface streams and groundwater. Water inputs to the lake from groundwater show lagged behaviour. A sustained growing groundwater head arising from cumulative rainfall in autumn and winter usually results in a discharge to the lakes between six and nine months later (Alvarez Cobelas *et al.*, 2006). Such a discharge mostly occurs into incoming creeks by springs

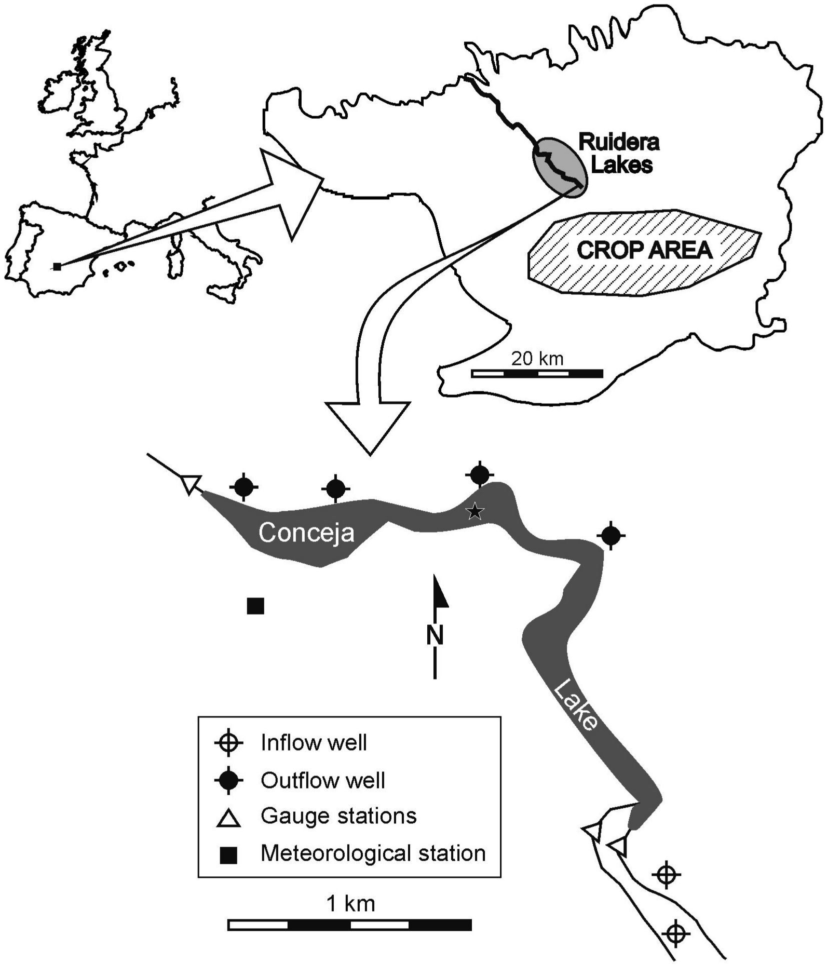

Figure 1. The study site and its location on the Iberian Peninsula (upper left). The groundwater catchment of the Ruidera Lakes is depicted and shows the area of intense agricultural practice (upper right). The lake basin is shown in the lower panel, along with the sampling sites and the location of the meteorological station. *Lugar de estudio y su situación en la Península Ibérica, donde se muestra la cuenca subterránea de las lagunas de Ruidera e indicamos las zonas de agricultura intensiva situadas en sus proximidades. La cubeta lacustre se presenta en la zona inferior de la figura, y en ella se señalan los lugares de muestreo y la situación de la estación meteorológica.*

located 500 m upstream of the lake. Therefore, our study was undertaken in a period when heavy rainfall occurred several months earlier and resulted in a strong delayed discharge from the upcoming wells to the upward streams and Conceja Lake, which increased lake water levels and diminished water retention. Hence, the hydrological conditions in the Conceja Lake catchment were not as simple as those of dry *vs*. wet year scheme at the time of our study.

The catchment is heavily polluted by nitrogen fertilizers from croplands, mostly barley and vineyards. Preferential flow paths drive N-rich waters through groundwater towards the chain of lakes, the upper of which is Conceja Lake. This N pollution enters the lake through streams, seepage and springs located within the lake basin. As a result, N:P atomic ratios higher than 15 000 are usual in surface water and groundwater of the entire region.

The small, calcite-rich, moderately deep, always oxic and monomictic Conceja Lake (Table 1) is surrounded by a fringe of helophytes encompassed primarily by *Cladium mariscus* plants. Submerged plants (mainly charophytes) that form lakewide meadows in years of higher water retention were absent during our study period because of strong water discharge. Additional information on the system can be found in Alvarez Cobelas *et al*. (2006).

Table 1. Basic limnological features of Conceja Lake in 2009. Annual ranges are reported. DIC: dissolved inorganic carbon, DOC: dissolved organic carbon; POC: particulate organic carbon; and DIN: dissolved inorganic nitrogen. *Características limnológicas de la laguna Conceja en 2009. Rangos anuales. DIC: carbono inorgánico disuelto, DOC: carbono orgánico disuelto, POC: carbono orgánico particulado, DIN: nitrógeno inorgánico disuelto.*

Surface catchment area (km^2)	750
Groundwater catchment area (km^2)	1200
Lake area (km^2)	0.38
Lake volume (10^6 m^3)	3.14
Max depth (m)	14.5
Average depth (m)	8.2
Water residence time (yr)	0.1
pH	7.51-7.95
Conductivity (µS/cm)	659-840
DIC (mg C/l)	49-69
DOC (mg C/l)	2.1-4.7
POC (mg C/l)	0.01-0.69
DIN (mg N/l)	6.1-18.2
Total nitrogen (mg N/l)	7.9-18.5
Total phosphorus (µg P/l)	1-10
Chlorophyll *a* (µg/l)	0.1-3.2

Field sampling, hydrological and laboratory methods

The study was undertaken in June and July 2009, when lake stratification was fully developed and strong (surface water and groundwater) discharge to the lake occurred. The discharge of stream water into the lake was recorded daily at noon in three gauging stations (Fig. 1) using an FP101 FlowProbe (Global Water, Gold River, California, USA). Two stations were located above the basin at different incoming creeks and were aggregated, and one station was placed at the outlet of the lake. A portable BWS200 basic meteorological station (Cambell Scientific Inc., Logan, Utah, USA) was installed in the vicinity of the lake (≈100 m, Fig. 1). Rainfall was absent during the study period; thus, runoff from the catchment and atmospheric wet deposition of nutrients were negligible. Air temperature, wind velocity, relative humidity, air pressure and solar irradiance were recorded at 10-minute intervals. Evaporation was measured with a class A evaporation pan (Hydrological Services PTY, Ltd., Liverpool, Australia) located close to the lake surface, following the procedures of Shuttleworth (1993). Transpiration was ascertained by the combined use of meteorological and littoral plant cover data (S. Cirujano, unpublished data), as proposed by Sánchez-Carrillo *et al.* (2001). A Solinst pressure transducer for water level (Solinst Canada Ltd., Georgetown, Ontario, Canada) was deployed from a buoy at the surface of the lake centre, and it recorded level changes at ten-minute intervals. This enabled us to estimate lake-water volume changes using an equation relating water level and lake volume (Alvarez Cobelas, unpublished data) after the integration of daily data. Net seepage was ascertained from the water budget on a daily basis, and the uncertainty of the estimations was also taken into account (see below). Water renewal time and areal hydraulic load were calculated from all of these data. All terms were estimated in m^3/d.

Sampling for the chemical budgets was performed weekly, roughly at noon at: 1) the incoming and outgoing lake streams; 2) wells that represented groundwater inputs and down-gradient outputs; and 3) in the middle of the lake at 1-m depths in the water column. While the stream samples were gathered manually, the groundwater and lake samples were collected with a 1-L Nordmeyer device (Nordmeyer Geotool Ltd., Berlin, Germany) and a 5-L van Dorn bottle (Eijkelkamp Soil and Water, Giesbeek, The Netherlands), respectively. Ultraclean PVC bottles were used to store water samples at 4 °C until analysis, which was conducted within two days of sampling. Samples for organic C were stored in glass vials. *In situ* water column profiles of conductivity, temperature and dissolved oxygen were recorded with a CTD SeaBird-19 (Sea-Bird Electronics Inc., Bellevue, Washington State, USA). A portable Crison MM-40 multimeter (Crison Instruments, Alella, Spain) was calibrated weekly and enabled us to register the pH and conductivity of all samples. Total alkalinity was measured *in situ* shortly after water sampling, with end-point titration in all of the surface and groundwater samples (APHA, 2005).

A surrogate of sedimentation was estimated using sediment traps, following the methods of Bloesch & Burns (1980). Four sediment traps were filled with distilled water, deployed in a 14 m deep central area of the lake and retrieved weekly. Once retrieved, their concentrations were gently mixed and stored for subsequent analysis.

Nitrate, nitrite, ammonia, total N, soluble reactive P (SRP) and total P were measured colourimetrically with a Seal-3 QuAAtro AQ2 autoanalyzer (SEAL Analytical Gmbh, Norderstedt, Germany). Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured with a Shimadzu TOC-V_{CSH} analyzer (Shimadzu, Kyoto, Japan), following the methods of APHA (2005). In-lake nutrient concentrations were integrated in the whole water column and, hence, reported on an areal basis (*e.g.*, g C/m^2), which enabled an easier calculation of fluxes.

Estimation of nutrient fluxes

The main carbon terms in this lake during the study period were the following: stream input and output, groundwater input and output, CO_2 efflux to the atmosphere, photosynthesis and respiration by emergent plants, photosynthesis and respiration by water column (including benthic) populations, particulate organic carbon (POC) sedimentation and CO_2 production from $CaCO_3$ formation. All methods will be fully described below.

The well-developed *Cladium* population fixed and respired carbon in sufficient amounts to influence the lake carbon budget. Part of the built-up biomass was accumulated later in the lake sediments, when dead leaves fell and entered the lake. We measured *Cladium* photosynthesis and respiration once a week with an infrared gas analyzer (ADC 225 MK3, ADC Bioscientific Ltd., Hoddeston, UK) in the more accessible populations of a nearby wetland and discovered an appropriate explanation for net production, such as plant gross photosynthesis minus respiration, with irradiance during daylight, and air temperature with plant respiration in dark conditions.

Photosynthesis and respiration of the water column (plankton, submerged macrophytes and microphytes, benthic animals, bacteria and fish) were measured by the method of Cole *et al.* (2000) using a YSI 6920-V2 sonde (Yellow Springs Instruments, Yellow Springs, Ohio, USA). Temperature and dissolved oxygen were recorded at 10-min intervals throughout the study period by deploying the sonde at 0.5 m in a central station of the lake. The calculations followed Cole *et al.* (2000) algorithms.

We estimated CO_2 efflux using the Cole & Caraco (1998) method. The CO_2 concentration of the upper layers of the lake was calculated from the alkalinity, pH, temperature and ionic strength, following the equations from Stumm & Morgan (1982). The CO_2 partial pressure in the lower layer of the atmosphere above the lake was measured with a WMA-4 IRGA equipment

(PP Systems, Amesbury, Massachusetts, USA), which continuously registered data in a nearby wetland, amounting to 370.3 ± 30.1 μatm for the period under study. The enhanced flux caused by hydration reactions of CO_2 at the air-lake boundary layer (Wanninkhof & Knox, 1996) was negligible because the lake waters were only slightly basic (Table 1), thereby preventing atmospheric CO_2 invasion into unsaturated upper layers.

The net flux of groundwater nutrients (total C, organic C, inorganic C, N and P) was calculated by multiplying the weekly difference in nutrient concentration recorded in upper wells and at the deeper lake layer by the weekly net groundwater flow, the latter being estimated from weekly water budgets (see above).

Carbonate formation can be a source of CO_2, particularly in karstic environments, such as Conceja Lake. It is well known that net $CaCO_3$ formation produces equimolar amounts of CO_2 (Stets *et al.*, 2009). Hence, it is possible to ascertain this source of CO_2 because net CO_2 hydrological inputs (both surface water and groundwater) enable the formation of calcium carbonate in equimolar amounts; this procedure was used in this study.

Sedimentation of particulate nutrients is an important term in the nutrient budget. It was de-

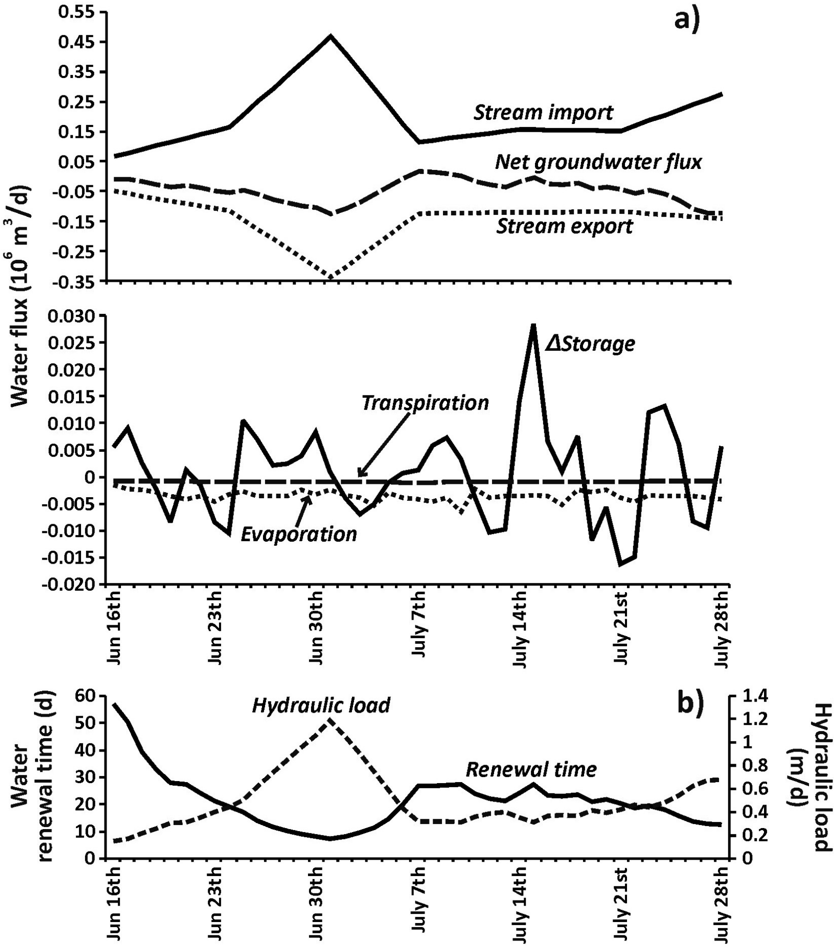

Figure 2. Water budget (a) and renewal (b) in Conceja Lake for the study period. *Balance hídrico (a) y renovación del agua (b) en la laguna Conceja durante el periodo de estudio.*

termined on a daily basis by dividing the settling rates of particulate C, N and P (see above) by the number of days between two consecutive sampling events.

While the N and P terms were stream inputs and outputs, particulate nutrient sedimentation and groundwater flux, N fluxes must also take denitrification into account. Denitrification was computed from data obtained by the isotope pairing technique method (Steingruber *et al.*, 2001) during the same stratification period of the earlier year (Eugercios, 2013). A multiple regression model of 2008 denitrification rates, as a function of measured environmental variables, enabled us to calculate denitrification in Conceja Lake in 2009.

Mass balances were calculated using all input and output fluxes of the water column for a given nutrient (total C, inorganic C, organic C, total N and total P).

Error estimation

Most nutrient fluxes were compounded estimations, including discharge and concentration. These measurements were both subjected to error. Assigning errors to our calculations was difficult because of the variety of data required when constructing nutrient budgets. Water discharge estimates were assigned an error of 10%, which arose from repeated discharge measurements with a flowmeter for several diel periods. For other flux variables, such as those arising from direct measurements (*i.e.*, photosynthesis, respiration), the average and standard deviations were used. Error propagation methods were employed for all derived values by using additive error propagation on all values and then applying the resulting CV to the sum of all terms, as suggested by Stets *et al.* (2009).

RESULTS

Hydrology

While the stream import to the lake amounted to 0.28 ± 0.20 10^6 m^3/d (temporal mean±standard deviation), the stream export was 0.15 ± 0.07 10^6 m^3/d for the 44 days of the study. Both parameters peaked in early July, with a minimum indicated shortly after the peak and an upward trend found afterwards (Fig. 2a). The water budget enabled us to estimate the net groundwater flux, which reached 0.05 ± 0.04 10^6 m^3/d and mostly corresponded to output from the lake (Fig. 2a). Therefore, the lake gained water via surface inputs and lost water through surface water and groundwater outputs. On average, groundwater outflow comprised roughly one fifth of stream inputs and one third of the stream outflow. Other terms of the budget were much smaller, with storage showing strong fluctuations throughout the study period (0.7 ± 8.8 10^3 m^3/d). Open water evaporation and transpiration by emergent plants were negligible in comparison because they were usually lower than 6.0 10^3 m^3/d and 1.0 10^3 m^3/d, respectively (represented as negative amounts in Fig. 2a). No rainfall occurred during the study period, but discharge to the lake was not a straightforward function of rainfall because it depended on a complex set of processes involving the local groundwater hydrogeology. Long lagged responses (see Site description) to rainfall appeared, thus causing oscillations in surface discharge that occurred in the middle of the study period.

The water renewal time spanned 7-57 d (21 ± 10 d), was lower in early July and was inversely related to the areal hydraulic load, which amounted to 0.50 ± 0.25 m/d (Fig. 2b).

Lake nutrient dynamics

Nutrients evolved differently in the lake water column throughout the study period (Fig. 3). While total C and inorganic C showed an upward trend, total P peaked on intermediate dates, and total N and TOC displayed a fluctuating course. POC accounted for 3-9% of the overall organic C. Inorganic C and inorganic N were the dominant forms of C and N. SRP was often below the detection limit; therefore, the organic forms of P and polyphosphate could be considered the dominant forms of phosphorus. The total nutrient concentrations (C, N and P) in the water column were unrelated to each other (Spearman correlation, $p > 0.05$).

Nutrient fluxes

Throughout the study period, most fluxes depended on the hydrology because the highest fluxes were those of stream inputs and outputs and groundwater exchange (Table 2). The variability was high in most of the fluxes. While input and output surface inorganic C fluxes amounted to 9.09-45.56 g C/m^2/d and 7.39-26.41 g C/m^2/d, respectively, the input and output surface organic C amounts were 0.66-4.01 g C/m^2/d and 0.49-2.68 g C/m^2/d, respectively. The change in DIC and organic C flux through the groundwater was almost always net output, amounting to –16.61–(+)2.18 g C/m^2/d and -0.77-(+)0.10 g C/m^2/d, respectively, with the minus sign indicating net output. Inorganic C fluxes were one order of magnitude higher than those of organic C. POC sedimentation (0.006-0.112 g C/m^2/d) was one order of magnitude lower than CO_2 efflux and only accounted for 0.1 % of the total C inputs on average. The CO_2 efflux showed low variability, ranging from 0.31-0.42 g C/m^2/d. Net C export via groundwater was roughly one fourth of the total C stream inputs.

The biogenic C flux might arise from the metabolism of emergent plants (mostly *Cladium*) and the water column. Gross primary production by *Cladium* plants was the highest biogenic C input to the lake (3.92-4.33 g C/ m^2/d), and its respiration was 1.15-2.05 g C/m^2/d (Table 2). Submerged macrophytes, often covering littoral and deeper benthic environments when the lake

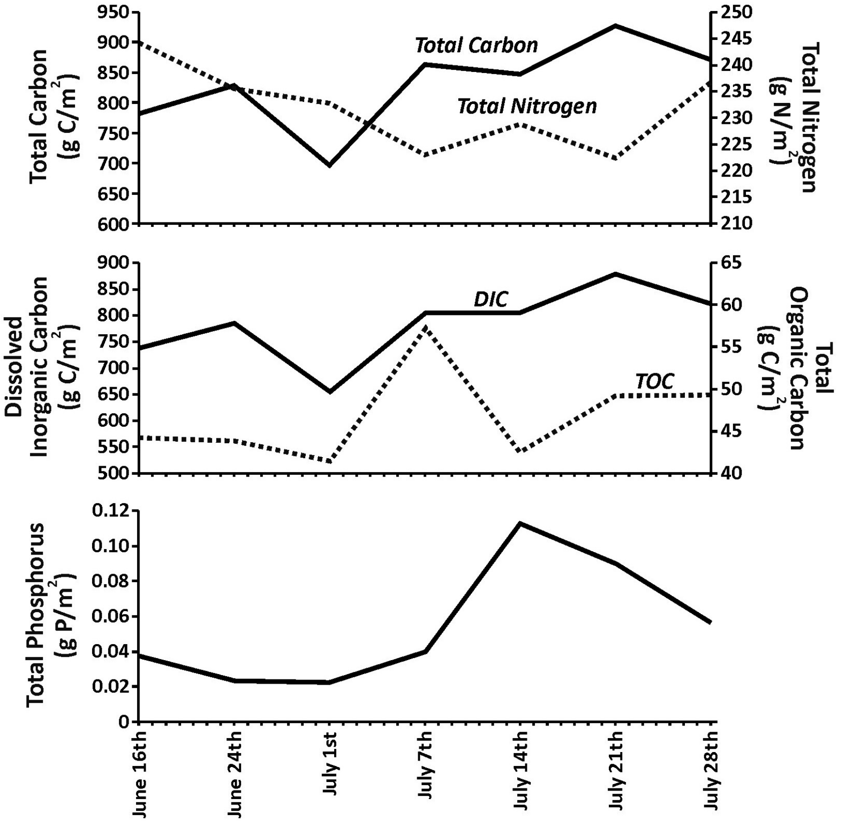

Figure 3. Nutrient concentrations in the water column of Conceja Lake during the study period. *Concentraciones de nutrientes en la columna de agua de la laguna Conceja durante el periodo de estudio.*

water retention was higher, were washed out during the study period and did not significantly contribute to the water column C budget. While the water column gross primary production ranged between 2.05 g C/m^2/d and 4.50 g C/m^2/d, its respiration was 1.35-2.93 g C/m^2/d; therefore, the lake was mostly net autotrophic throughout the study period. Gross photosynthesis by all plants reached from 6.02 g C/m^2/d to 8.20 g C/m^2/d, and it was the highest at the time of the phytoplankton peak on July 14th. The overall respiration was 2.66-4.72 g C/m^2/d. Therefore, the metabolism of the water column was 32-55% and 45-70% of the overall primary production and respiration, respectively. Calcium carbonate formation could sometimes provide a source of CO$_2$ (range: 0-0.06 g C/m^2/d; Table 2). The C biogenic fixation *vs.* C hydrological surface input ratio was 6-29% throughout the study period, and it did not show any trend. If *Cladium* C net inputs were removed (*i.e.*, only accounting for water column biogenic C), that ratio would be 1-7%.

Table 2. The carbon, nitrogen and phosphorus fluxes for Conceja Lake during the study period. GPP: gross primary production, IC: inorganic carbon, OC: organic carbon, POC: particulate organic carbon, PON: particulate organic nitrogen, and PP: particulate phosphorus. Negative values in some output dates (*e.g.*, some of net groundwater N) mean that the lake did not export that nutrient; as a result of negative and positive values, the average value can be negative. The error propagation of fluxes was ascertained by the method of Stets *et al.* (2009) (see text). *Flujos de carbono, nitrógeno y fósforo en la laguna Conceja durante el periodo de estudio. GPP: producción primaria bruta, IC: carbono inorgánico, OC: carbono orgánico, POC: carbono orgánico particulado, PON: nitrógeno orgánico particulado, PP: fósforo particulado. Los valores negativos de flujo de salida en algunas fechas (por ejemplo, en la salida neta de nitrógeno subterráneo) significan que el lago no exportó ese nutriente; como resultado de valores positivos y negativos, el promedio puede ser negativo. La propagación de errores se determinó siguiendo el método de Stets* et al. *(2009) (véase el texto).*

Inputs		June 16th	June 24th	July 1st	July 7th	July 14th	July 21st	July 28th	Average	Error
Surface C flux	g C/m^2/d	9.7	23.8	44.1	19.3	26.0	25.5	46.9	27.9	28.6
Surface OC flux	g C/m2/d	0.66	1.18	4.01	1.02	0.84	0.95	1.87	1.50	1.58
Surface IC flux	g C/m^2/d	9.0	22.6	40.1	18.3	25.1	24.5	45.0	26.4	25.7
Water column GPP	g C/m^2/d	2.33	2.05	2.05	2.97	4.50	3.33	3.29	2.93	0.88
Cut-sedge GPP	g C/m^2/d	3.92	3.97	4.33	3.93	3.70	4.33	4.06	4.03	0.23
N surface flux	g N/m^2/d	3.304	8.074	22.787	5.655	7.618	7.141	13.409	9.713	7.820
P surface flux	mg P/m^2/d	0.34	4.33	6.62	0.49	1.67	1.65	3.19	2.61	4.18
Outputs										
Surface C flux	g C/m^2/d	7.9	16.7	29.1	19.5	18.5	19.1	23.1	19.1	15.5
Surface OC flux	g C/m^2/d	0.49	0.98	2.68	1.18	1.07	0.75	1.52	1.24	0.97
Surface IC flux	g C/m^2/d	7.4	15.7	26.4	18.3	17.4	18.3	21.6	17.9	14.7
POC settling flux	mg C/m^2/d	6	7	12	53	112	22	9	32	39
CO$_2$ efflux	mg C/m^2/d	398	327	407	409	306	416	308	367	51
Groundwater net C flux	mg C/m^2/d	17	−71	−6587	−47	48	141	312	884	2518
Groundwater net OC flux	mg C/m^2/d	0.04	−0.87	−1.97	0.04	−0.14	0.12	0.02	0.39	0.77
Groundwater net IC flux	mg C/m^2/d	17	−70	−6585	−47	48	140	312	884	2517
CaCO$_3$ formation	mg C/m^2/d	0	0	0	47	50	62	0	23	29
Water column respiration	g C/m^2/d	1.72	1.35	1.38	2.12	2.69	2.68	2.93	2.13	0.66
Cut-sedge respiration	g C/m^2/d	1.65	1.31	1.71	1.33	1.15	2.05	1.51	1.53	0.30
N surface flux	g N/m^2/d	2.38	5.43	16.00	5.84	5.54	5.61	6.49	6.76	4.34
PON settling flux	mg N/m^2/d	16	36	17	13	10	4	12	16	10
Denitrification	mg N/m^2/d	11	17	16	20	28	28	9	19	8
Groundwater net N flux	mg N/m^2/d	103	−164	−388	102	−121	−299	1451	−98	624
P surface flux	mg P/m^2/d	0.65	1.82	1.51	0.56	1.89	1.22	1.12	1.25	1.38
PP settling flux	mg P/m^2/d	0.16	0.37	0.07	0.06	0.06	0.01	0.01	0.10	0.13
Groundwater net P flux	mg P/m^2/d	−0.18	−1.14	−2.60	−0.001	−0.14	−0.27	−0.002	0.62	0.96

Hydrologic flow paths were also far more important than sedimentation and denitrification in the N budget (Table 2). The lake lost N during much of the study period, but only infrequently via groundwater export because net groundwater flux only occurred on some dates. While surface N inputs ranged from 3.30-22.78 g $N/m^2/d$, surface outputs were 2.38-16.00 g $N/m^2/d$. The net groundwater N flux varied between –1.12 g $N/m^2/d$ and 1.45 g $N/m^2/d$. On average, particulate N sedimentation (0.004-0.036 g $N/m^2/d$) amounted to 1.6% of the stream N inputs and was in the same order of magnitude as denitrification (0.008-0.028 g $N/m^2/d$). The sedimentation of particulate P was rather low (0.003-0.161 mg $P/m^2/d$), approximately 0.1% of the hydrologically controlled P fluxes (0.34-6.62 mg $P/m^2/d$, 0.65-1.89 mg $P/m^2/d$ and –2.60-(+)0.96 mg $P/m^2/d$) for surface inputs, surface outputs and net groundwater flux, respectively; Table 2). The net export of P occurred 42% and 100% of the time through surface outlet water and groundwater, respectively. The organic C, total N and total P surface inflows and outflows differed significantly (Wilcoxon test, $p = 0.044 – 0.031$).

While C and N hydrological fluxes covaried ($R^2 = 0.76$ and 0.74, $p = 0.020$ and 0.023, for input and output fluxes, respectively), the P input or output fluxes were unrelated to those of other nutrients ($p > 0.05$). The net groundwater C and P fluxes covaried ($R^2 = 0.82$, $p = 0.017$), but their relationships with those of N were not statistically significant ($p > 0.05$). The sedimentation of N and P covaried ($R^2 = 0.83$, $p = 0.015$), but they were unrelated with that of organic C.

Nutrient export and accumulation

The net export of OC, N and P from the lake took place at times (Fig. 4). Total C accumulation ranged from 2.74-27.75 g $C/m^2/d$ and was mostly comprised by DIC. N accumulation varied between –0.32 g $N/m^2/d$ and 7.14 g $N/m^2/d$, and the P accumulation varied between –0.13 mg $P/m^2/d$ and 7.64 mg $P/m^2/d$ (Fig. 3). The accumulations of OC, N and P covaried ($R^2 = 0.68 – 0.85$,

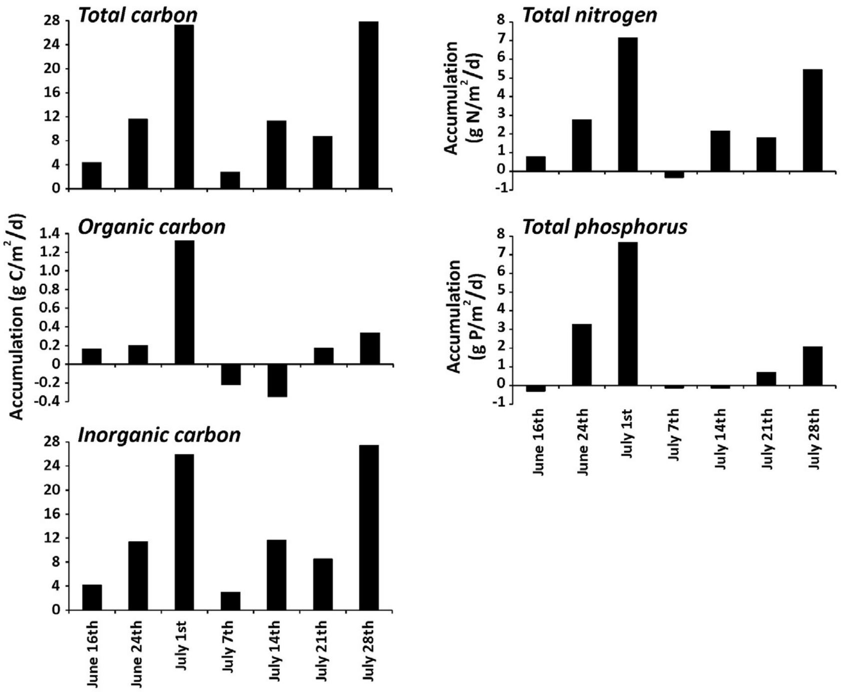

Figure 4. Nutrient accumulation in Conceja Lake during the study period. *Acumulación de nutrientes en la columna de agua de la laguna Conceja durante el periodo de estudio.*

$p = 0.003 - 0.013$). No statistically significant relationship was found between the water renewal time and accumulation ($p > 0.05$).

DISCUSSION

Nutrient fluxes, nutrient accumulation and their relationships

Nutrient fluxes in Conceja Lake mostly depended on the hydrology, and their input and output fluxes via surface water and groundwater were the highest of all of the measured fluxes (Table 2), as other studies reported for a small, groundwater-fed lake (Stets *et al.,* 2009) and a hard-water lake chain (Finlay *et al*., 2010). Our results for this lake of mixed (surface water and groundwater) water exchanges suggested that the spatial variability of the nutrient fluxes was partially regulated by flow paths but also by element-specific processing time along a flow path. For example, we observed that the nutrient contents in the lake did not covary, and the net groundwater fluxes of N and P did not covary. Degassing, uptake by organisms and the sedimentation of particulate matter appeared to vary temporally, as suggested by the error propagations listed in Table 2. In fact, Conceja Lake is surrounded by a forest fringe, beyond which croplands dominate in the wider catchment draining into this lake, so diffuse fertilizer pollution and its leakage to groundwater is expected to enter the lake and influence nutrient biogeochemistry. Nevertheless, these fluxes, their time lags and impact on lake biogeochemistry are highly complex and, despite recent modelling efforts (Eugercios, 2013), they are still not fully understood due to the groundwater anisotropy of flow paths and variable time lengths of passage arising from the complex hydrogeology of the aquifer.

CO_2 degassing was higher than POC sedimentation in Conceja Lake, as Stets *et al.* (2009) found for Shingobee Lake (Minnesota), which is an ecosystem fed by groundwater and surface inputs, and as Finlay *et al.* (2010) found for two headwater lakes in Saskatchewan. Variability was high in all C fluxes and was much higher than that reported by Stets *et al.* (2009) for a year-long study. Degassing implies a net heterotrophy of the lake during the study period, but this was at odds with the gross primary production:respiration ratio of the water column, which was mostly positive throughout the study period. These seemingly contradicting results can be reconciled if we take into account the strong input of inorganic carbon flux to the lake, which resulted in a positive CO_2 outgassing from the lake. This fact was already demonstrated by McDonald *et al.* (2013) for at least 12% of net autotrophic lakes in the coterminous United States.

CO_2 production from $CaCO_3$ formation in calcareous lakes is a process that has seldom been quantified in lakes (McConnaughey *et al.*, 1994). Our results showed high variability, which was often attained for negligible lakes (Table 2), and values lower than those recorded for marl lakes (Stets *et al.*, 2009). As previously reported (see the site description section), charophytes were washed out during the study period, and CO_2 production from $CaCO_3$ formation was therefore restricted to the metabolism of microalgae in the lake. It is likely that this process could increase CO_2 outgassing in this lake when charophyte meadows are fully developed, which would occur when the water retention time increases, but this fact still awaits confirmation.

Biogenic C mainly resulted from *Cladium* photosynthesis, and the water column activity was an approximate ratio of 0.7:1. Therefore, the net C inputs by metabolism of *Cladium* was another important source of C to Conceja Lake, and this occurred often with helophytes around lakes (Wetzel, 2001; Sobek *et al*., 2006). The net photosynthesis of *Cladium* in Conceja Lake was lower than that measured in *Cladium* in a French Mediterranean wetland (Saltmarsh *et al*., 2006).

The sedimentation of particulate C was lower (6-112 mg $C/m^2/d$), albeit more variable, than those recorded in oligotrophic boreal lakes of Canada (30-150 mg $C/m^2/d$) (Teodoru *et al.,* 2013). Water-column production, which was not negligible (see above), might result in the increasing sedimentation of particulate nutrients. However, this was not the case due to the short renewal time of lake water, resulting in lower settling rates than expected. Therefore, the oligotrophic Conceja Lake might have had more settling seston than it actually had during our period of study, if the amount of water entering the lake was lower. These results did not support the old idea of a relationship between trophic status and the settling rates of organic matter. Teodoru *et al.* (2013) reported the same and stated that other environmental features must be taken into account, such as lake morphometry and the relative contribution of in-lake particles *vs.* particles of terrestrial sources.

The biogenic C to hydrological surface input C ratio was always below 30% and varied greatly (6-29%) during the short timescale of our study. Stets *et al.* (2009) reported 4.5% on an annual basis for Shingobee Lake, but they did not take into account the inputs by littoral plants. If we disregard the contribution of *Cladium*, that ratio would amount to 1-7%, a range around that of Shingobee Lake. Therefore, when strong hydrological processes occur in a lake, it seems likely that water-column biogenic processes would contribute to less than 10% of the overall C budget.

The denitrification was roughly in the same order of magnitude as the PON sedimentation, a strikingly different result from what was found in more productive lakes downstream within the same lake chain (Piña-Ochoa, 2007), where sedimentation was higher than denitrification. Despite the high nitrate contents of the lake water, the denitrification rates were not as high as expected because of the low levels of soluble reactive phosphorus and dissolved organic carbon (Alvarez Cobelas, unpublished data). The sedimentation of particulate N might have been lower than that during years with higher water retention, which enabled the development of charophyte meadows (Rodrigo *et al.*, 2007). Such meadows did not develop in 2009; therefore, the contribution of charophytes to the settling particulate N, an important fraction of this element in these lakes (Piña-Ochoa *et al.*, 2006), was negligible. The particulate P sedimentation was low, and inorganic P co-precipitation with Ca was also unlikely because the low phytoplankton biomass did not increase pH by photosynthesis (Hartley *et al.*, 1997). Furthermore, the low concentrations of soluble P at the sediment-water interface might have limited denitrification because SRP is required for bacteria to carry out that process (Meyer *et al.*, 2005). The high N:P ratios in the catchment waters also took place in the lake, despite the fact that some denitrification occurred in soils and groundwater before they entered the lake (Alvarez Cobelas, unpublished data). In Conceja Lake, this imbalance might strongly limit primary production; however, our community metabolism data revealed a net autotrophic metabolism on most of the dates recorded (Gross Primary Production:Respiration ratio> 1.0), which suggested that P sources were enough to fuel primary production to that extent. In fact, naturally-hydrological P fluxes to Conceja Lake during our study period were within the range of those used in the well-known fertilizing experiments of Wisconsin lakes (Pace & Cole, 2000), hence supplying enough P to enhance the water column primary production in Conceja Lake.

The accumulations of OC, N and P covaried, which suggested that the process of build-up biomass might be controlling the accumulations of these nutrients. This was supported by two facts: i) the fluxes of these nutrients due to other processes, such as sedimentation, were mostly been unrelated with each other, and ii) the accumulation was not related to water renewal. Thus, the role of organisms in nutrient fluxes could be higher than expected in flow-through lakes. Harris (1999) established an opposite relationship between water renewal and organismal metabolism, but our results showed that it was not always the case and that organisms can be more influential on lake metabolism even in harsh conditions for them, such as those of short water residence.

Lake biogeochemistry and the role of hydrogeology

Lohse *et al.* (2009) concluded that changes in the hydrologic regime, which can be episodic fluctuations in water availability or hydrologic transport of reactants, will likely result in the disturbances of biogeochemical processes. This statement only partially covers the biogeochemical variability because it ignores other non-hydrological processes that can also promote changes in nutrient dynamics, such as those of biogenic metabolism (*e.g.*, denitrification, CO_2 degassing and nutrient uptake; Table 2), that proceed at different rates. In groundwater, such dynamics are controlled by recharge rates, the depth and length of flow paths and the supply of reactants (Lohse *et al.*, 2009). However, when a lake intersects an aquifer, as occurs in Conceja Lake, the net export of N and P from the lake and the net input of both nutrients to groundwater did not appear to be related to those processes. Instead, it is more likely to be controlled by groundwater regional flow, lake geology, and the oxic conditions of sediments that promote diffusive leaching to groundwater, rather than remaining trapped in sediments. It also appeared that phosphorus binding in the lake bottom could be limited by oxic conditions (McCulloch *et al.,* 2013), which might enhance its export through the groundwater. The nature of the underlying rock may enhance N and P export via the groundwater if: i) sediments are oxic and do not diffuse SRP to the overlying water and ii) the groundwater outflow is significant. Karst aquifers, such as that underlying Conceja Lake, contain a wealth of conduits arising from multiple geochemical processes, such as dedolomitization and karstification (Screaton *et al.*, 2004), which can affect sediments on the lake bottom, and these conduits may be used for the rapid export of water and soluble and particulate nutrients. However, the precise outcome of this export not only depends on these bottom flow paths but also on the interactions between nutrients and the sediment matrix. This might be the reason why the time series of net groundwater export of N and P did not match. Therefore, nutrient fluxes in flow-through lakes, where groundwater exchange is also occurring, are clearly dependent upon the interactions between them and the hydrogeological setting of the lake basin. A proper characterization of these fluxes cannot be truly accurate without a good knowledge of the hydrogeological site. Further studies are required to improve our knowledge of these interactions. We will gain that knowledge through a much closer relationship between limnologists and hydrogeologists, as previously advocated (Alvarez Cobelas, 2006).

CONCLUDING REMARKS

This short-term study demonstrated the important role that organisms play in nutrient fluxes of flow-through lakes, which was higher than expected. Hydrological nutrient fluxes dominated lake processes, but their input and output fluxes differed, which was related to the nutrient export to groundwater but also to the significance of biogenic fluxes. These facts were also supported by the lack of a relationship between the water renewal and nutrient accumulation in Conceja Lake.

The water column of the oligotrophic Conceja Lake was a net autotrophic environment during our study period, despite the fact that CO_2 outgassing was observed throughout. Hydrological inputs of inorganic carbon were responsible for that positive outgassing, a feature that was also observed in other oligotrophic lakes. Most biogenic nutrient fluxes recorded in Conceja Lake were within the ranges measured in P-limiting lakes, but P hydrological inputs enabled the lake to sustain a relatively high water column production.

This study was conducted for several weeks during the thermal stratification of the lake. Our results suggested an unexpected behaviour of the lake when it experienced high water inputs, *i.e.*, the role of biogenic nutrient fluxes was higher than expected in flow-through lakes. It was clear that studies carried out for longer time periods in flow-through lakes are necessary to enhance the strength of our conclusions. However, studies of that type appear to face two likely shortcomings: 1) there are too many processes involved that would be rather expensive for a long-term (a year or longer) study, and 2) there are very few flow-through lakes in the Mediterranean area in which to undertake this type of study. We encourage these studies to be tackled because we are certain that they will provide interesting and unexpected results.

Finally, this study showed that there are neglected fields in the discipline of lake biogeochemistry, namely, the hydrogeological setting of the lake basin (which is very important to understand the water exchange between the lake and the underlying aquifer) and the role of littoral plants. Clearly, they deserve closer scrutiny in the future to cover the large gaps of knowledge in this limnological area of expertise.

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