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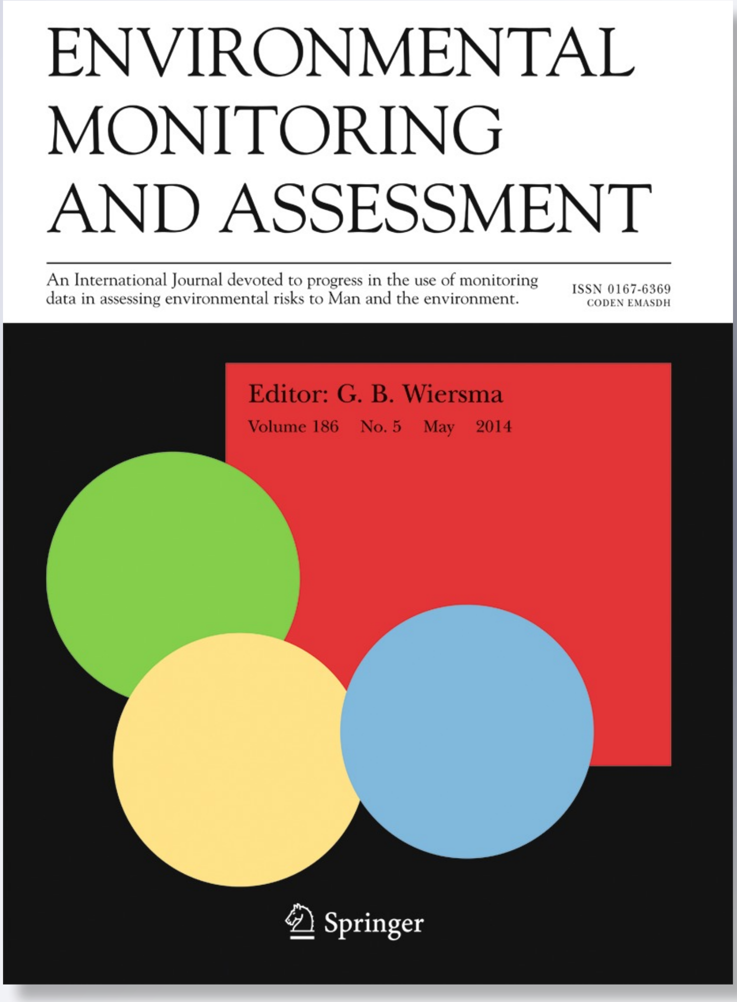

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Seasonal baseline of nutrients and stable isotopes in a saline lake of Argentina: biogeochemical processes and river runoff effects

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Abstract The seasonal variability of inorganic and organic nutrients and stable isotopes and their relations with plankton and environmental conditions were monitored in Lake Chasicó. Principal component analysis evidenced the strong influence of the river runoff on several biogeochemical variables. Silicate concentrations were controlled by diatom biomass and river discharge. Higher values of nitrate and soluble reactive phosphorus (SRP) indicated agricultural uses in the river basin. Elevated pH values (~9) inhibiting nitrification in the lake explained partially the dominance of ammonium: ~83 % of dissolved inorganic nitrogen (DIN). The low DIN/SRP ratio inferred nitrogen limitation, although the hypotheses of iron and CO_2 limitation are relevant in alkaline lakes. Particulate organic matter (POM) and dissolved organic matter (DOM) were mainly of autochthonous origin. The main allochthonous input was imported by the river as POM owning to the arid conditions. Dissolved organic carbon was likely top-down regulated by the bacterioplankton grazer *Brachionus plicatilis*. The $\delta^{13}C$ signature was a good indicator of primary production and its values were influenced probably by CO_2 limitation. The $\delta^{15}N$ did not evidence nitrogen fixation and suggested the effects of anthropogenic activities. The preservation of a good water quality in the lake is crucial for resource management.

Keywords Drought · Organic matter · pH · $\delta^{13}C$ · $\delta^{15}N$ · Rotifers · Pampa

Introduction

The development of strategies for the successful management of lakes depends on our knowledge of biogeochemical dynamics and their dependence on hydrological regimes. Some of the most valuable tools to comprehend biogeochemical processes and the origin of organic matter in aquatic systems are the stable isotope ratios of carbon and nitrogen (Cunha et al. 2006; Lara et al. 2010; Maya et al. 2011). The signature of $\delta^{13}C$ in the particulate organic matter (POM) is a good indicator of primary productivity, CO_2 concentration in water and carbon speciation (Lehmann et al. 2004; Gu et al. 2011). Generally, the $\delta^{15}N$ of POM indicates planktonic

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nitrogen fixation, denotes anthropogenic disturbance and establishes trophic baselines (Wigand et al. 2007; Carlier et al. 2009; Gu 2009).

Organic nutrients alter several physicochemical features of water and are substantial nutritional sources for aquatic organisms. Dissolved organic matter (DOM) often surpasses POM by an order of magnitude (Wetzel 1984). DOM attenuates UV radiation, modifies nutrient availability and contaminants toxicity, and is generally the largest source of carbon and nitrogen for microorganisms (Williamson et al. 1999; Jiao et al. 2010; Nguyen et al. 2011). Subsequent consumption of bacteria by heterotrophic flagellates and microzooplankton provides a pathway to transfer DOM into food webs (Pace et al. 2004). According to Elser et al. (2000), nutrient input and food web structure are two of most important forces governing lake function.

Inorganic nutrients are critical in limiting primary production and determining community structure in lakes. The increasing load of organic and inorganic nutrients in water bodies is the main cause of eutrophication, one of the most widespread and serious anthropogenic disturbances of aquatic ecosystems (Sánchez-Carrillo et al. 2007; Karydis and Kitsiou 2012; Cotovicz Junior et al. 2013). Potential effects are reduction in water transparency, deterioration of benthic primary producers, cyanobacteria blooms, oxygen depletion, fish mortalities and reduction in species biodiversity. In the Argentinean Pampa, the lakes range from eutrophic to hypereutrophic (Kopprio et al. 2010).

Several saline lakes in the Argentinean Pampa are also relevant for the cycle of carbon. Saline lakes are mainly situated in endorheic watersheds representing terminal points for carbon flow (Duarte et al. 2008). Geomorphologically, shallow lakes together with extensive wetlands in the Argentinean Pampa emerged as a consequence of alternating dry and wet periods (Iriondo 1989). The drainage of basins in a great part of the Pampa region is endorheic or arheic, for that reason recurrent floods and droughts lead to strong hydrological and biogeochemical variations (Quirós et al. 2002).

The aims of the present study are to contribute to the understanding of mechanisms and factors controlling the seasonal variability of nutrients and stable isotopes and to identify the relative importance of the main sources of organic matter in the nature reserve Lake Chasicó. We hypothesize that river runoff and anthropogenic impacts will strongly influence the biogeochemical characteristics and processes in the endorheic watershed river-lake Chasicó.

Material and methods

Study site and sampling

Lake Chasicó is a water body in the semiarid region of the Argentinean Pampa (Fig. 1) with a high biomass of the commercial fish *Odontesthes bonariensis*. This lake is shallow, polymictic, saline and eutrophic (Kopprio et al. 2012, 2013). The monitoring period was from August 2007 to September 2008 and coincided with one of the recurrent droughts in the Pampa region. Three sites were sampled monthly (n=42) in the lake: (1) Station CV, near Chapalcó Village; (2) Station EE at a place called "El Embudo" and (3) Station RM, near the river mouth. A further station was located upstream in River Chasicó (Station RC) and was sampled four times.

Hydrological and biogeochemical survey

Physicochemical water parameters were determined in situ at each sampling station with electronic probes (U-10, Horiba Ltd.). Turbidity was expressed as nephelometric turbidity units (NTU). Additionally, water transparency was measured with a Secchi disk. For the biogeochemical survey, lake water (0.5 to 1 L) was sampled at 1 m below the surface with a Van Dorn sampler and filtered immediately through glass-fibre filters (Whatman GF/F, precombusted at 500 °C for 5 h) by duplicate.

Filters for chlorophyll *a* determination were placed in buffered acetone (90 % in water), kept in dark for 24 h at 4 °C and quantified spectrophotometrically. Filters for POM and stable isotope determinations were dried overnight at 60 °C and kept at room temperature in a desiccator until analysis. The dried filters were homogenised with a ball mill (Retsch PM 100) and particulate organic carbon (POC) and particulate organic nitrogen (PON) were quantified by high-temperature flash combustion with a Carlo Erba NA 2100 elemental analyser. Stable isotopes of carbon (^{13}C) and nitrogen (^{15}N) of POC and PON were analysed with a Thermo Finnigan Delta Plus mass spectrometer coupled to a Flash EA 1112 elemental analyser. Homogenised filters were put in silver vials, acidified with 0.1 N HCl to remove inorganic carbon, dried for 12 h at 50 °C and completely oxidised in the elemental analyser by flash combustion at temperatures

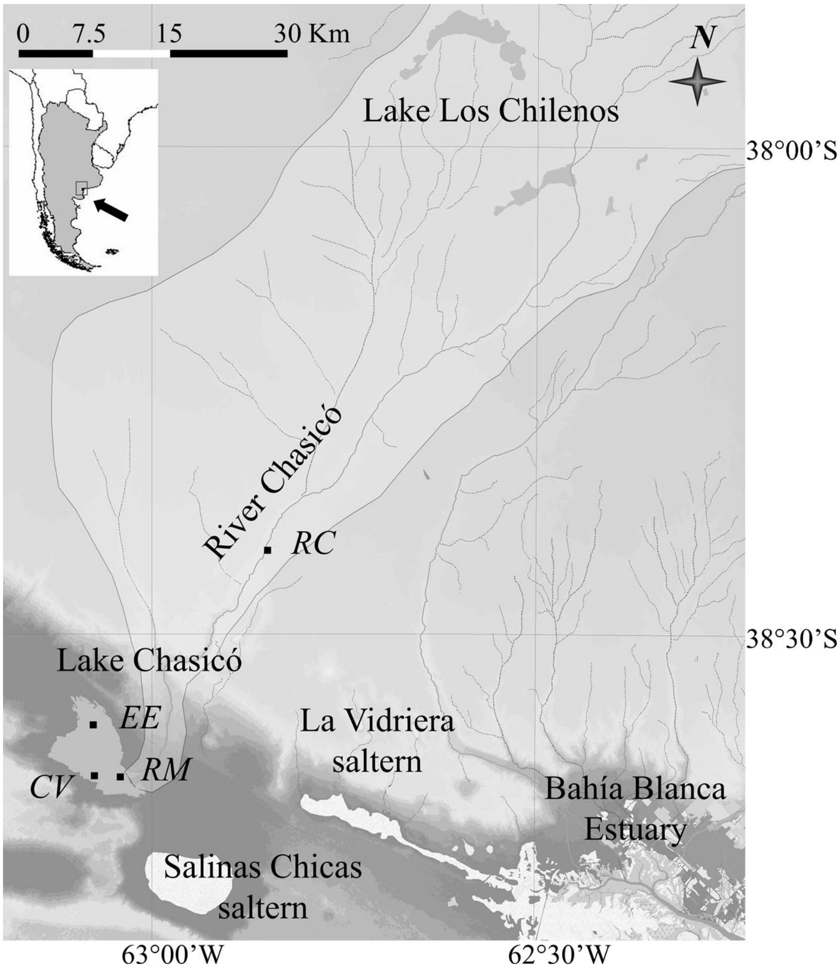

Fig. 1 Main hydrographic basins around Lake Chasicó. Sampling stations: *CV* Chapalcó Village, *EE* El Embudo, *RM* River Mouth, and *RC* River Chasicó

above 1,000 °C under pure O_2. The isotope composition of N_2 and CO_2 was analysed by mass spectrometry.

Sample analysis was carried out in duplicate including an internal standard and a blank every four samples. The amount of isotope per sample was within the analytical range. The relative standard deviation between the duplicates never exceeded 3 %. Results were normalised to the Pee Dee Belemnite (PDB) and atmospheric N_2 standards calculating isotope ratios (R) given as ‰ deviation from the standard values where:

$$R = {}^{13}\mathrm{C}/{}^{12}\mathrm{C} \text{ or} {}^{15}\mathrm{N}/{}^{14}\mathrm{N} \text{ and } \delta(‰) = \left[\left(R_{\text{sample}} - R_{\text{standard}}\right) - 1\right] \times 1{,}000$$

The isotope ratios were determined in accordance with the international standards of the International Atomic Energy Agency (Vienna): IAEA-N1 and IAEA-N2 were used for ^{15}N, NBS 22 and USGS-24 for ^{13}C, and peptone as internal standard.

Filtrates for inorganic nutrients were preserved with mercuric chloride (Kattner 1999) at 4 °C in 50 ml PE bottles and analysed according to standard methods with a nutrient analyser (Evolution III, Alliance Instruments). Filtrates for DOM were adjusted after filtration to pH=2 with H_3PO_4 and kept frozen (−20 °C) in 10 ml precombusted glass ampoules. DOM was estimated as DOC and DON. DOC was determined by high-temperature catalytic oxidation with a Shimadzu TOC-V_{CPN} analyser. In the autosampler, 6 ml of filtrates were sparged with oxygen for 5 min to remove inorganic carbon. In total, 50 μl sample volume was injected directly on the platinum catalyst (heated to 720 °C). Detection of the generated CO_2 was performed with an infrared detector. Total dissolved nitrogen (TDN) was measured simultaneously with DOC by chemiluminescence detection with a Shimadzu TNM-1. Dissolved organic nitrogen was calculated by difference as DON=TDN−dissolved inorganic nitrogen (DIN).

For the plankton survey, lake water was preserved with Lugol solution. Phytoplankton and microzooplankton were counted in duplicate by the Utermöhl method under inverted microscope. The microalgal biovolume was calculated using a standardised set of equations for biovolume calculations from microscopically measured linear dimensions (Hillebrand et al. 1999). The statistical analyses were performed using the programs Statistica 6.0 and XLStat 3.0.

Results

Table 1 describes the main limnological characteristics of Lake Chasicó. The waters of the lake were well oxygenated although the sediments were detected to be anoxic. The pH was alkaline and their values were relatively constant. Differently, salinity showed an increasing significant tendency from ~21 at the begin to ~23 practical salinity units (PSU) at the end of the sampling period, while precipitation displayed an opposite trend due to the extended drought (from ~150 to ~30 mm). Mean summer values of soluble reactive phosphorus (SRP), chlorophyll *a* and Secchi disk were 3.8 μM, 9.1 μg L^{-1} and 1.2 m, respectively. In January, after occasional rainfall and subsequent runoff of River Chasicó, peaks of turbidity (~550 NTU) and chlorophyll *a* (30.5 μg L^{-1}) were detected at Station RM. During this strong runoff, the maximum of nitrate (12.8 μM) and SRP (5.5 μM) and one of the highest concentrations of ammonium (9.3 μM) and silicate (132 μM) were recorded. Higher values of nitrate and chlorophyll *a* were also related to Station RM and negatively correlated with salinity at r values of 0.70 ($p<0.001$) and 0.58 ($p<0.001$), respectively.

Table 1 Main limnological characteristics of Lake Chasicó

Lake variables	Values
Surface area (km^2)	65
Altitude (m.s.l.)	−20
Mean and maximum depth (m)	10 and 15
Temperature range (°C)	5–25
Conductivity (mS cm^{-1})	35.3±2.0[a]
pH	8.9±0.6[a]
Salinity (PSU)	22.1±1.2[a]
Dissolved oxygen (mg L^{-1})	8.6±2.1[a]
Turbidity (NTU)	31±83[a]
Secchi disk depth (m)	1.4±0.6[a]
Chlorophyll *a* (μg L^{-1})	5.8±4.5[a]
Soluble reactive phosphorus (μM)	3.6±0.5[a]
Dissolved inorganic nitrogen (μM)	6.7±3.5[a]

[a] Annual mean

Silicate concentrations were linked to the river discharge (Fig. 2a) and also negatively correlated with salinity at Station RM ($r=0.63$, $p<0.001$). Taking into consideration the stations CV and EE to avoid the strong local influence of river discharge, the peak of diatom biovolume from October to December coincided with the reduction in silicate (Fig. 2b). After the decrease of diatoms from March to May, silicate increased to its initial concentration. Furthermore, the logarithm of the biovolume of diatoms was negatively correlated with the logarithm of silicate ($r=0.61$, $p<0.01$). Diatoms, particularly *Cyclotella* spp., dominated generally the biovolume of phytoplankton (2.4±1.6 mm^3 L^{-1}); whereas flagellates characterised the abundance (8.9±5.7×10^6 cells L^{-1}). At lower abundance and biovolume, cyanobacteria were found particularly in summer and dinoflagellates in autumn.

Ammonium (5.2±1.7 μM) was the main inorganic nitrogenous nutrient: 83±13 % of DIN (sum of the ammonium + nitrate + nitrite) and had values higher than 2 μM throughout the sampling period. Ammonium reached its maximum concentration (9.9 μM) at Station

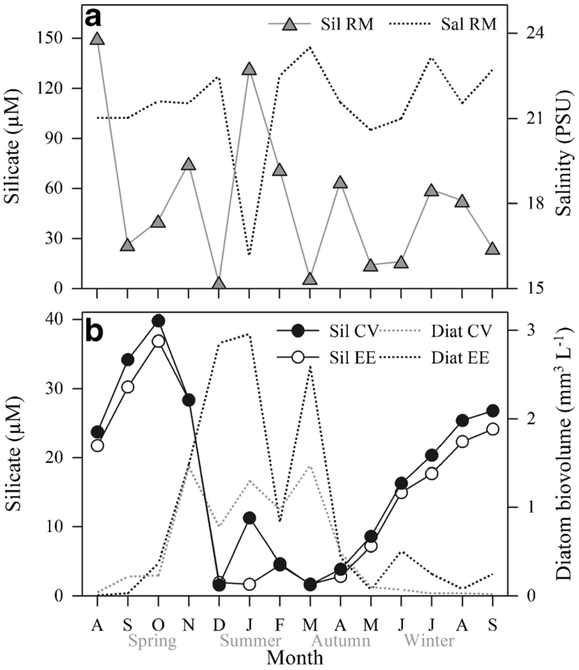

Fig. 2 **a** Monthly silicate concentrations (*Sil*) and salinity (*Sal*) at Station RM (River Mouth). **b** Monthly silicate concentrations and biovolume of diatoms (*Diat*) at stations CV (Chapalcó Village) and EE (El Embudo)

RM in March. The DIN/SRP molar ratio was 1.8±0.7. Unlike in the lake, at the riverine station (RC) the main inorganic nitrogenous compound (82±5 % of DIN) was nitrate (24.2±12.4 µM), SRP was lower (0.7 ±0.7 µM) and the DIN/SRP ratio was several times higher (72.9±35.1). At this station, salinity was ~0.2 and silicate concentrations were extremely elevated (782.5±134.3 µM).

The distribution of PON was very similar to POC ($r=0.99$, $p<0.001$). Elevated values of POC (Fig. 3a) and PON were generally associated to Station RM and were negatively correlated with salinity ($r=0.74$, $p<0.001$ and $r=0.69$, $p<0.001$, respectively). The maximum concentration of POC (2264 µM) and PON (196 µM) coincided with the stronger runoff of River Chasicó at Station RM in January. During this event, POC/PON (molar ratio) was 11.6; higher compared to the annual mean (7.9±1.5). DOC (Fig. 3b) increased during the dryer period (from April to September of 2008) by about 2000 µM, while DON described a relatively stable trend. The mean molar C/N ratio of DOM was 16.1±4.0. In contrast to the particulates, lower concentrations of DOC and DON were usually detected at Station RM and the minimum was during the river runoff (2,200 and 180 µM, respectively).

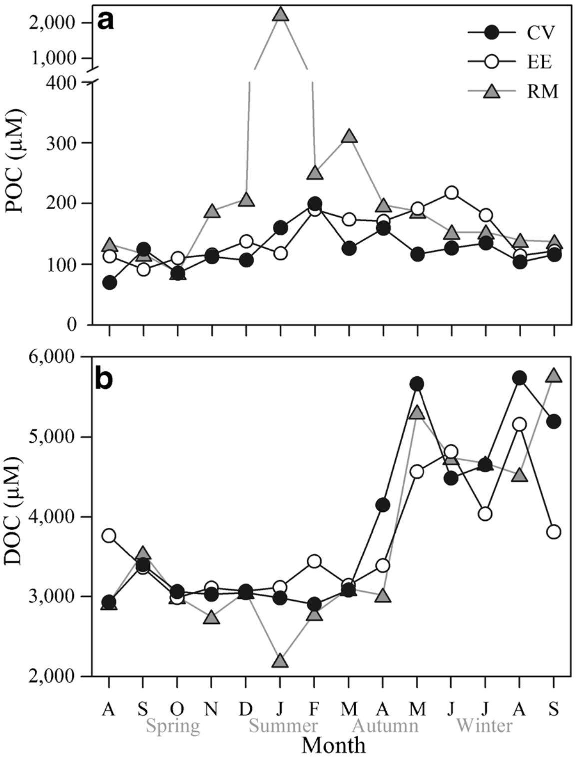

Fig. 3 Seasonal variability of **a** particulate organic carbon (POC) and **b** dissolved organic carbon (DOC) at the three sampling stations of Lake Chasicó (*CV*, *EE* and *RM*)

DOC was correlated with microzooplankton on a logarithmic scale ($r=0.55$, $p<0.05$). The period of higher abundance of the rotifer *Brachionus plicatilis*, which characterised the microzooplankton from March to September of 2008, coincided with a marked increase of 2000 µM in DOC concentration. Moreover, a multiple regression with DOC as dependent variable and *B. plicatilis* abundance and temperature as independent variables, was highly significant ($r=0.76$, $p<0.001$) and explains 58 % of the variance. Temperature was used as an indicator of mesophilic bacterial growth. Beta values were significantly positive for *B. plicatilis* (0.54) and negative for temperature (0.56).

The annual trend of δ^{13}C had a bell shape (Fig. 4a) and there were positive correlations with temperature ($r=0.79$, $p<0.001$) and chlorophyll *a* ($r=0.63$, $p<0.01$). Elevated values of δ^{15}N (Fig. 4b) were found at Station CV and EE (~9‰) from the beginning of the sampling period to summer of 2008; this trend decrease by about 1 ‰ from March to September of 2008. During the warmer months, higher δ^{13}C and lower δ^{15}N values were generally found at Station RM. Moreover, the maximum value of δ^{13}C (−23.0 ‰) and minimum of δ^{15}N (7.1 ‰) were detected during river runoff. The annual mean values of δ^{13}C and δ^{15}N were -25.9±1.0‰ and 8.1±0.6‰, respectively.

The principal component analysis (PCA) explains 67 % of the variation: 48 % for the first axis and 19 % for the second one (Fig. 5). Table 2 shows the correlations of the first two components with each variable. The first component can be related to the river influence: stronger at positive values, while lower at negative values. Indeed, the samples of Station RM more influenced by the river were ordinated positively due to the higher levels of chlorophyll *a*, nitrate, POC, PON and δ^{13}C. Conversely, the other cases were grouped negatively owing to lower values of the mentioned variables and elevated concentrations of DOC and DON. The second component indicates mainly seasonality and sampling period. Generally, the samples from winter and September of 2008 (Sep′) with higher DOC and SRP concentrations were arranged positively. On the other hand, the samples from September of 2007 to April of 2008 (spring, summer and early autumn) with higher δ^{15}N, δ^{13}C and ammonium values were negatively ordinated.

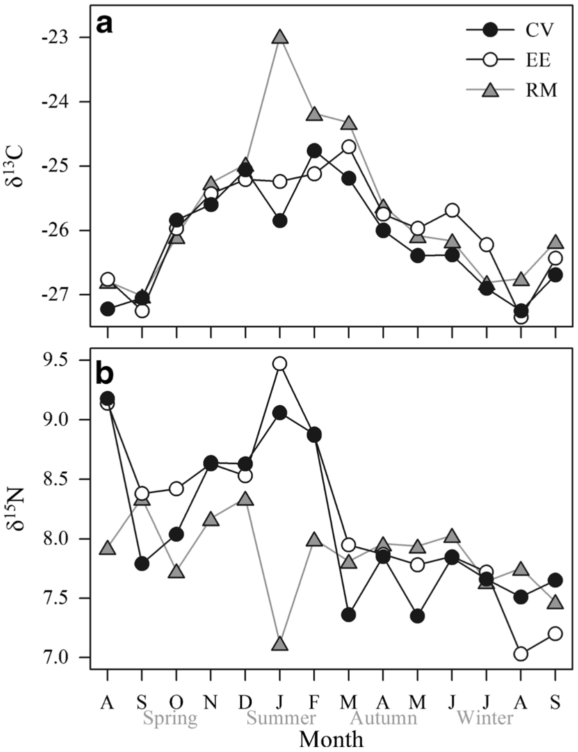

Fig. 4 Seasonal dynamic of **a** stable carbon isotope ($\delta^{13}C$) and **b** stable nitrogen isotope ($\delta^{15}N$) at the three sampling station of Lake Chasicó (*CV*, *EE* and *RM*)

Table 2 Correlations between initial variables and principal components (PC) of the analysis (PCA)

Variables	PC 1	PC 2
Chlorophyll *a*	0.86	−0.01
Soluble reactive phosphorus (SRP)	0.49	0.52
Silicate	0.64	0.20
Ammonium	0.57	−0.48
Nitrate	0.93	0.20
Particulate organic carbon (POC)	0.95	0.13
Particulate organic nitrogen (PON)	0.94	0.10
Dissolved organic carbon (DOC)	−0.43	0.79
Dissolved organic nitrogen (DON)	−0.51	0.02
Stable nitrogen isotope ($\delta^{15}N$)	−0.21	−0.75
Stable carbon isotope ($\delta^{13}C$)	0.62	−0.53

Discussion

River Chasicó was the main source of nitrate and silicate to the lake. The river receives considerable groundwater input (Bonorino et al. 1989) and the pampean aquifer is characterised by elevated concentrations of dissolved silica and nitrate (Miretzky et al. 2001). Silicate was highly utilised by diatoms and reached in some months values close to depletion. Moreover, the dry period likely influenced the aquifer discharge and therefore the silicate and nitrate outflow to the lake was reduced. Agricultural runoff also alters nitrate concentration of River Chasicó. In basins, where agriculture is the primary land use, nitrate is commonly the main nitrogen species of concern (Shanafield et al. 2010). The elevated concentrations of SRP at Station RM could be also linked to agricultural runoff. Furthermore, the river current may facilitate the diffusion of SRP and ammonium from the anoxic sediment explaining partially higher concentrations at Station RM.

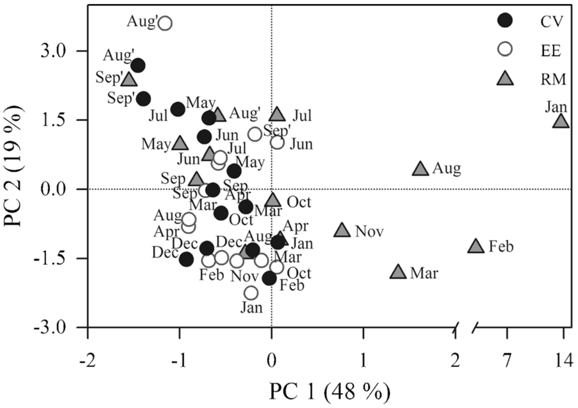

Fig. 5 Principal component analysis (PCA) based on the correlation matrix among chlorophyll *a*, inorganic and organic nutrients and stable isotopes content at the three sampling station of Lake Chasicó (*CV*, *EE* and *RM*); *prime symbol* in 2008

Elevated phosphorus content in Lake Chasicó is a common characteristic of pampean lakes and the low DIN/SRP ratio infers nitrogen limitation. Phosphorus-rich loess soils and human use of land and water resources are the basic reasons for the phosphate-rich status of these water bodies (Quirós and Drago 1999; Gómez et al. 2007). Considering well-established eutrophication indices for P-limited freshwater lakes (Carlson 1977) and even calculating the trophic state index of total phosphorus with SRP, which is an underestimation because it does not include the particulate phosphorus, the lake is classified as hypereutrophic. However, summer chlorophyll *a* concentrations and Secchi disk values were lower and indicated mesotrophic or eutrophic conditions. This difference may also point out primary production limitation by nitrogen and the nitrate from the river may stimulate primary production as was indicated by the higher values of chlorophyll *a*, POC, PON and $\delta^{13}C$ at Station RM. However, natural phytoplankton communities typically prefer to take up nitrogen in the reduced form of ammonium (York et al. 2007) which was the main nitrogen compound of DIN in the lake.

The dominance of ammonium was likely due to inhibition of nitrification processes by the high pH. Ammonium usually indicates oxygen depletion supported by the anoxic sediment. However, the water in Lake Chasicó was well oxygenated owing to the mixing of the water column by the strong winds characteristic of the region. Fish and zooplankton excretion enriched additionally the water with ammonium. Anyway, the activity of the two enzymes involved in nitrification processes, the ammonia monooxygenase and the hydroxylamine oxidoreductase decreases considerably at pH higher than 8 (Frijlink et al. 1992; Stein and Arp 1998). Furthermore, complete inhibition of nitrification takes place at the pH of the lake (Ruiz et al. 2003).

Alkalinity can also limit phytoplankton growth in saline lakes and consequently reduce their chlorophyll *a* concentrations and increase their water transparency. Prairies saline lakes have remarkably lower chlorophyll *a* levels relative to total phosphorus and nitrogen (Campbell and Prepas 1986). At the pH of the lake, dissolved inorganic carbon is present mostly as bicarbonate (HCO_3^{-}) and carbonate (CO_3^{-2}) and not as CO_2. Photosynthesis is limited by low CO_2 concentrations during phytoplankton blooms in hardwater alkaline lakes (Hein 1997). Moreover, ferrous solutions at the pH of the lake form a highly stable precipitate (Jickells et al. 2005; Hove et al. 2008). Evans and Prepas (1997) suggest that low iron bioavailability is the major factor restricting phytoplankton biomass in lakes of higher salinity and that iron limitation in these lakes is likely due to the high concentrations of alkaline anions. The lower pH in the River Chasicó may also stimulate phytoplankton growth at Station RM and explain the higher values of POC, PON, chlorophyll *a* and $\delta^{13}C$.

The main allochthonous input of organic matter occurred during the strong runoff of River Chasicó and was imported as POM. Excluding this event, POM in the lake was mostly produced autochthonously as inferred from the comparison of the C/N ratio of POM with the Redfield ratio (6.6). DOM in Lake Chasicó was basically of autochthonous origin, as deduced from the fact that the river runoff had a diluting impact on DOM and that DOC concentration increased during the dryer months. Floods and rainfall constitute the principal source of allochthonous organic matter and nutrients in arid streams (Vidal-Abarca et al. 2001). Although lake ecosystems frequently receive large inputs of terrestrial carbon in the form of DOM, the arid conditions of the River Chasicó basin did not favour the formation of a major allochthonous DOM pool.

DOC was likely top-down regulated by microzooplankton and its main sources were probably organic matter decomposed in the anoxic sediment of the lake particularly during the dryer months. Microalgae should also influence DOC concentrations since higher DOC values can be attributed to aquatic photosynthetic activity (Dittmar and Lara 2001). The constant concentrations of DOC during summer, when photosynthesis is generally higher in temperate lakes, may be caused by heterotrophic uptake or photolytic degradation of labile DOC. Microzooplankton and particularly *B. plicatilis* graze directly on bacterioplankton or indirectly on protozoa that predate on bacteria. Bacteria are important nutritional sources for *B. plicatilis* (Temerova et al. 2002; Martínez-Díaz et al. 2003) and bacterial abundance is partly controlled by grazers and temperature (Freese et al. 2007). The variability of DOC can be explained by a multiple regression between the abundance of the bacterial grazer *B. plicatilis* and temperature as a bacterial growth indicator.

The marked DOC increase from April to September of 2008 may be additionally attributed to enhanced sedimentary resuspension and consequent DOC liberation as a result of stronger wind conditions in wintertime combined with decreased uptake by bacterioplankton at colder temperatures and reduced photolytic degradation at less solar irradiation. However, clearly lower DOC concentrations than in winter of 2008 were observed in the three samples of winter of 2007, which were characterised by the absence of the bacterial grazer *B. plicatilis* and the dilution effect of higher precipitations. The explanation of the driving forces behind the DOC dynamics is not valid for DON. The values of DON were more constant throughout the year and higher DOM C/N ratios during autumn and winter support the hypothesis that a considerable part of DON is suspended from the lake sediments, a recalcitrant material scarcely utilised by bacterioplankton.

Primary production and CO_2 limitation driven by temperature and pH are the main reasons for the seasonality of $\delta^{13}C$. The $\delta^{13}C$ distribution is a good indicator of primary production, as suggested by the strong correlation with chlorophyll *a*. The variation in $\delta^{13}C$ during the seasonal cycle was relatively large, as is expected for eutrophic lakes in temperate regions. This variation in high latitude eutrophic lakes is due to temperature and light regime, which lead to large seasonal variations in CO_2 concentrations and phytoplankton growth (Gu et al. 2011). As inferred from the pH, the main form of dissolved inorganic carbon in Lake Chasicó was HCO_3^-, which is enriched by about 8 ‰ compared to CO_2 (Ostrom et al. 1997). Microalgae capable of using HCO_3^- are cyanobacteria and diatoms (Moschen et al. 2009; Van den Meersche et al. 2009), which were more abundant during the warmer months and thus certainly CO_2 limited. The higher values of $\delta^{13}C$ at Station RM indicate that river water stimulated the primary productivity. Particularly during stronger runoff events POM with a higher $\delta^{13}C$ signature was imported from Lake Los Chilenos through River Chasicó.

There was no evidence of nitrogen fixation during the period studied. The seasonal $\delta^{15}N$ POM amplitude in eutrophic lakes is generally large (mean of 10.3 ‰) and increases from low to high latitudes (Gu 2009). The values of $\delta^{15}N$ in Lake Chasicó, nevertheless, were lower and relatively constant and the largest difference between stations was found during the plume event (~2.5). The low DIN/SRP ratio may favour N-fixing cyanobacteria blooms. However, phytoplankton in Lake Chasicó was dominated by diatoms and flagellates. Nitrogen limitation does not necessarily lead to cyanobacteria dominance (Kosten et al. 2009) and the polymictic nature of Lake Chasicó may not permit severe cyanobacteria blooms. Moreover, the nitrogenase responsible for nitrogen fixation requires iron as a cofactor (Jarvie et al. 2012), but the bioavailability of iron is theoretically reduced at the pH of the lake.

Human activities involved in the nitrogen cycle influence also the $\delta^{15}N$ dynamic of POM in the lake. The use of fertiliser derived from the fixation of atmospheric nitrogen in the River Chasicó basin may explain lower values of $\delta^{15}N$ at Station RM. The higher signature of $\delta^{15}N$ during spring and summer is attributed to lower fractionation of ammonium during the diatom bloom period. The $\delta^{15}N$ is also a good marker of pollution in aquatic environments. Human waste-water discharge during the fishing season at Station CV and EE increased likely the $\delta^{15}N$. Higher microalgae fractionation at lower temperatures in autumn and winter of 2008 and the ammonium of lower $\delta^{15}N$ derived from the denitrification of nitrate decreased possibly the $\delta^{15}N$ of PON.

Summary and conclusions

River discharge had a strong influence on the dynamic of inorganic and organic nutrients. The lower groundwater discharge driven by the dry period and the diatom bloom contributed to the reduction in silicate concentrations. Agricultural uses in the river watershed were the likely cause of higher values of SRP and nitrate at Station RM. The anoxic sediments were also responsible of SRP and ammonium peaks. The elevated pH of the lake inhibited likely nitrification processes and explained also the dominance of ammonium. The low DIN/SRP ratio indicated nitrogen limitation of phytoplankton growth, though the hypotheses of high pH limitation of CO_2 and iron are pertinent in alkaline lakes. The origin of POM and DOM was mainly autochthonous and the main allochthonous import through the river was as POM. DOC concentrations were likely top-down regulated by microzooplankton and influenced by hydrological changes. The $\delta^{13}C$ dynamic of POM was driven by phytoplankton growth and CO_2 limitation. The $\delta^{15}N$ amplitude did not indicate atmospheric nitrogen fixation and its spatial-temporal variability denoted the influence of anthropogenic activities.

This survey is the first to contribute to the understanding of the seasonal dynamics of nutrients and POM isotopes in a saline lake of South America; to characterise the stochastic events (e.g., river runoff) that typically alter nutrient dynamics in shallow lakes; and to propose *B. plicatilis* as top-down regulator of DOC in lakes of the Argentinian Pampa. Further and long-term research is needed in saline lakes of South America to reach a better understanding of the factors interacting in these not only ecologically but also commercially valuable but poorly studied ecosystems. Increased human uses of water resources, hydrological extremes and climate change will represent considerable challenges for water managers. Water management strategies should be focused to sustain a good water quality.

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References

Campbell, C. E., & Prepas, E. E. (1986). Evaluation of factors related to the unusually low chlorophyll levels in prairie saline lakes. *Canadian Journal of Fisheries and Aquatic Sciences, 43*(4), 846–854. doi:10.1139/f86-104.

Carlier, A., Riera, P., Amouroux, J.-M., Bodiou, J.-Y., Desmalades, M., & Grémare, A. (2009). Spatial heterogeneity in the food web of a heavily modified Mediterranean coastal lagoon: stable isotope evidence. *Aquatic Biology, 5*(2), 167–179. doi:10.3354/ab00147.

Carlson, R. E. (1977). A trophic state index for lakes. *Limnology and Oceanography, 22*(2), 361–369.

Cotovicz Junior, L. C., Brandini, N., Knoppers, B. A., Mizerkowski, B. D., Sterza, J. M., Ovalle, A. R. C., et al. (2013). Assessment of the trophic status of four coastal lagoons and one estuarine delta, eastern Brazil. *Environmental Monitoring and Assessment, 185*(4), 3297–3311. doi:10.1007/s10661-012-2791-x.

Cunha, M. E. T., Yabe, M. J. S., Lobo, I., & Aravena, R. (2006). Isotopic composition as a tool for assessment of origin and dynamic of organic matter in tropical freshwater. *Environmental Monitoring and Assessment, 121*(1–3), 459–476. doi:10.1007/s10661-005-9146-9.

Dittmar, T., & Lara, R. J. (2001). Driving forces behind nutrient and organic matter dynamics in a mangrove tidal creek in north Brazil. *Estuarine, Coastal and Shelf Science, 52*(2), 249–259. doi:10.1006/ecss.2000.0743.

Duarte, C. M., Prairie, Y. T., Montes, C., Cole, J. J., Striegl, R., Melack, J., et al. (2008). CO2 emissions from saline lakes: a global estimate of a surprisingly large flux. *Journal of Geophysical Research: Biogeosciences, 113*(G4), G04041. doi:10.1029/2007JG000637.

Elser, J. J., Sterner, R. W., Galford, A. E., Chrzanowski, T. H., Findlay, D. L., Mills, K. H., et al. (2000). Pelagic C:N:P stoichiometry in a eutrophied lake: responses to a whole-lake food-web manipulation. *Ecosystems, 3*(3), 293–307. doi:10.1007/s100210000027.

Evans, J. C., & Prepas, E. E. (1997). Relative importance of iron and molybdenum in restricting phytoplankton biomass in high phosphorus saline lakes. *Limnology and Oceanography, 42*(3), 461–472.

Freese, H. M., Görs, S., Karsten, U., & Schumann, R. (2007). Dissolved inorganic nutrients and organic substrates in the River Warnow (north-eastern Germany)—utilisation by bacterioplankton. *Limnologica - Ecology and Management of Inland Waters, 37*(3), 264–277. doi:10.1016/j.limno.2007.03.001.

Frijlink, M., Abee, T., Laanbroek, H., Boer, W., & Konings, W. (1992). The bioenergetics of ammonia and hydroxylamine oxidation in *Nitrosomonas europaea* at acid and alkaline pH. *Archives of Microbiology, 157*(2), 194–199. doi:10.1007/BF00245290.

Gómez, S., Menni, R., Naya, J., & Ramirez, L. (2007). The physical–chemical habitat of the Buenos Aires pejerrey, *Odontesthes bonariensis* (Teleostei, Atherinopsidae), with a proposal of a water quality index. *Environmental Biology of Fishes, 78*(2), 161–171. doi:10.1007/s10641-006-9086-4.

Gu, B. (2009). Variations and controls of nitrogen stable isotopes in particulate organic matter of lakes. *Oecologia, 160*(3), 421–431. doi:10.1007/s00442-009-1323-z.

Gu, B., Schelske, C., & Waters, M. (2011). Patterns and controls of seasonal variability of carbon stable isotopes of particulate organic matter in lakes. *Oecologia, 165*(4), 1083–1094. doi:10.1007/s00442-010-1888-6.

Hein, M. (1997). Inorganic carbon limitation of photosynthesis in lake phytoplankton. *Freshwater Biology, 37*(3), 545–552. doi:10.1046/j.1365-2427.1997.00180.x.

Hillebrand, H., Dürselen, C.-D., Kirschtel, D., Pollingher, U., & Zohary, T. (1999). Biovolume calculation for pelagic and benthic microalgae. *Journal of Phycology, 35*(2), 403–424. doi:10.1046/j.1529-8817.1999.3520403.x.

Hove, M., van Hille, R. P., & Lewis, A. E. (2008). Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH. *Chemical Engineering Science, 63*(6), 1635. doi:10.1016/j.ces.2007.11.016.

Iriondo, M. (1989). Quaternary lakes of Argentina. *Palaeogeography, Palaeoclimatology, Palaeoecology, 70*(1–3), 81–88.

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., et al. (2010). Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. *Nature Reviews Microbiology, 8*(8), 593–599. doi:10.1038/nrmicro2386.

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., et al. (2005). Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science, 308*(5718), 67–71. doi:10.1126/science.1105959.

Karydis, M., & Kitsiou, D. (2012). Eutrophication and environmental policy in the Mediterranean Sea: a review. *Environmental Monitoring and Assessment, 184*(8), 4931–4984. doi:10.1007/s10661-011-2313-2.

Kattner, G. (1999). Storage of dissolved inorganic nutrients in seawater: poisoning with mercuric chloride. *Marine Chemistry, 67*(1–2), 61–66. doi:10.1016/S0304-4203(99)00049-3.

Kopprio, G. A., Freije, R. H., Strussmann, C. A., Kattner, G., Hoffmeyer, M. S., Popovich, C. A., et al. (2010). Vulnerability of pejerrey *Odontesthes bonariensis* populations to climate change in pampean lakes of Argentina. *Journal of Fish Biology, 77*(8), 1856–1866. doi:10.1111/j.1095-8649.2010.02750.x.

Kopprio, G. A., Kattner, G., Graeve, M., Freije, R. H., & Lara, R. J. (2012). Exceptional lipid storage mode of the copepod *Boeckella poopoensis* in a pampean salt lake, Argentina. *Aquatic Biology, 15*(3), 275–281. doi:10.3354/ab00432.

Kopprio, G. A., Freije, R. H., Arias-Schreiber, M., & Lara, R. J. (2013). An ecohydrological adaptive approach to a salt lake in the semiarid grasslands of Argentina: future management perspectives. *Sustainability Science*, 1-10, doi:10.1007/s11625-013-0207-7.

Kosten, S., Huszar, V. L. M., Mazzeo, N., Scheffer, M., Sternberg, L. S. L., & Jeppesen, E. (2009). Lake and watershed characteristics rather than climate influence nutrient limitation in shallow lakes. *Ecological Applications, 19*(7), 1791–1804. doi:10.1890/08-0906.1.

Lara, R. J., Alder, V., Franzosi, C. A., & Kattner, G. (2010). Characteristics of suspended particulate organic matter in the southwestern Atlantic: influence of temperature, nutrient and phytoplankton features on the stable isotope signature. *Journal of Marine Systems, 79*(1–2), 199–209. doi:10.1016/j.jmarsys.2009.09.002.

Lehmann, M. F., Bernasconi, S. M., McKenzie, J. A., Barbieri, A., Simona, M., & Veronesi, M. (2004). Seasonal variation of the δ13C and δ15N of particulate and dissolved carbon and nitrogen in Lake Lugano: constraints on biogeochemical cycling in a eutrophic lake. *Limnology and Oceanography, 49*(2), 415–429. doi:10.4319/lo.2004.49.2.0415.

Martínez-Díaz, S., Álvarez-González, C. A., Moreno Legorreta, M., Vázquez-Juárez, R., & Barrios-González, J. (2003). Elimination of the associated microbial community and bioencapsulation of bacteria in the rotifer *Brachionus plicatilis. Aquaculture International, 11*(1–2), 95–108. doi:10.1023/A:1024117109362.

Maya, M. V., Soares, M., Agnihotri, R., Pratihary, A. K., Karapurkar, S., Naik, H., et al. (2011). Variations in some environmental characteristics including C and N stable isotopic composition of suspended organic matter in the Mandovi estuary. *Environmental Monitoring and Assessment, 175*(1–4), 501–517. doi:10.1007/s10661-010-1547-8.

Miretzky, P., Conzonno, V., & Fernández Cirelli, A. (2001). Geochemical processes controlling silica concentrations in groundwaters of the Salado River drainage basin, Argentina. *Journal of Geochemical Exploration, 73*(3), 155–166. doi:10.1016/S0375-6742(01)00194-7.

Moschen, R., Lücke, A., Parplies, J., & Schleser, G. H. (2009). Controls on the seasonal and interannual dynamics of organic matter stable carbon isotopes in mesotrophic Lake Holzmaar, Germany. *Limnology and Oceanography, 54*(1), 194–209. doi:10.4319/lo.2009.54.1.0194.

Nguyen, H.-M., Shin, J.-K., & Hur, J. (2011). Multivariate analysis for spatial distribution of dissolved organic matters in a large river-type dam reservoir. *Environmental Monitoring and Assessment, 183*(1–4), 425–436. doi:10.1007/s10661-011-1930-0.

Ostrom, N. E., Macko, S. A., Deibel, D., & Thompson, R. J. (1997). Seasonal variation in the stable carbon and nitrogen isotope biogeochemistry of a coastal cold ocean environment. *Geochimica et Cosmochimica Acta, 61*(14), 2929–2942. doi:10.1016/S0016-7037(97)00131-2.

Pace, M. L., Cole, J. J., Carpenter, S. R., Kitchell, J. F., Hodgson, J. R., Van de Bogert, M. C., et al. (2004). Whole-lake carbon-13 additions reveal terrestrial support of aquatic food webs. *Nature, 427*, 240–243. doi:10.1038/nature02227.

Quirós, R., & Drago, E. (1999). The environmental state of Argentinean lakes: an overview. *Lakes & Reservoirs: Research and Management, 4*(1–2), 55–64. doi:10.1046/j.1440-1770.1999.00076.x.

Quirós, R., Rosso, J. J., Rennella, A., Sosnovsky, A., & Boveri, M. (2002). Análisis del estado trófico de las lagunas pampeanas (Argentina). *Interciencia, 27*(11), 584–591.

Ruiz, G., Jeison, D., & Chamy, R. (2003). Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration. *Water Research, 37*(6), 1371–1377. doi:10.1016/S0043-1354(02)00475-X.

Sánchez-Carrillo, S., Alatorre, L. C., Sánchez-Andrés, R., & Garatuza-Payán, J. (2007). Eutrophication and sedimentation patterns in complete exploitation of water resources scenarios: an example from northwestern semi-arid Mexico. *Environmental Monitoring and Assessment, 132*(1–3), 377–393. doi:10.1007/s10661-006-9541-x.

Shanafield, M., Rosen, M., Saito, L., Chandra, S., Lamers, J., & Nishonov, B. (2010). Identification of nitrogen sources to four small lakes in the agricultural region of Khorezm, Uzbekistan. *Biogeochemistry, 101*(1–3), 357–368. doi:10.1007/s10533-010-9509-3.

Stein, L. Y., & Arp, D. J. (1998). Ammonium limitation results in the loss of ammonia-oxidizing activity in *Nitrosomonas europaea. Applied and Environmental Microbiology, 64*(4), 1514–1521.

Temerova, T., Tolomeyev, A., & Degermendzhy, A. (2002). Growth of dominant zooplankton species feeding on plankton microflora in Lake Shira. *Aquatic Ecology, 36*(2), 235–243. doi:10.1023/A:1015607304508.

Van den Meersche, K., Van Rijswijk, P., Soetaert, K., & Middelburg, J. J. (2009). Autochthonous and allochthonous contributions to mesozooplankton diet in a tidal river and estuary: integrating carbon isotope and fatty acid constraints. *Limnology and Oceanography, 54*(1), 62–74. doi:10.4319/lo.2009.54.1.0062.

Vidal-Abarca, M. R., Suárez, M. L., Guerrero, C., Velasco, J., Moreno, J. L., Millán, A., et al. (2001). Dynamics of dissolved and particulate organic carbon in a saline and semiarid stream of southeast Spain (Chicamo stream). *Hydrobiologia, 455*(1–3), 71–78. doi:10.1023/A:1011939418723.

Wetzel, R. G. (1984). Detrital dissolved and particulate organic carbon functions in aquatic ecosystems. *Bulletin of Marine Science, 35*(3), 503–509.

Wigand, C., McKinney, R., Cole, M., Thursby, G., & Cummings, J. (2007). Varying stable nitrogen isotope ratios of different coastal marsh plants and their relationships with wastewater nitrogen and land use in New England, USA. *Environmental Monitoring and Assessment, 131*(1–3), 71–81. doi:10.1007/s10661-006-9457-5.

Williamson, C. E., Morris, D. P., Pace, M. L., & Olson, O. G. (1999). Dissolved organic carbon and nutrients as regulators of lake ecosystems: resurrection of a more integrated paradigm. *Limnology and Oceanography, 44*(3 part 2), 795–803. doi:10.4319/lo.1999.44.3_part_2.0795.

Withers, P. J. A. (2012). Climate change and coupling of macronutrient cycles along the atmospheric, terrestrial, freshwater and estuarine continuum. *Science of The Total Environment, 434*, 252–258. doi:10.1016/j.scitotenv.2012.07.051.

York, J. K., Tomasky, G., Valiela, I., & Repeta, D. J. (2007). Stable isotopic detection of ammonium and nitrate assimilation by phytoplankton in the Waquoit Bay estuarine system. *Limnology and Oceanography, 52*(1), 144–155. doi:10.4319/lo.2007.52.1.0144.