

Oxic–anoxic conditions in the water column of a tropical freshwater reservoir (Peña-Larga dam, NW Venezuela)

Boris Bellanger^{a,*}, Sylvain Huon^{a,*}, Philipp Steinmann^b, François Chabaux^c, Fernando Velasquez^d, Vincent Vallès^e, Kaspar Arn^b, Norbert Clauer^c, André Mariotti^a

^aUMR 7618 (UPMC-INRA-CNRS) BIOMCO, Université Pierre Marie Curie (UPMC), Case 120, 4 place Jussieu, Paris Cedex 05, 75252, France

^bInstitut de Géologie, Université de Neuchâtel, Case postale 2, 11 rue Emile Argand, Neuchâtel CH-2007, Suisse

^cCGS (UMR 7517 CNRS-ULP), Ecole et Observatoire des Sciences de la Terre, 1, rue Blessig, Strasbourg 67084, France

^dUnidad PLANINDECH, Centro de Ecología de Boconó, Universidad de los Andes, Boconó, Estado Trujillo, Venezuela

^eINRA Science du Sol Domaine St Paul, Site Agroparc, Avignon Cedex 9, 84914, France

Abstract

A freshwater reservoir (area: 122 km², volume: 2850 × 10⁶ m³, maximum depth: 72 m) located at the outlet of a tropical Andean watershed (Rio Boconó, 1620 km², 08°57'–09°31'N, 70°02'–70°34'W, NW Venezuela) was studied combining: (1) high resolution monitoring of the major environmental parameters using a CTD probe; (2) dissolved (major and trace) element concentration measurements; (3) water (δ¹⁸O, δ²H) isotope measurements and; (4) organic carbon (C) concentration – δ¹³C measurements on suspended matter and on sediments. Composed of two sub-reservoirs with contrasted water inputs, the Peña Larga dam provides the opportunity to better constrain C budgets and source – composition of suspended organic matter within two parts of a unique freshwater system with contrasted redox conditions. The redox status is reflected by drastic differences between the two parts of the reservoir, pictured by water residence time, water column ventilation, dissolved trace element concentration and suspended organic matter composition. Seasonal renewal of water near the main inlet supports higher surface productivity, oxic water column conditions, homogenous water chemical composition and, below the thermocline, the transport of suspended organic matter mainly derived from soil erosion on the watershed. Calculated sediment and organic C storages amount to 5.6 × 10⁶ t a⁻¹ and 21 ± 5 × 10³ t C a⁻¹, respectively. Despite a markedly lower suspended sediment load, outflow waters exhibit POC-δ¹³C values similar to those in inflow waters, due to a short water residence time and a rapid recycling of primary products. In the more isolated parts of the reservoir, where water discharge is thoroughly reduced, hypoxic to anoxic conditions are found immediately below the thermocline (ca. 16 m, [O₂] < 30 μmol L⁻¹). They induce a correlative increase of trace element concentrations with water depth. Suspended organic matter display ¹³C-depleted compositions, contrasting sharply with that of photosynthetic organisms and land-derived detritus, that either reflect the contribution of microbial biomass (chemoautotrophic and/or methanotrophic bacteria) or the selective degradation of more labile organic compounds in the water column. The hypoxic to anoxic conditions displayed in the major part of the water column extend to the first cm of lake bottom sediments. A simplified budget based on the main redox processes active in the hypolimnion and on average water residence times, supports drastic differences in mineralization rate: 83–444 μmol C L⁻¹ a⁻¹ for the oxic reservoir and only 43 μmol C L⁻¹ a⁻¹ for the hypoxic to anoxic reservoir. This study shows that, if water renewal is not sufficient, tropical freshwater lakes may be subject to severe dissolved O₂ depletion conditions at shallow depths, comparable to those observed in deep sections of the water column of temperate eutrophic lakes.

* Corresponding authors.

Present address: Laboratoire Chimie et Environnement, Université de Provence, 3 Place Victor Hugo, 13331 Marseille Cedex 3, France. Fax: +33-1-44-27-41-64 (V. Vallès).

E-mail addresses: bbellan@ccr.jussieu.fr (B. Bellanger), huon@ccr.jussieu.fr (S. Huon).

1. Introduction

Eutrophication of natural and artificial lakes and water reservoirs is a major environmental problem because of their importance to human settlement, in particular for flood control, irrigation, fishing and energy production. Critical conditions may arise when the dissolved O_2 concentration available to decompose organic matter falls below a minimum level ($[O_2] < 1 \text{ mg L}^{-1}$, equivalent to $31 \mu\text{mol L}^{-1}$, Chapra and Dobson, 1981). In the absence of O_2 , bacterially mediated reduction processes may lead to the degradation of water quality through NH_4^+ production, SO_4^{2-}/H_2S conversion, dissolved metal release from oxide/hydroxide phases (and possibly also clay minerals) and, control CH_4 production (e.g. Davison and Woof, 1984; De Vitre et al., 1988; Davison, 1993; Hamilton-Taylor and Davison, 1995; Stumm and Morgan, 1996; Hongve, 1997). Several major processes control O_2 depletion in freshwater lakes (Likens, 1972): (1) enhanced biological productivity resulting from high input of nutrients (autochthonous organic matter input), (2) high organic matter supply provided by soil erosion in the drainage areas (allochthonous organic matter input) and, (3) low water turnover (hydrological eutrophication). Natural O_2 depletion may also result from gradual sedimentary filling over long periods of time, but human activities accelerate this process. This is particularly obvious in tropical regions where deforestation and cultivation enhance soil erosion (Lal, 1990, 1995). Important amounts of organic matter are thus displaced to streams and; water reservoirs may constitute ultimate receptacles for runoff when located at the outlet of cultivated mountainous watersheds.

In sufficiently deep lakes, changes in water chemistry are mainly driven by the temperature gradient prevailing in the water column, and by photosynthetic/respiration processes. In tropical regions, temperature is high and nearly constant over the year so that persistent thermal stratification may arise, leading to drastic chemical differences between the epilimnion (in contact with atmosphere) and the hypolimnion (isolated from atmosphere). Deep waters may be isolated from surface if inlet (and outlet) flows or stirring by winds do not support sufficient mixing and renewal of water. Hydro-

logical eutrophication may also arise from reduced ventilation conditions in the water column. The aim of this study was to characterize the oxic to anoxic conditions prevailing in the water column of a tropical freshwater reservoir, the Peña Larga water dam, set up at the outlet of a mountainous cultivated watershed (Boconó watershed, NW Venezuelan Andes) and in which soil erosion is suspected of inducing severe eutrophic conditions through enhanced soil organic matter supply (Lewis, 1984; Brock, 1985). Composed of two sub-reservoirs with different hydrological regimes, the Peña Larga dam also provides the opportunity to constrain geochemical budgets within two parts of a unique freshwater system with equivalent climatic conditions but different ventilation rates of the water column. This study was carried out in order to: (1) better assess the relationship between suspended matter and oxidation/reduction processes taking place in the water column, (2) discriminate terrigenous and autochthonous sources of suspended organic matter and, (3) identify the main process driving the water column to hypoxic-anoxic conditions (i.e., reduced bottom water ventilation vs. excess organic matter supply). The study was focussed on the characterization of water column redox status combining geochemical analyses carried out on water sample aliquots collected at several depths in the water column (water stable isotopes, dissolved element concentrations, particulate organic C concentration and $^{13}C/^{12}C$ measurements) along with high resolution monitoring of freshwater most relevant environmental parameters (temperature, dissolved O_2 concentration, total chlorophyll-*a* concentration, pH, Eh, water electrical conductivity and suspended organic matter load using light backscattering measurements).

2. Materials and methods

2.1. Physiographic setting

The Peña Larga water dam, built for water and electricity production in 1983, is located at the outlet of the Rio Boconó watershed (1620 km^2 , NW Venezuelan Andes, $08^{\circ}57' - 09^{\circ}31'N$, $70^{\circ}02' - 70^{\circ}34'W$; Fig. 1). The

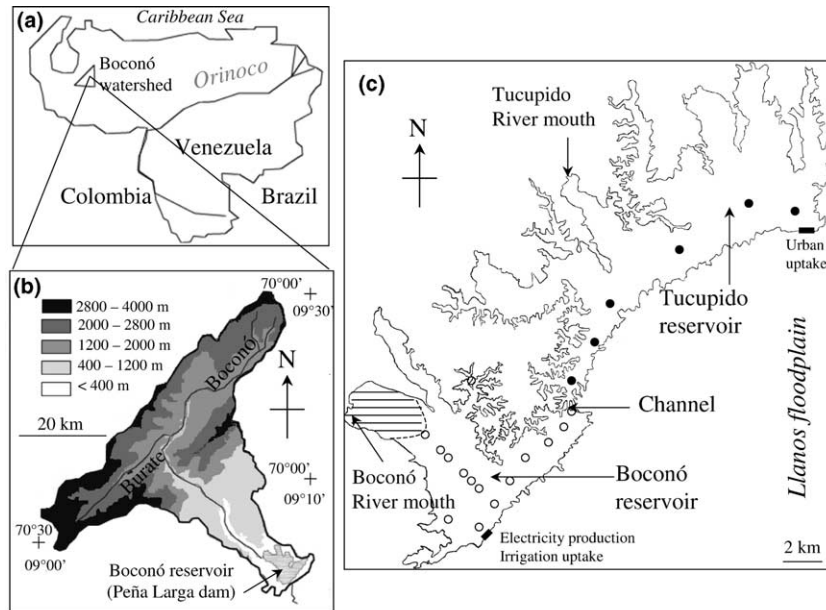


Fig. 1. Location of the Boconó Watershed in Venezuela (a) and physiographic maps of the watershed (b) and of the Peña Larga water reservoir (c). Horizontal lines in (c) correspond to the alluvial fan of the Boconó River. Locations of the bathymetric profiles are reported for the Boconó reservoir (open circles) and for the Tucupido reservoir (closed circles).

geological basement of the watershed is composed of Palaeozoic meta-sedimentary rocks and Tertiary – Quaternary alluvial deposits in the southern part and, crystalline rock formations in the northern part (Gonzales de Juana et al., 1980; Pouyllau, 1989; Edmond et al., 1996). The resulting reservoir can be divided into two parts (Fig. 1(c)), the Boconó and the Tucupido reservoirs, that communicate through a narrow and shallow

channel with a maximum depth of 20 m. The Boconó River (Fig. 1) provides 90% of the inflow water volume (see Table 1 for detailed hydrological data). With a maximum storage capacity of $3590 \times 10^6 \text{ m}^3$ (267.75 m a.s.l.), the two reservoirs cover a surface area of 122 km^2 with a maximum water depth of 72 m (information provided by the MARNR, Ministerio del Ambiente y de los Recursos Naturales Renovables, Caracas, 2001).

Table 1
Hydrological data for the Peña Larga water dam

	Boconó reservoir	Tucupido reservoir
Mean water level (m a.s.l.) ^a	260.5	260.5
Mean water depth (m) ^b	26	27
Maximum water depth (m)	62	72
Area (km ²) ^c	38.4	68.6
Volume (10 ⁶ m ³) ^c	1010	1870
Drainage area (km ²)	1620	440
River input (10 ⁶ m ³ a ⁻¹)	2490	277
Water uptake for electricity production (10 ⁶ m ³ a ⁻¹)	2763	–
Water uptake for urban use (10 ⁶ m ³ a ⁻¹)	–	4
Direct precipitation (10 ⁶ m ³ a ⁻¹) ^d	61	110
Evaporation (10 ⁶ m ³ a ⁻¹) ^d	50	89
Water transfer between reservoirs (10 ⁶ m ³ a ⁻¹)	+273	–273
Water residence time (a) ^e	0.36	6.20

^a 1997–2000 Period.

^b Volume:area ratio.

^c Calculated for the mean water level (260.5 m a.s.l.) using hypsometric data.

^d Mean precipitation: 1600 mm a^{-1} , mean evaporation: 1300 mm a^{-1} .

^e Water volume/water outflow.

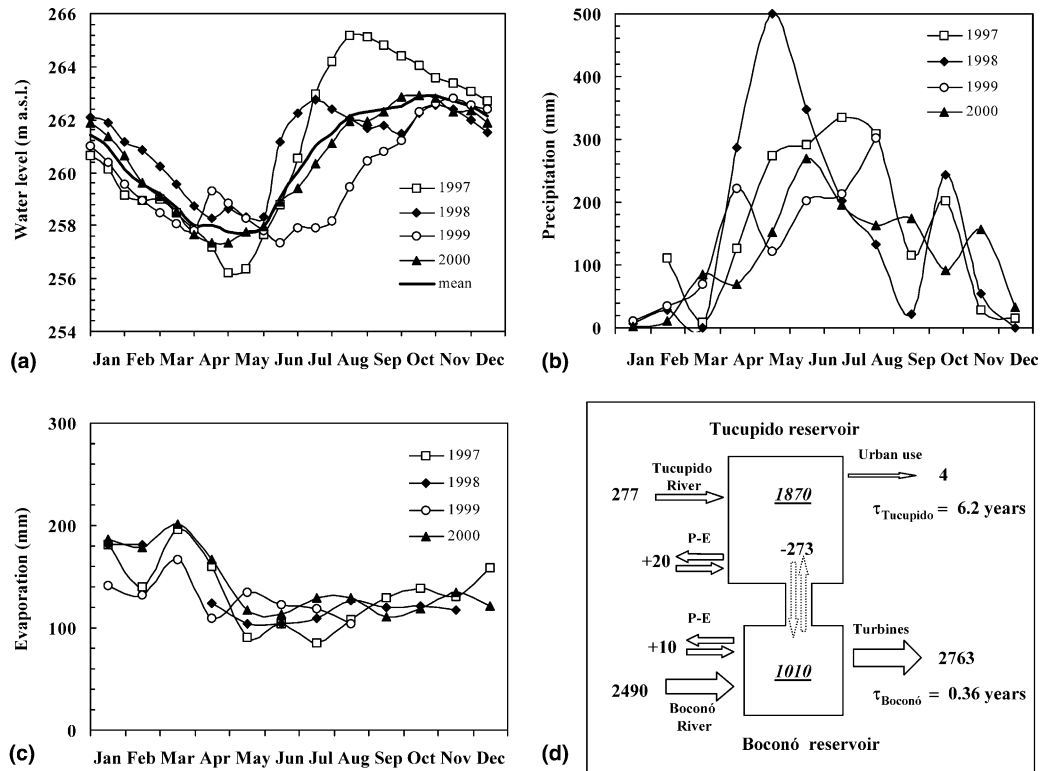


Fig. 2. Plots of: (a) bi-monthly water level, (b) average monthly precipitation, (c) average monthly evaporation and (d) annual water budget, for the whole lake over the 1997–2000 period. Flux unit is $10^6 \text{ m}^3 \text{ a}^{-1}$, volume unit (underlined, *Italic style*) is 10^6 m^3 . P–E corresponds to precipitation minus evaporation over the reservoir surfaces. τ is the average water residence time (the ratio of water volume to annual water flux) calculated for each reservoir.

Water uptakes for electricity production, irrigation, and urban use are performed at mid-water depth (ca. 20–40 m) in both reservoirs. The mean water level is 260.5 m a.s.l. (1997–2000) with seasonal variations of several meters (Fig. 2(a)). The tropical climatic conditions prevailing in the study area result in a mean annual temperature of 25 °C, with maximum precipitation between April and October during the rainy season (Fig. 2(b)), and maximum evaporation between December and April during the dry season (Fig. 2(c)). Bathymetric mapping of the Boconó reservoir in 1998 and 2001 showed that sediment delivery reduced the water storage capacity by $4 \times 10^6 \text{ m}^3 \text{ a}^{-1}$ (MARNR, 2001). According to this sedimentary filling rate, the Peña Larga dam should theoretically cease being useful in 47 a. Using a bulk sediment density of 1.4 g cm^{-3} , the sedimentation rate (volume loss rate \times sediment density) reaches $5.6 \times 10^6 \text{ t a}^{-1}$, a value very close to the average $6.0 \times 10^6 \text{ t a}^{-1}$ obtained by direct sediment yield monitoring of the Boconó River discharge (Cornielès, 1998). These data imply that approximately 90% of the suspended sediment discharge is stored in alluvial deposits in the Boconó reservoir.

2.2. Analytical procedures

Environmental parameters were obtained using a CTD (conductivity–temperature–depth) probe that allows high resolution (every 30 cm, sensor response time below 1 s) and simultaneous monitoring of pressure (expressed as water depth), temperature, pH, electrical conductivity (EC), dissolved oxygen concentration, total chlorophyll-*a* concentration, turbidity and light backscatter. Accurate monitoring of turbidity in the water column could only be performed in November 2000 and the results are not displayed in this study. Sampling for suspended matter collection, redox potential (Eh), dissolved organic and inorganic C (DOC, DIC, respectively), major and trace element concentrations and water stable isotope ($\delta^{18}\text{O}$, $\delta^2\text{H}$) measurements was carried out for selected water depths in June 1998, March 1999, September 1999 and November 2000. Water sample aliquots for DOC and DIC analyses were poisoned with sodium azide (1 g L^{-1} , NaN_3) and filtered with Millipore $0.8 \mu\text{m}$ glass fiber filters the day of collection. All samples were stored in dark Pyrex bottles and kept in refrigerated places. Analyses were performed

Table 2
Analytical procedures

Parameter	Method	Material	Precision
Water depth (pressure)	In situ measurements with additional sensors	OTS-094, Meerestechnik	0.1%
Temperature		Backscat I-Fluorometer 1910 (Dr Haardt Optik Mi- croelectronik)	0.01 °C
pH			0.1 pH unity
Electrical conductivity			1 $\mu\text{S cm}^{-1}$
Dissolved oxygen			2% sat. O ₂
Chlorophyll- <i>a</i>			0.01 $\mu\text{g Chlorophyll-}a$ L ⁻¹
Light backscatter			0.01% Backscatter
Redox potential	Manual probe (Pt electrode)	Hanna instruments	20 mV
Dissolved Inorganic Carbon (DIC)	CO ₂ with H ₃ PO ₄	Dohrmann analyser DC-190	0.5 ppm
Dissolved Organic Carbon (DOC)	Combustion and oxidation (DOC = TOC – DIC)		0.5 ppm
Ca, Mg, Na, K	Atomic absorption	Hitachi Z 8200	$0.001 \times 10^{-3} \text{ mol L}^{-1}$
F, Cl, SO ₄ , NO ₃ , NO ₂ , PO ₄	Ionic chromatography	Dionex 2000 I	$0.001 \times 10^{-3} \text{ mol L}^{-1}$
NH ₄ , Si	Colourimetry	Technicon autoanalyser II	$0.001 \times 10^{-3} \text{ mol L}^{-1}$
Fe, Mn, Al, and trace elements	ICP-AES	JY 124	2–3%
Sr, Ba, U	ICP-MS	Fisons PQ 2	5–10%
$\delta^{18}\text{O}$ (Epstein and Mayeda, 1953)	CO ₂ –H ₂ O equilibrium	VG Fisons Optima IRMS	0.1‰ vs. SMOW
$\delta^2\text{H}$ (Bigeleisen et al., 1952)	H ₂ O reduction by uranium	Finnigan IRMS	1‰ vs. SMOW
Particulate Organic Carbon (POC)	EA-IRMS	Carlo-Erba NA-1500 NC	0.1 mg C g ⁻¹
Particulate nitrogen (PN)		Elemental analyser on line	0.05 mg N g ⁻¹
POC- $\delta^{13}\text{C}$		With a Fisons Optima IRMS	0.1‰ vs. PDB

the following month. Separate water sample aliquots were filtered with Millipore 0.45 μm cellulose filters for major dissolved element analyses. Major cation and trace element measurements were carried out on subsamples, acidified with 1 N HCl the day of collection. Particulate organic C concentration (POC), particulate N concentration (PN) and C stable isotope analyses ($\delta^{13}\text{C}$) were performed on sieved <50 μm size fractions of the filtered residues from un-poisoned samples collected in polyethylene bottles. Carbonate removal for POC analyses was performed using 1 N HCl under pH control (above 4.0) in order to reduce possible leaching effects (e.g. Huon et al., 2002). All analytical procedures are summarized in Table 2.

3. Results

3.1. Water budget of the Peña Larga water dam

An annual water budget was calculated using the hydrological data available for the 1997–2000 period (Fig. 2(d) and Table 1, data provided by the MARNR). Water supply was estimated using the av-

erage discharges of the Boconó and Tucupido Rivers, 79 and 9 $\text{m}^3 \text{s}^{-1}$ (2490×10^6 and $277 \times 10^6 \text{ m}^3 \text{ a}^{-1}$), respectively, and from local precipitation data. Calculation of water output includes intakes for electricity production and irrigation (Boconó reservoir), urban use (Tucupido reservoir) and direct evaporation. Due to the establishment of a forested protection area around the water reservoirs, overland runoff can be considered as negligible with respect to river discharges. Ground water seepage is limited to the main alluvial deposits and directly linked to the Boconó river discharge. The overall water movements indicate a net annual water transfer ($\approx 273 \times 10^6 \text{ m}^3 \text{ a}^{-1}$) from the Tucupido reservoir to the Boconó reservoir. According to the seasonal water level changes observed over the 1997–2000 period, a mean annual rise of 30 cm was derived, corresponding to additional water storage of $30 \times 10^6 \text{ m}^3$. Because the water volume of the reservoirs is nearly constant year to year (the additional water storage only represents 1% of lake volume), steady state conditions may be assumed. The average water residence time (ratio of volume to flow rate) is 0.36 years for the Boconó reservoir and 6.20 years for the Tucupido reservoir.

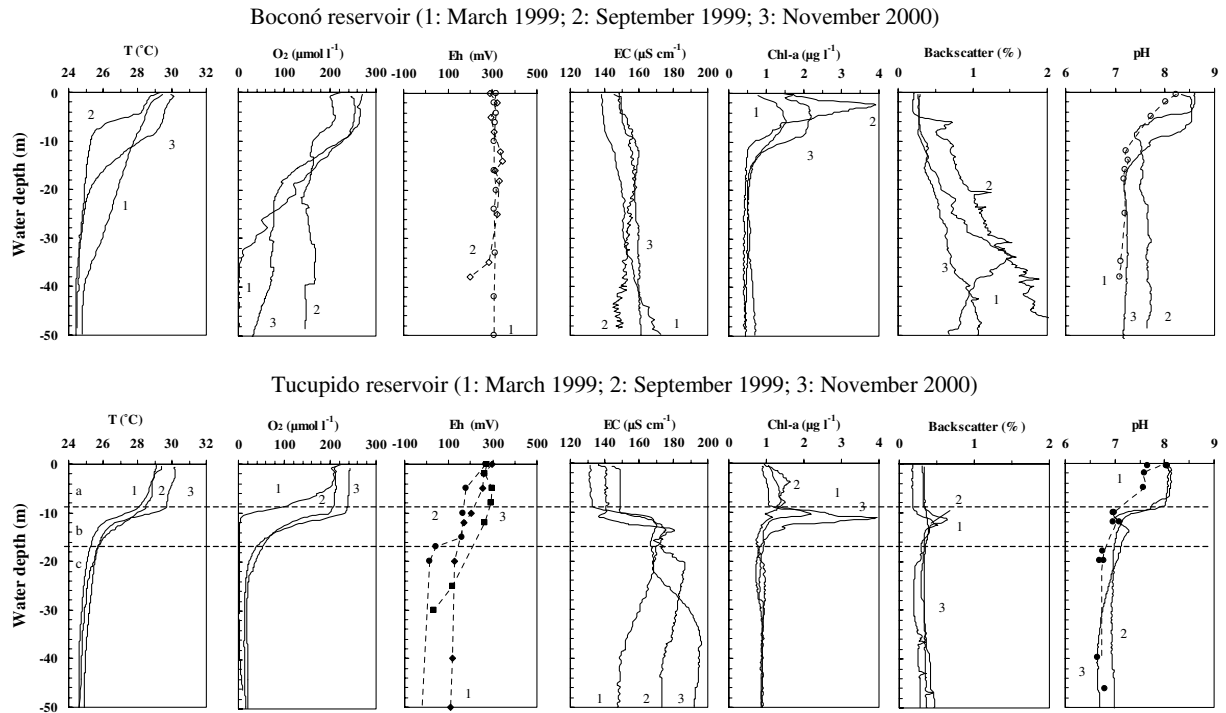


Fig. 3. Plots of mean values for environmental parameters in the water column (mean of 3–14 profiles). a, epilimnion; b, metalimnion (mixing zone); c, hypolimnion. T, temperature; O₂, dissolved O₂ concentration; Eh, redox potential; EC, water electrical conductivity; Chl-*a*, total chlorophyll-*a* concentration.

Table 3

Mean of standard deviations* for environmental parameters calculated over n bathymetric profiles for all water depths

Parameter	March 1999		September 1999		November 2000	
	Boconó ($n = 14$)	Tucupido ($n = 4$)	Boconó ($n = 6$)	Tucupido ($n = 3$)	Boconó ($n = 9$)	Tucupido ($n = 7$)
Temperature (°C)	0.1	0.1	0.07	0.45	0.1	0.06
Conductivity ($\mu\text{S cm}^{-1}$)	1.9	2.0	1.5	7.0	1.2	4.1
Chlorophyll- <i>a</i> ($\mu\text{g L}^{-1}$)	0.09	0.18	0.17	0.26	0.10	0.13
Backscatter (%)	0.14	0.06	0.10	0.12	0.05	0.02
Dissolved O ₂ (mg L^{-1})	1.1	0.5	0.8	1.0	0.6	0.2
pH	–	–	0.10	0.14	0.10	0.04

* $\sum_{z_i}^{z_f} \sigma_z / n_z$, where z_i = initial depth, z_f = final depth, σ_z = standard deviation at depth z for n profiles, n_z = number of depths.

3.2. Environmental parameters monitoring

Average values of 3 to 14 CTD probe casts for the Boconó and the Tucupido reservoirs are reported as a function of water depth in Fig. 3 for several monitoring surveys, performed in 1999 and 2000. The average standard deviations (Table 3) show that spatial variability within each reservoir is low with respect to instrumental precision in terms of water temperature, pH, electrical conductivity and backscatter (a proxy for suspended

organic matter load, see further in the text) and higher for chlorophyll-*a* and dissolved O₂ concentrations (Table 2). The variability of measured parameters is higher between the two reservoirs than inside each individual reservoir. Except for the Boconó basin in March 1999, thermal stratification was observed in both reservoirs leading to well-defined epilimnion, metalimnion (mixing zone) and hypolimnion (Fig. 3). This stratification was apparently stable throughout the year for the Tucupido reservoir with a thermocline located ca. 10 m and a

temperature gradient of 4–5 °C. In contrast, thermal stratification was only temporary for the Boconó reservoir. In November 2000, the thermocline was located 6 m below that of September 1999 and was not observed in March 1999. Due to lower temperatures (ca. 24 °C), the river inflow sinks below the thermocline in the Boconó reservoir. Dissolved O₂ concentrations have different depth-patterns for the two reservoirs. Hypoxic to anoxic conditions prevail in the Tucupido basin below 15 m ([O₂] < 14 μmol L⁻¹), whereas the water column remains oxic to hypoxic in the Boconó reservoir ([O₂] > 30 μmol L⁻¹), except in March, during the dry season, where hypoxic to anoxic conditions are observed below 35 m. Dissolved O₂ concentrations range from 203 to 266 μmol L⁻¹ (6.5–8.5 mg L⁻¹, respectively) in the epilimnion and indicate conditions close to equilibrium with atmosphere near the surface (O₂ solubility is 240 μmol L⁻¹ at 29 °C, equivalent to 7.7 mg L⁻¹, Benson and Krause, 1984). Redox potentials (Eh) are also contrasted between the

two reservoirs (Fig. 3). High and constant Eh values (≈300 mV), indicating oxic conditions (e.g.: Stumm and Morgan, 1996), characterize Boconó reservoir waters, whereas depth-decreasing trends are displayed in the Tucupido reservoir below the thermocline for all CTD casts. The latter reflects low water column ventilation and subsequent evolution towards suboxic to anoxic conditions (e.g.: Stumm and Morgan, 1996). Surface and deep-water temperatures are rather constant (average ± 1σ: 29.5 ± 0.4 and 24.6 ± 0.2 °C, respectively) for both reservoirs. In contrast, electrical conductivity ranges from 140 ± 10 to 200 μS cm⁻¹ with different depth trends in each reservoir. In the Boconó reservoir, electrical conductivity values slightly increase with water depth, whereas in the Tucupido reservoir sharp increases (ca. +40 μS cm⁻¹) occur in the mixing zone, immediately followed by varying trends. Average chlorophyll-*a* concentration ranges from 0.5 to 4.0 μg L⁻¹ with prominent peaks near the surface for the Boconó reservoir. Lower

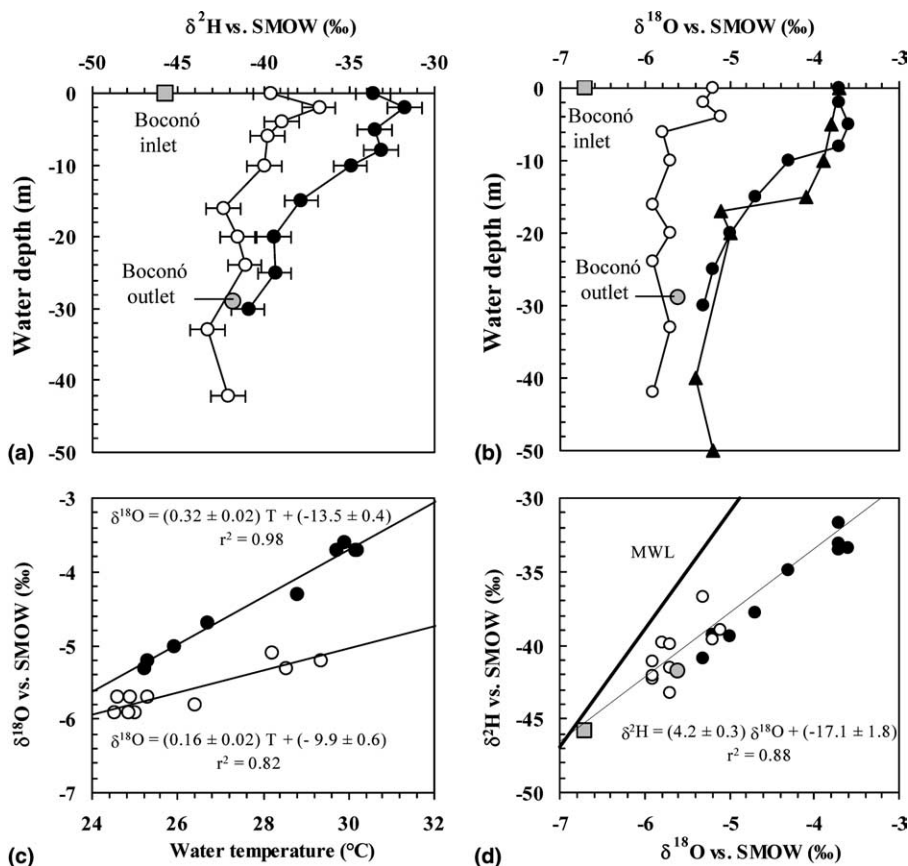


Fig. 4. Plots of stable isotope data in the water column: (a) δ²H, (b) δ¹⁸O and plots of correlations: (c) δ¹⁸O vs. temperature, (d) δ²H vs. δ¹⁸O. Open circles refer to Boconó reservoir data (September 1999); closed circles and triangles refer to Tucupido reservoir data (September 1999 and November 2000, respectively). Grey squares correspond to the Boconó River and grey circles refer to the Boconó reservoir outlet. GMWL = global meteoric water line. Regression lines are calculated using a least squares fit with a reduced major axis procedure (Payne, 1991).

concentrations are observed in surface waters of the Tucupido reservoir, along with a second chlorophyll-*a* peak in the metalimnion (Fig. 3). In the Boconó reservoir, backscatter values are high and continuously increasing with water depth, except in March 1999, when a prominent peak is observed between ca. 30 and 40 m (Fig. 3). Backscatter values are low and nearly constant in the water column of the Tucupido reservoir with small peaks in the metalimnion. The pH values are high (8.0–8.5) in the epilimnion, decrease sharply in the mixing zone (by 1.0–1.5 pH unit), and remain nearly constant in deep parts of the water column with values between 6.5 and 7.0 near the bottom. Boconó waters display an average shift of 0.5 pH units with respect to Tucupido waters.

3.3. Stable isotopes composition of water

Water $\delta^{18}\text{O}$, and $\delta^2\text{H}$ are displayed in Figs. 4(a)–(b). The values decrease with water depth below the thermocline for both reservoirs. Water is enriched in ^{18}O and ^2H in the Tucupido reservoir with respect to the Boconó

reservoir, in particular for surface waters. This depth-related distribution is linked to the thermal stratification and correlations between stable isotope values and water temperature can be derived (Fig. 4(c)). Using a least square fitting method with a reduced major axis procedure (Payne, 1991), the overall $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values could be fitted by an “evaporation” line (Fig. 4(d)) with a slope of 4.2 ± 0.3 , consistent with the 4.0 value usually reported for surface lake waters (e.g.: Gat, 1995). The observed relationship can be improved if only Tucupido reservoir data are taken into account. A local meteoric water line could be derived from average monthly precipitation data reported for the Boconó watershed (IAEA, 2001). This local meteoric line [$\delta^2\text{H} = (7.99 \pm 0.14)\delta^{18}\text{O} + (10.6 \pm 1.0)$, $r = 0.99$, $n = 59$] is very closed to the global meteoric water line (GMWL, Craig, 1961; GNIP, 1996). The intercept of the GMWL with the evaporation line ($\delta^{18}\text{O} \approx -7\text{‰}$ and $\delta^2\text{H} \approx -45\text{‰}$) provides a first order estimate of the isotopic composition of the water before evaporation. This composition is closely approached by that of the Boconó River ($\delta^{18}\text{O} = -6.7\text{‰}$ and $\delta^2\text{H} = -45.8\text{‰}$, Fig. 4(d)). At the

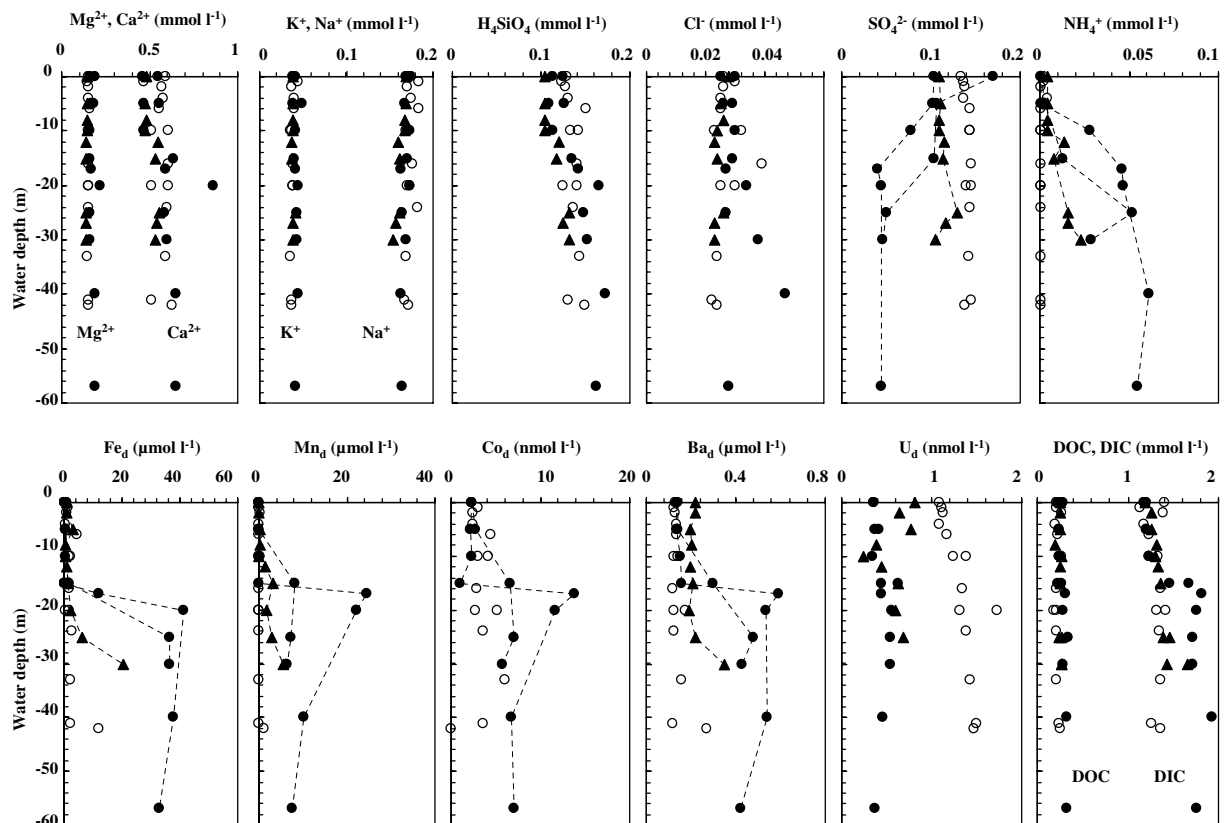


Fig. 5. Plots of dissolved element concentrations in the water column. Open and closed circles refer to two bathymetric profiles in the Boconó and Tucupido reservoirs, respectively, in September 1999. Triangles refer to one bathymetric profile in the Tucupido reservoir in November 2000. DOC concentrations are 0.1 mmol L^{-1} higher in the Tucupido reservoir.

outlet of the dam, water provides $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions (-5.6‰ and -41.8‰ , respectively) that match those in the water column of the Boconó reservoir at the depth of water intake (ca. 30 m).

3.4. Dissolved element concentrations

Depth-variations of major element and selected trace element concentrations are displayed in Fig. 5. Depth-variations of electrical conductivity are correlated with total dissolved load and mainly linked to the behaviour of DIC, which represents 40–50 mol% of the total dissolved species (Fig. 5). The ionic balance is accurately tightened if DIC concentrations are assigned to HCO_3^- and the average uncertainty between major cations and anions concentrations is below 2.5%. Several major element (Na, K, Mg, Ca, Si, Cl) concentrations are equivalent and constant with water depth and time in both reservoirs. In contrast, SO_4 , NH_4 and dissolved metal and trace elements (Fe, Mn, Co, Ba, U) display a different behaviour in each reservoir. Despite equivalent concentrations in surface waters for both reservoirs, samples located immediately below the thermocline in the Tucupido reservoir display a marked decrease in SO_4 concentrations and concomitant increases in NH_4^+ , dissolved Fe, Mn, Co and Ba concentrations (Fig. 5). These trends are more pronounced in September 1999 than in November 2000. In contrast with other trace elements, U concentrations are lower in the Tucupido reservoir than in the Boconó reservoir. Waters in both reservoirs are markedly depleted in nitrates with concentration ranging from 2 to 4 $\mu\text{mol L}^{-1}$ or even below the detection limit (1 $\mu\text{mol L}^{-1}$). Phosphate concentrations are always below detection limit (data not shown). Finally, DOC and DIC also differ from one reservoir to the other below the thermocline, with nearly constant values in the Boconó reservoir and higher, depth-increasing concentrations in the Tucupido reservoir that mirror electrical conductivity changes (Fig. 3). The dissolved element concentrations in the Boconó reservoir closely match those of the Boconó River (Table 4), the main water supply to the Peña Larga dam.

3.5. Composition of suspended matter

In the Boconó reservoir high and depth-increasing suspended sediment concentrations (16–140 mg L^{-1}) are observed whereas, the Tucupido water column only bears very low sediment concentrations (<10 mg L^{-1}) with no depth-related change (Fig. 6(a)). All particles are smaller than 50 μm in the Boconó reservoir but 7–51 wt% of suspended matter debris are above 50 μm in the Tucupido reservoir. Optical observations as well as total organic matter analyses (POC = $415 \pm 98 \text{ mg C g}^{-1}$, POC/PN = 27 ± 10 , and $\delta^{13}\text{C} = -26 \pm 1\text{‰}$; $n = 9$) support high occurrence of land derived detritus in the >50

Table 4

Data for the Boconó River at the inlet (inflow, September 1999) and the outlet of the Peña Larga water dam (outflow: November 1997 for water data, and September 1999 for suspended sediment data)

	Inflow	Outflow
Ca^{2+} (mmol L^{-1})	0.55	0.41
Mg^{2+} (mmol L^{-1})	0.14	0.10
Na^+ (mmol L^{-1})	0.16	0.10
K^+ (mmol L^{-1})	0.04	0.02
SO_4^{2-} (mmol L^{-1})	0.15	0.12
NO_3^- (mmol L^{-1})	0.02	bd ^a
Cl^- (mmol L^{-1})	0.02	0.02
DOC (mmol L^{-1})	0.22	0.13
DIC (mmol L^{-1})	1.46	1.31
Fe ($\mu\text{mol L}^{-1}$)	0.72	–
Mn ($\mu\text{mol L}^{-1}$)	0.18	–
Ba ($\mu\text{mol L}^{-1}$)	0.07	–
U (nmol L^{-1})	1.09	–
$\delta^{18}\text{O}$ vs. SMOW (‰)	–6.7	–5.6
$\delta^2\text{H}$ vs. SMOW (‰)	–45.8	–41.8
T ($^{\circ}\text{C}$)	23.9	24.9
TSS <50 μm (g L^{-1})	1.46	0.09
POC <50 μm (mg C g^{-1})	10.3	13.0
PN <50 μm (mg N g^{-1})	1.1	1.4
POC: PN <50 μm	8.9	9.0
$\delta^{13}\text{C}_{\text{POC}}$ <50 μm vs. PDB (‰)	–25.8	–24.8

^a Below detection limit.

μm size fraction of suspended matter in the Tucupido reservoir ($\text{C/N} > 20$; Meyers, 1994). An additional contrast between the two reservoirs is displayed by the POC concentrations and their $\delta^{13}\text{C}$ values (Fig. 6). The POC contents (in mg C g^{-1}) of suspended sediments decrease with water depth in both reservoirs but values are much lower for the Boconó reservoir, indicating the presence of organic C-poor material (Fig. 6(b)). However, POC concentrations (in mg C L^{-1}) are higher in the Boconó reservoir than in the Tucupido reservoir, due to higher suspended sediment concentrations (Fig. 6(c)). While both reservoirs display relatively similar $\delta^{13}\text{C}$ values in their epilimnion, contrasting compositions are observed below the thermocline (Fig. 6(d)). In the hypolimnion of the Boconó reservoir, $\delta^{13}\text{C}$ values decrease moderately from -25.6‰ to -26.3‰ near lake bottom whereas they decrease sharply to -29.9‰ in the Tucupido reservoir. The POC:PN ratios decrease with water depth in both reservoirs (Fig. 6(e)), indicating the increase of N with respect to organic C in the water column and/or the mixing of particles originating from organic matter pools with a different composition. The input of suspended organic matter linked to the Boconó river discharge is reflected in the water column (ca. 20–30 m) by concomitant changes in POC, POC:PN and $\delta^{13}\text{C}$ values (Table 4 and Fig. 6). The lowest POC: Chlorophyll-*a* ratio coincides with the highest POC: PN value (ca. 2 m, Fig. 6(f)) but no evident direct link be-

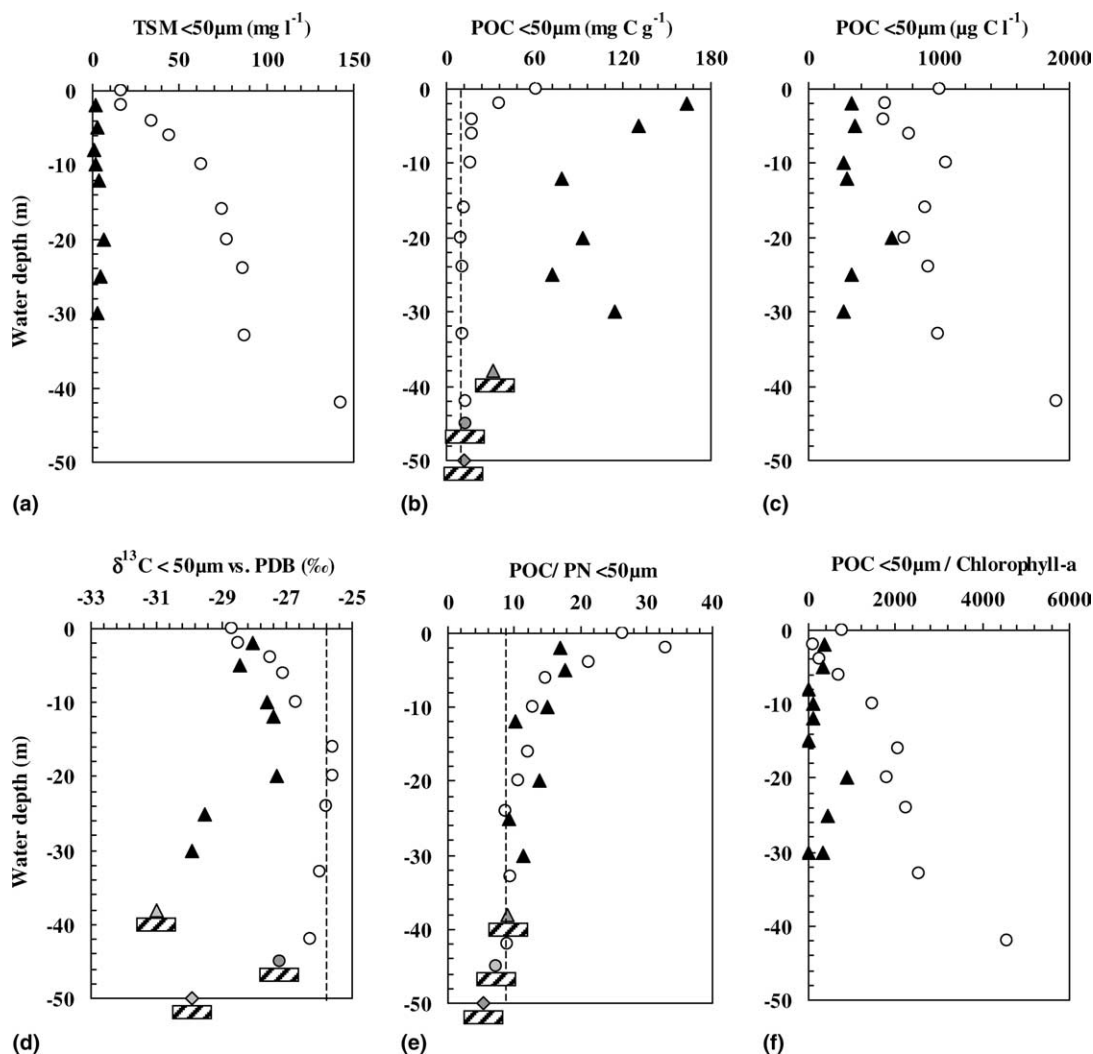


Fig. 6. Plots of data for suspended fine size (<50 μm) fractions in the water column: (a) total suspended matter (TSM) concentrations, (b) POC concentrations (mg C g^{-1}), (c) POC concentrations (mg C L^{-1}), (d) POC - $\delta^{13}\text{C}$, (e) POC:PN atomic weight ratios, and (f) POC:Chlorophyll-*a* ratios. Open circles refer to Boconó reservoir data (September 1999), and closed triangles refer to Tucupido reservoir data (November 2000). Grey diamonds and triangles refer to the composition of lake bottom sediment collected in the Tucupido reservoir (September 1999 and November 2000). Grey circles refer to the composition of lake bottom sediment collected in the Boconó reservoir (September 1999). Vertical dashed lines refer to the average composition of organic matter in the Boconó River suspended sediments. Horizontal dashed squares refer to bottom sediment collection depths.

tween chlorophyll-*a*, POC concentration or stable C isotope values can be put forward.

3.6. Lake bottom and alluvial sediment compositions

Three lake bottom sediments were collected using a grab sampler at a depth of 45 m in the Boconó reservoir, and of 38 and 50 m in the Tucupido reservoir. These sediments display moderate to highly reducing conditions with Eh values of 35 mV and -100/-190 mV

for the Boconó and the Tucupido reservoirs, respectively. In both cases, redox conditions in the overlying water column are less reducing than in the sediment (Fig. 3). The organic matter composition of the lake bottom sediments extends the decreasing POC, POC/PN and $\delta^{13}\text{C}$ trends observed in the water column to the first cm of sediments (Fig. 6). In both reservoirs, $\delta^{13}\text{C}$ values in bottom sediments are up to 1‰ lighter than in bottom water suspended sediments. Furthermore, a 3–4‰ contrast in bottom sediment $\delta^{13}\text{C}$ was

observed between the two reservoirs (ca. -30.5% vs. -27.0% for the Tucupido and the Boconó reservoirs, respectively).

Additional information on sedimentary organic C was obtained from 6 sedimentary cores sampled in the alluvial fan of the Boconó River. These deposits represent the greatest part of the sedimentary supply to the Boconó reservoir. Organic C concentrations range from 12 mg C g^{-1} in surface sediments to 3 mg C g^{-1} at a depth of 3 m (Fig. 7). Except for a few C-rich surface sediments, organic C concentrations are rather homogeneous with depth, with an average POC concentration of $4 \pm 1 \text{ mg C g}^{-1}$. The measured pH–Eh values ($T = 26 \text{ }^\circ\text{C}$, $\text{pH} = 6.29$, $-100 \text{ mV} < \text{Eh} < -190 \text{ mV}$) indicate slightly more reducing conditions than in the top first cm of lake bottom sediments (Fig. 9).

3.7. Sediment and organic carbon budgets

Suspended matter mass concentrations and light backscatter values are correlated for the Boconó reservoir (September 1999; Fig. 8(a)). Because POC and suspended sediment concentrations are also correlated (hyperbolic trend, Fig. 8(b)), both the amount of suspended matter and of POC can be derived from backscatter values for each profile in the water column (Figs. 8(c)–(d)). Using water depth–water volume relationships ($v = 0.53z^2 + 63.99z + 1907.81$ and $v = 0.32z^2 + 36.66z + 1041.19$ for the Boconó and Tucupido reservoirs, respectively, with v = water volume in 10^6 m^3 and z = water depth in m, range: -0 m to -70 m ,

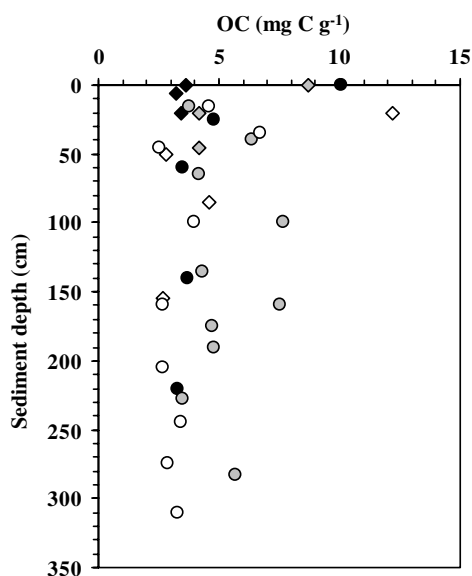


Fig. 7. Plots of organic C concentration in 6 sediments cores located in the alluvial fan of the Boconó River.

MARNR, 2001), average backscatter values and the relationships previously established, for September 1999 an estimate can be derived of the instantaneous amount of suspended sediment ($80 \times 10^3 \text{ t}$) and POC ($0.95 \times 10^3 \text{ t C}$) in the Boconó reservoir water column. Correlative hyperbolic trends between POC and suspended sediment are generally observed in rivers (e.g.: Meybeck, 1982) and are thought to reflect either the dilution of organic matter by minerals for high concentrations of suspended sediment or a change in the nature of organic matter (i.e., vegetation debris vs. soil organic matter). However, if organic C-rich samples collected near the surface are disregarded (Fig. 6), and a constant POC concentration is assumed throughout the water column (average $\pm 1\sigma$: $13 \pm 3 \text{ mg C g}^{-1}$), the POC budget does not significantly change ($1.0 \pm 0.2 \times 10^3 \text{ t C}$ vs. $0.95 \times 10^3 \text{ t C}$). Suspended sediment concentrations and backscatter values being almost constant throughout the water column in the Tucupido reservoir, an average $10 \times 10^3 \text{ t}$ of sediment and $0.5 \times 10^3 \text{ t}$ of POC can be calculated, using a mean suspended sediment concentration of 5 mg L^{-1} and a mean POC concentration of 0.3 mg C L^{-1} in the water column (Fig. 6). The suspended sediment concentration in the Boconó reservoir was one order of magnitude higher than in the Tucupido reservoir but the POC concentration was only 3 times higher. Assuming that backscatter/sediment and sediment/POC relationships are also valid in November 2000, the suspended sediment content in the water column of the Boconó reservoir during this period was half of that of September 1999, but the POC content remained similar (Fig. 8(c)–(d)). Equivalent estimations could not be performed for March 1999 because backscatter values recorded the presence, in the hypolimnion between ca. 28–40 m, of incompletely mixed river/lake water masses with different suspended loads and, most likely also, different types of organic matter. The total POC content in the water column of the dam amounted to $1.5 \times 10^3 \text{ t C}$ in September 1999. The DOC: POC ratios also differed from one reservoir to the other, reflecting the difference in suspended sediment concentrations (DOC/POC ≈ 3 in the Boconó reservoir and DOC/POC ≈ 10 in the Tucupido reservoir).

The Boconó River discharges $32 \times 10^3 \text{ t C a}^{-1}$ (calculated with an average POC content of 5 mg C g^{-1}). Of this, $21 \pm 5 \times 10^3 \text{ t C a}^{-1}$ is stored in bottom sediments (calculated with an average POC content of $4 \pm 1 \text{ mg C g}^{-1}$) and ca. $2 \times 10^3 \text{ t C a}^{-1}$ is exported from the water dam (calculated with an average POC content of 10 mg C g^{-1} measured at the depth of water intake). Because POC mainly accumulates in the Boconó reservoir (38.4 km^2), an organic C burial rate between 416 and $703 \text{ t C km}^{-2} \text{ a}^{-1}$ was derived, which is an order of magnitude higher than that usually reported for small lakes ($<500 \text{ km}^2$, rate: $20\text{--}80 \text{ t C km}^{-2} \text{ a}^{-1}$; e.g.: Einsele et al., 2001). This high burial rate results both from high inputs of

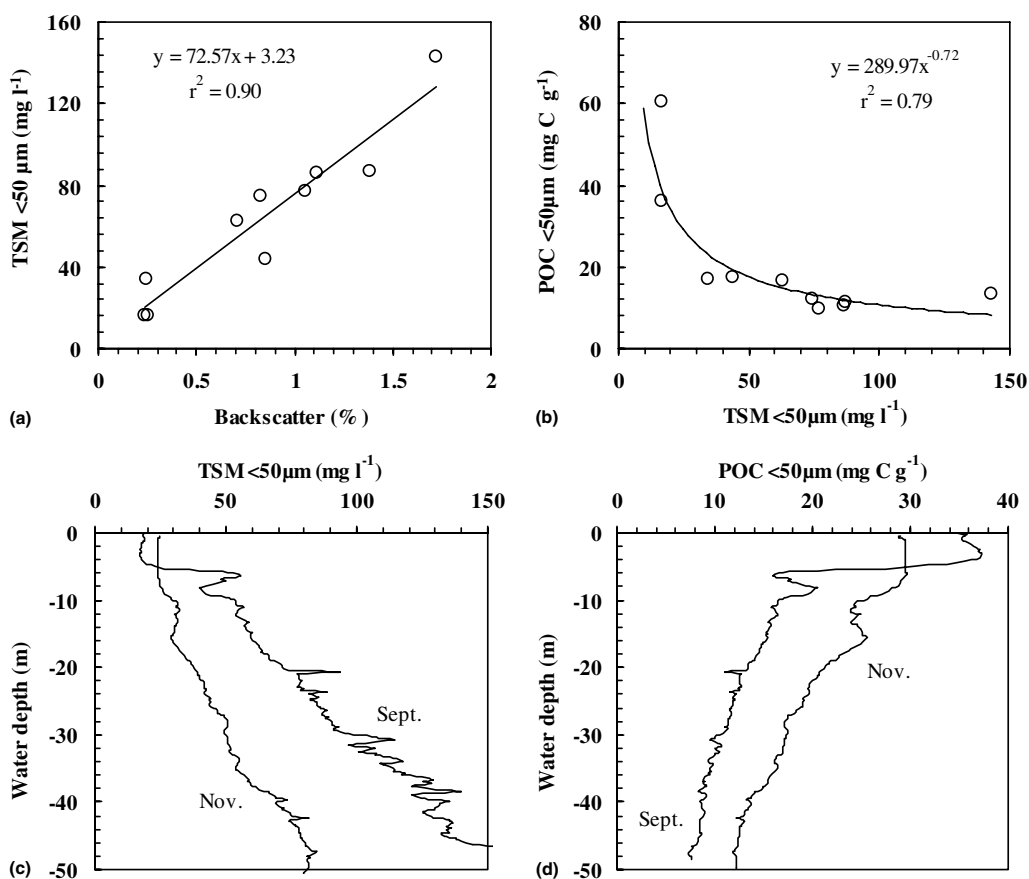


Fig. 8. Plots of: (a) correlation between fine (<50 μm) size suspended matter concentrations and backscatter in the Boconó reservoir (September 1999), (b) correlation between fine (<50 μm) size suspended matter and POC concentrations in the Boconó reservoir (September 1999), (c) calculated suspended matter concentrations in the Boconó reservoir (September 1999 and November 2000) derived from backscatter profiles and correlation in (a), (d) calculated POC concentrations (September 1999 and November 2000) derived from backscatter profiles and correlations in (a) and (b).

land-derived organic matter, and a high drainage area: lake area ratio (≈ 40 for the Boconó reservoir).

4. Discussion and interpretation

4.1. Contrasted water budgets between the two reservoirs of the Peña-Larga water dam

Monitoring of environmental parameters in the Peña-Larga dam demonstrates significant differences between and within the two water reservoirs that are mainly related to the hydrological budget of each reservoir. Indeed, the average residence time of water in each reservoir should be markedly different due to contrasting water intake and river discharge (Fig. 1 and Table 1). A rapid turnover is found for the Boconó reservoir with an average residence time of 0.36 a. The dissolved element composition of the Boconó reservoir

waters closely reflects that of the Boconó River indicating that regular mixing of waters minimizes the extent of redox processes in the water column below the thermocline. Seasonally varying flow rates of the Boconó River control suspended sediment load as well as ventilation conditions in the water column of the Boconó reservoir. The colder waters of the Boconó River dive below the thermocline and could even be traced in March 1999, using the backscatter record, at a depth ca. 28–40 m. In contrast, the smaller water input/output budget of the Tucupido reservoir leads to a long turnover time of 6.2 a. Local meteorological events are apparently insufficient to stir and homogenize the water column so that stable thermal stratification and water hypoxia to anoxia may develop below 10 m. The narrow depth of the channel connecting the two reservoirs (≈ 20 m) also controls the ventilation conditions in the Tucupido reservoir by reducing advection and mixing of fresh bottom water from the Boconó reservoir (on the

model of the Black sea and the Bosphorus sill; e.g.: Demaison and Moore, 1980). The isotopic composition of water also reflects the impact of contrasted water residence times. The extent of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ isotopic fractionation due to evaporation was reduced in the Boconó reservoir with respect to that of the Tucupido reservoir (Fig. 4).

4.2. Linkages between environmental parameters and geochemical data

The evolution of environmental parameters through the water column indicates that photosynthetic processes control the water chemistry above the thermocline (high chlorophyll-*a* and dissolved O_2 concentrations, high pH) whereas, respiration processes lead to dissolved O_2 depletion and low pH in the deeper water strata. The impact of these processes can be clearly seen in the calcite equilibrium diagram (Fig. 9(a)). Over saturation with respect to calcite equilibrium is observed in surface water, and under saturation in bottom water. However, there is no evidence for precipitation of carbonates in the Peña Larga water dam, because no seasonal or water depth related depletions in Ca^{2+} , Mg^{2+}

or DIC concentrations have been observed (e.g.: McConnaughey et al., 1994; McConnaughey and Whelan, 1997).

In contrast to the Boconó reservoir in which organic matter undergoes aerobic mineralization, microbially mediated redox-driven processes induced by dissolved O_2 depletion control water chemical composition below 15 m in the Tucupido reservoir. Thus, the narrow chlorophyll-*a* concentration and backscatter peaks observed in the thermocline ca. 11 m (Fig. 3) indicate accumulation of suspended debris and reflects the location of high microbial activity. It coincides with a major “dissolution zone” characterized by a sharp increase of EC, and a decrease to near zero of dissolved O_2 concentration. The location of high photosynthetic activity at this depth is linked to high nutrient concentrations induced by the degradation of suspended organic matter and by the penetration of light. In O_2 -depleted waters, the oxidation of organic matter is coupled with a succession of reduction reactions using other electron acceptors that theoretically follow decreasing free energy yields (Stumm and Morgan, 1996). These processes have been widely described in lakes and fjords (e.g.: Balistrieri et al., 1992a, 1994; Yao and Millero, 1995; Hamilton-

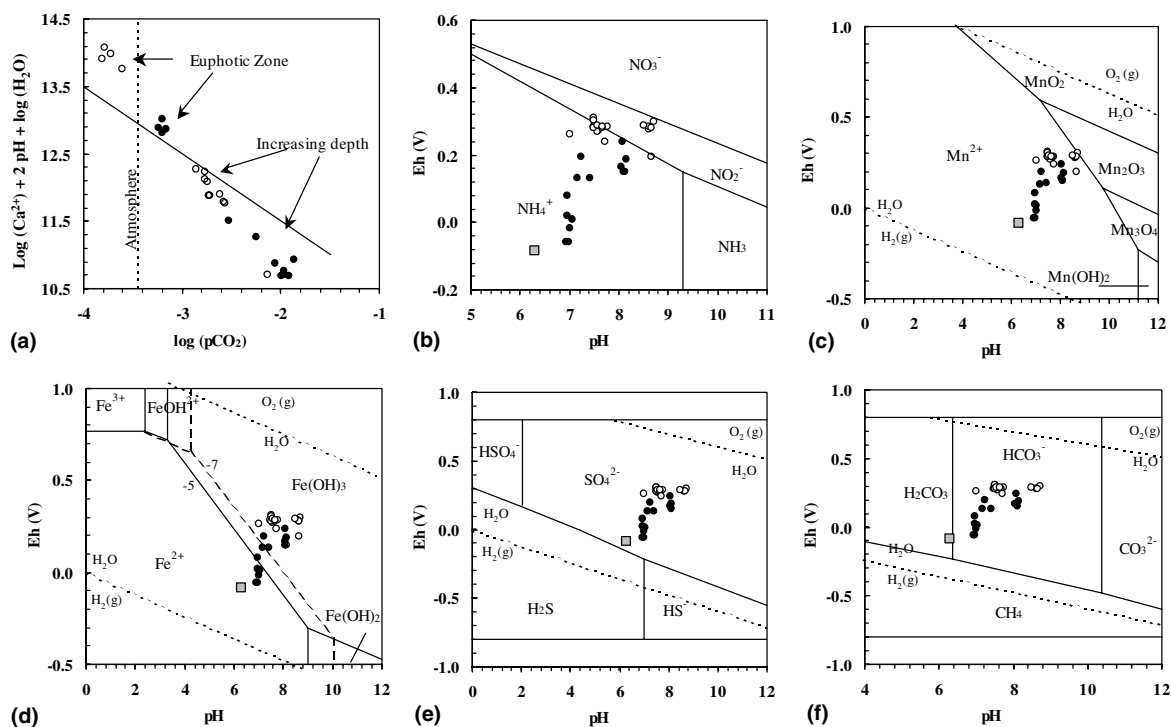


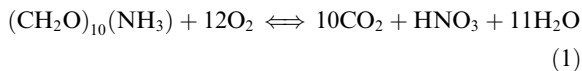
Fig. 9. Equilibrium diagrams for: (a) calcite and water in the two reservoirs and Eh–pH diagrams (at 25 °C) for: (b) dissolved N species, (c) Mn species, (d) Fe species, (e) dissolved S species and (f) dissolved C species. N_2 is considered as a redox-inert component and therefore ignored. Boundaries in equilibrium diagrams are calculated for total Mn concentrations = 10^{-6} mol L^{-1} , total Fe concentrations = 10^{-5} and 10^{-7} mol L^{-1} . Oxidation states involved are S (–II) and S (+VI), C (–IV) and C (+IV). Open and closed circles refer to Boconó and Tucupido reservoirs, respectively (September 1999 and November 2000). Grey squares refer to lake bottom sediments in the Tucupido reservoir (November 2000).

Taylor et al., 1996; Sternbeck, 1996; Stumm and Morgan, 1996; Hongve, 1997; Wann et al., 1997; Zaw and Chiswell, 1999). The main redox reactions can be pictured by thermodynamic equilibrium diagrams using Eh and pH values (Figs. 9(b)–(f)). It appears that conditions for a complete dissolution of Fe and Mn oxides/hydroxides and reduction of NO_3^- to NH_4^+ are predicted in the Tucupido reservoir for samples located below the thermocline. Sulphate reduction and, possibly also CH_4 formation, are operating but most likely, do not reach equilibrium. Additional information on active reduction processes taking place in the water column is displayed by the correlative distribution of dissolved Co and Ba concentrations with dissolved Fe and Mn concentrations below the thermocline in the Tucupido reservoir (Fig. 10). This behaviour has been previously observed in numerous lakes (e.g.: Balistrieri et al., 1992b, 1994; Hamilton-Taylor and Davison, 1995; Viollier et al., 1995; Achterberg et al., 1997; Taillefert and Gaillard, 2002) and attributed to microbially mediated reduction of metallic hydrous oxides accompanied by the release of adsorbed Co and Ba. The linear correlation between dissolved Mn and Co concentrations (Fig. 10) bears a slope of 4.5×10^{-4} , which falls in the range of the Co:Mn ratios described for other lakes (1×10^{-4} to 8×10^{-4} , see references above). Cobalt and Ba are most likely preferentially adsorbed onto Mn-oxides because the correlations are more accurately defined with Mn ($r^2 = 0.97$ and 0.75 , respectively) than with Fe ($r^2 = 0.68$ and 0.33 , respectively). Additional evidence for reducing conditions is pictured by the behaviour of U that is less soluble in O_2 -depleted waters, suggesting out to possible removal to sediments (Anderson et al., 1989).

4.3. Estimates of the mineralization rate of suspended organic matter in the water column

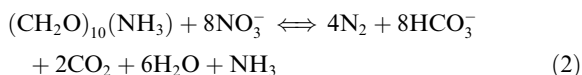
On the basis of suspended organic matter with a C/N ratio of 10, the sequence of oxidants, determined by their energy yield can be expressed, for the Tucupido reservoir, by the following equations (Froelich et al., 1979; Stumm and Morgan, 1996):

Nitrification (coupled oxic respiration and nitrification):



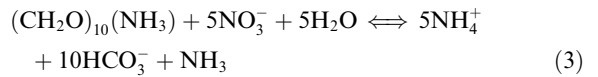
$$\Delta[\text{O}_2] = (12/10) \times \Delta[\text{CH}_2\text{O}] = -12 \times \Delta[\text{NO}_3^-] = -12 \times \Delta[\text{Alk}]$$

Denitrification:



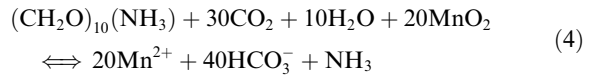
$$\Delta[\text{NO}_3^-] = (4/5) \times \Delta[\text{CH}_2\text{O}] = -8 \times \Delta[\text{NH}_3] = -\Delta[\text{Alk}]$$

Nitrate reduction:



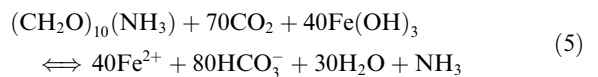
$$\Delta[\text{NO}_3^-] = (1/2) \times \Delta[\text{CH}_2\text{O}] = -\Delta[\text{NH}_4^+] = -(1/2)\Delta[\text{Alk}]$$

Mn (IV) reduction:



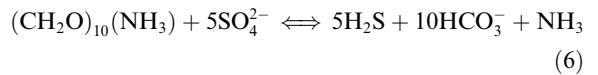
$$\begin{aligned} \Delta[\text{Mn}^{2+}] &= -2 \times \Delta[\text{CH}_2\text{O}] = 20 \times \Delta[\text{NH}_3] \\ &= (1/2) \times \Delta[\text{Alk}] \end{aligned}$$

Fe (III) reduction:



$$\Delta[\text{Fe}^{2+}] = -4 \times \Delta[\text{CH}_2\text{O}] = 40 \times \Delta[\text{NH}_3] = (1/2) \times \Delta[\text{Alk}]$$

Sulfate reduction:



$$\begin{aligned} \Delta[\text{SO}_4^{2-}] &= (1/2) \times \Delta[\text{CH}_2\text{O}] = -5 \times \Delta[\text{NH}_3] \\ &= -(1/2) \times \Delta[\text{Alk}] \end{aligned}$$

Assuming the hypolimnion (water depth below 10 m in September 1999) as a closed system, we estimated the theoretical amount of oxidized organic C ($\Delta[\text{CH}_2\text{O}]$), using the stoichiometry of the operating redox processes in each reservoir and integrating the average variations in element concentrations ($\Delta[\text{O}_2]$, $\Delta[\text{NO}_3^-]$, $\Delta[\text{Mn}^{2+}]$, $\Delta[\text{Fe}^{2+}]$ and $\Delta[\text{SO}_4^{2-}]$) in the hypolimnion between an assumed initial status (t_0 time, oxic conditions) where the dissolved element composition is constant with water depth and equivalent to that of the Boconó River ($[\text{O}_2] = 220 \mu\text{mol L}^{-1}$, $[\text{SO}_4^{2-}] = 100 \mu\text{mol L}^{-1}$, $[\text{NO}_3^-] = [\text{Mn}^{2+}] = [\text{Fe}^{2+}] = 0 \mu\text{mol L}^{-1}$) and, a final status (t time, hypoxic to anoxic conditions) where the dissolved element composition is given by that of the concentration profiles achieved in September 1999 (Fig. 11). Mean variations in concentration $\Delta[\text{X}]$ in the hypolimnion between t_0 and t can be calculated using the following equation:

$$\Delta[\text{X}] \times V = ([\text{X}] \times V)_{t_0} - \left(\sum [\text{X}]_z \times V_z \right) t,$$

where t_0 and t are indices that refer to initial and final redox status, respectively; $[\text{X}]$ is the dissolved element concentration (O_2 , SO_4^{2-} , Mn^{2+} , Fe^{2+} in $\mu\text{mol L}^{-1}$) in the hypolimnion; $[\text{X}]_z$ is the element concentration at depth z (in $\mu\text{mol L}^{-1}$) extrapolated from their distribution in

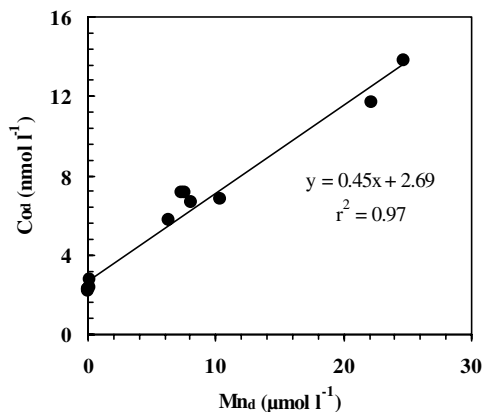


Fig. 10. Correlation between dissolved Mn and Co (Tucupido reservoir, September 1999).

the water column in September 1999; V is the water volume in the hypolimnion (in m^3) and V_z is the water volume in the hypolimnion at depth z (in m^3) calculated using hypsometric data (water volume vs. water depth relation, see above). When solved for $\Delta[\text{X}]$, the changes in dissolved element concentration amounted to $-180 \mu\text{mol L}^{-1}$ for O_2 , $-42 \mu\text{mol L}^{-1}$ for SO_4^{2-} , $+12 \mu\text{mol L}^{-1}$ for Mn^{2+} , $+30 \mu\text{mol L}^{-1}$ for Fe^{2+} (Table 5). Because NO_3^- concentrations in the oxic reservoir are very low throughout the water column ($<1 \mu\text{mol L}^{-1}$), it was assumed that NO_3^- essentially derived from organic N through the oxic respiration of organic matter. Respiration of organic matter, between t_0 and t , induced an O_2 depletion of $-180 \mu\text{mol L}^{-1}$ and, according to Eq. (1), should have released $15 \mu\text{mol L}^{-1}$ of NO_3^- . In the absence of marked variation in NO_3^- concentrations the authors could not determine if this organic N-derived NO_3^- underwent denitrification (Eq. (2)) or nitrate reduction (Eq. (3)). However, denitrification is much more thermodynamically favourable (Stumm and Morgan, 1996) and should be considered as the only NO_3^- reduction process. Accordingly, it was assumed that NH_4^+ accumulation in the water column below the thermocline mainly results from the degradation of organic matter under hypoxic to anoxic conditions (Eqs. (4)–(6)). Using the stoichiometry given by Eqs. (1)–(6) and the variations in element concentration calculated between time t_0 and time t , a total estimate was derived of $266 \mu\text{mol L}^{-1}$ of mineralized organic matter $[\Delta(\text{CH}_2\text{O})]$ in the water column of the Tucupido reservoir (Table 5), assuming that nitrates released (Eq. (1)) are completely reduced through denitrification (Eq. (2)). Organic matter is mainly degraded in the hypolimnion through aerobic oxidation ($150 \mu\text{mol L}^{-1}$, ca. 56.4%), SO_4^{2-} reduction ($84 \mu\text{mol L}^{-1}$, ca. 31.6%) and denitrification ($19 \mu\text{mol L}^{-1}$, ca. 7.1%). The contribution of Fe and Mn reduction processes to organic matter degradation is apparently low with respect to the other redox

reactions (ca. $<3\%$ each). The budgets do not take into account the cycling of Fe and Mn at the oxic–anoxic boundary, the potential oxidation of Fe^{2+} by Mn-oxides (Davison, 1993) and the removal of dissolved Fe as Fe sulphide. Therefore, it is possible that the amount of dissolved Fe generated by organic matter degradation and, accordingly, the amount of oxidized organic matter are underestimated (Eq. (5)). The authors are aware that the overall estimations involve large uncertainties, in particular with respect to microbially – mediated reactions that may not reach equilibrium. This point will be addressed further in the discussion, with alkalinity and C budgets.

Because dissolved element concentrations are constant throughout the water column in the Boconó reservoir (Figs. 3 and 5), mineralization of organic matter can solely be related to the dissolved O_2 decrease observed below the thermocline (Eq. (1)). The amount of theoretically mineralized organic matter can be derived using the assumptions made in the calculations performed for the Tucupido reservoir (hypoxic part of the freshwater system). Assuming minimal and maximal O_2 depletion in the Boconó reservoir in September 1999 (end of the rainy season) and March 1999 (end of the dry season), respectively, the change in dissolved O_2 concentration below the thermocline can be calculated with respect to O_2 -saturated water above the thermocline. The stoichiometric oxidation of organic matter $[\Delta(\text{CH}_2\text{O})]$ related to O_2 depletion ranges between 30 and $160 \mu\text{mol L}^{-1}$ for March and September 1999, respectively.

Neglecting O_2 diffusion from the epilimnion (low diffusion rate with respect to distance; e.g.: Jorgensen, 2000) and advection through bottom water circulation (low depth of the sill between reservoirs), a mineralization rate model was derived for each reservoir based on the stoichiometry of the major redox processes. The mineralization rate can be expressed by:

$$r = \Delta[\text{CH}_2\text{O}]/\tau,$$

where r is the mineralization rate (in $\mu\text{mol C L}^{-1} \text{a}^{-1}$), $\Delta[\text{CH}_2\text{O}]$ is the variation in concentration per unit volume (in $\mu\text{mol L}^{-1}$) of organic matter deduced from the reactions involving O_2 depletion and other active redox reactions, and τ is the average water residence time (in years). The residence time used in the calculation is only a first order estimate that may not fully reflect the real residence time of water in the hypolimnion (Table 1, Fig. 2). However, because no additional water stratification is displayed below the thermocline for the Tucupido reservoir, it was assumed that hypolimnion waters are well mixed and that the average water residence time is representative of the biogeochemical processes observed. Additional evidence for water mass homogenisation is shown by constant Ca, Mg, Na, K concentrations throughout the water column (Fig. 5), and equivalent redox status from one year to the other

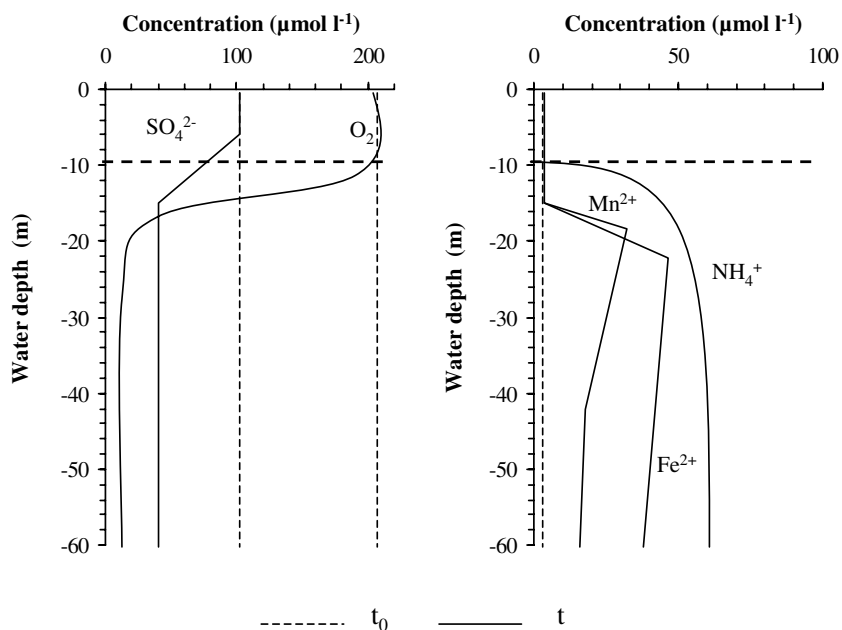


Fig. 11. Stoichiometric model for the evolution of redox element concentrations between an initial state under oxic conditions (t_0 , dotted line) and a final state under hypoxic to anoxic conditions (t , plain line) for the water column of the Tucupido reservoir (September 1999). The initial concentrations correspond to the composition of the Boconó River.

(Fig. 9). Mineralization rates amounted 83 to 444 $\mu\text{mol C L}^{-1} \text{ a}^{-1}$ (calculated with $\tau = 0.36 \text{ a}$, $\Delta[\text{CH}_2\text{O}] = 30$ and 160 $\mu\text{mol C L}^{-1}$, for March and September 1999, respectively) in the Boconó reservoir and only 43 $\mu\text{mol C L}^{-1} \text{ a}^{-1}$ for the Tucupido reservoir (calculated with $\tau = 6.2 \text{ a}$, $\Delta[\text{CH}_2\text{O}] = 266 \mu\text{mol C L}^{-1}$ for September 1999). Rates of organic matter decomposition have been determined using incubation experiments under oxic or anoxic conditions (e.g.: Lee, 1992; Kristensen and Holmer, 2001; Lehmann et al., 2002). The more labile fraction decomposes at similar rates regardless of oxic or anoxic conditions whereas, the more refractory fraction decays significantly more slowly under anoxic conditions, leading to higher organic C preservation (e.g.:

Harvey et al., 1995). The high and low estimates of organic C mineralization rate for the oxic and hypoxic reservoirs, respectively, are consistent with these experiments. The redox status of the two reservoirs was apparently controlled by low water turnover rate rather than by excess nutrient or organic matter supply, which would have thoroughly enhanced surface productivity. Moreover, given the C budget calculated above (see Section 3.7), a net amount of $8 \pm 5 \times 10^3 \text{ t C a}^{-1}$ is consumed in the Boconó basin (river POC input minus POC storage in suspended and bottom sediments and water dam POC output). Taking into account the total mineralization rates derived from the redox reactions (ca. 80–440 $\mu\text{mol C L}^{-1} \text{ a}^{-1}$), 1 to 5 10^3 t C a^{-1} is the-

Table 5

Organic matter mineralization and alkalinity generation calculated using the variation in dissolved element concentrations involved in the major redox reactions for the Tucupido reservoir

	$\Delta[\text{X}] (\mu\text{mol L}^{-1})^{\text{a}}$	$\Delta[\text{CH}_2\text{O}] (\mu\text{mol L}^{-1})^{\text{b}}$	$\Delta[\text{Alk}] (\mu\text{mol L}^{-1})^{\text{b}}$
Nitrification	$\Delta\text{O}_2 = -180$	-150	15
Denitrification ^c	$\Delta\text{NO}_3^- = -15$	-19	15
Mn reduction	$\Delta\text{Mn}^{2+} = +12$	-6	24
Fe reduction	$\Delta\text{Fe}^{2+} = +30$	-7	60
Sulphate reduction	$\Delta\text{SO}_4^{2-} = -42$	-84	84
Budget		-266	198

^a Average variation in the hypolimnion between t_0 and t .

^b Calculated using the stoichiometry of reactions (see Eqs. (1)–(6) in the text).

^c Organic nitrogen released by nitrification.

oretically respired for the Boconó basin. These values provide a first order match of the calculated C budget. The redox reactions involved with organic matter degradation are coupled with proton transfer and generate alkalinity (Lerman and Stumm, 1989; Sigg et al., 1991). Alkalinity increased by $350 \mu\text{mol L}^{-1}$ between assumed oxic initial conditions (t_0 , $1350 \mu\text{mol L}^{-1}$) and hypoxic final conditions (t , $1700 \mu\text{mol L}^{-1}$) for the Tucupido reservoir (Fig. 5). This value is of “similar order” to the $198 \mu\text{mol L}^{-1}$ calculated by adding all alkalinities induced by each redox reaction involved in organic matter degradation (see Eqs. (1)–(6) and Table 5). The stoichiometric approach, although subject to large uncertainties due to several assumptions, provides a first order estimate of the major acting redox processes and the rate of organic matter mineralization that are consistent with the organic C budget and the observed change in alkalinity.

4.4. Origin and evolution of particulate organic matter in the water column

Since the water column redox status apparently controls the extent of organic matter mineralization, one can expect the composition of suspended particles to be significantly different between the two reservoirs and to reflect the extent of bacterial degradation. However, differences in the composition of particulate organic matter (Fig. 6(d)) may also be explained by differences in the source of organic matter (i.e.: land derived vs. phytoplanktonic material). Furthermore, the mineralization rates are based on average residence times and involve steady state conditions that might not be directly addressed by the composition of suspended organic matter.

In the oxic reservoir, suspended matter is provided by the Boconó River whose discharge represents the major input of land-derived organic matter. This supply is reflected in the high and depth-increasing suspended matter concentrations observed in the Boconó reservoir water column (Fig. 6). Near the surface (0–10 m), high chlorophyll-*a* concentrations and pH values support high levels of primary production that typically displays ^{13}C -depleted organic matter compositions (e.g.: Fogel and Cifuentes, 1993) with atomic C:N ratios usually between 4 and 10 in freshwater environments (e.g.: Meyers, 1994). However, unexpectedly high POC:PN values were measured in surface waters (Fig. 6(e)). These values either suggest the occurrence of unusual phytoplanktonic material with high C:N ratios or high contribution of land vascular plant debris with respect to phytoplankton that bear similar ^{13}C -depleted compositions (e.g.: Meyers and Eadie, 1993). The authors cannot discriminate these two possible origins. Mineralization of suspended organic matter should theoretically leave a ^{13}C -depleted residue. Indeed, microbial degradation of organic matter induces a decrease of settling POC- $\delta^{13}\text{C}$

due to a selective loss of the more labile carbohydrate and amino-acids fractions (^{13}C -enriched with respect to bulk organic matter; Degens, 1969) and a selective preservation of the lipid and cellulose fractions (^{13}C -depleted with respect to bulk organic matter; Degens, 1969). Oxic and anoxic incubation decay experiments of phytoplankton concentrates tend to confirm this shift to lighter $\delta^{13}\text{C}$ values (Harvey and Macko, 1997a; Lehmann et al., 2002) although, in situ measurements of POC - $\delta^{13}\text{C}$ also show opposite trends with water depth that are interpreted as source variations or differential response to mineralization (Meyers and Eadie, 1993; Ostrom et al., 1998a; Hollander and Smith, 2001). In the water column of the Boconó reservoir, POC- $\delta^{13}\text{C}$ values (Fig. 6) support a mixing trend rather than a non-equivoque mineralization trend. Indeed, the correlation between $\delta^{13}\text{C}$ and POC/PN (Fig. 12) is best explained as a mixing line between a ^{13}C -depleted and C-enriched pool composed of phytoplankton and/or vascular plant debris near surface and, a ^{13}C -enriched and C-depleted soil-derived pool, transported in the water column. Indeed, the composition of suspended organic matter below 15 m (average $\pm 1\sigma$: $\delta^{13}\text{C} = -25.9 \pm 0.3\text{‰}$, POC/PN = 10.0 ± 1.3 , $n = 5$, water depth: 16–42 m) closely matches terrigenous supply of the Boconó River ($\delta^{13}\text{C} = -25.8\text{‰}$, POC/PN = 10).

In contrast, the very low suspended matter concentrations measured in the water column of the Tucupido reservoir (Fig. 6) are directly linked to the low discharge of the Tucupido River (Table 1) and by the distance from the Boconó River, the major source of suspended sediments (Fig. 1). For these reasons, suspended material in the Tucupido reservoir is thought to be mainly composed of aquatic-derived matter possibly mixed, near surface, with vegetation debris supplied by wind

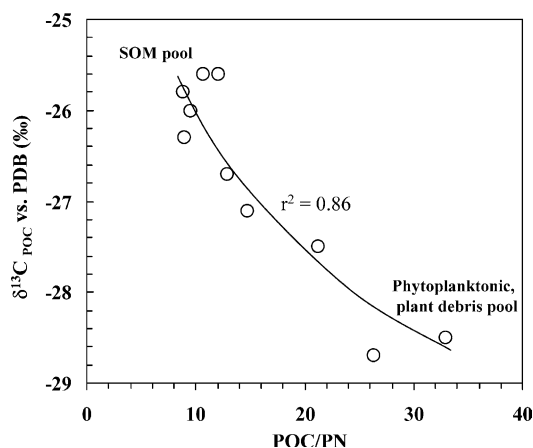


Fig. 12. Correlation between POC- $\delta^{13}\text{C}$ and POC:PN atomic weight ratios (Boconó reservoir, September 1999). SOM refers to soil organic matter.

(with high C:N ratios). The higher organic C contents (in mg C g⁻¹) measured in suspended sediments support this assumption with respect to the soil-derived POC recovered in the water column of the Boconó reservoir, typically diluted by clay minerals and / or fine clastic debris. Below the thermocline (ca. 12 m), the decreasing $\delta^{13}\text{C}$ trend towards light values (-30‰) could reflect the theoretical decreasing trend due to organic matter mineralization previously outlined. However, since reduced mineralization rate apparently take place in the Tucupido reservoir, suspended organic matter should be better preserved than for the Boconó reservoir. An alternative interpretation to the observed trend could be a change in the nature of suspended organic matter (e.g.: Hollander and Smith, 2001). Under hypoxic to anoxic conditions, settling material with ^{13}C -depleted values in the deeper part of the water column might reflect the contribution of chemoautotrophic and/or methanotrophic biomass. Indeed, chemoautotrophic bacteria usually display low $\delta^{13}\text{C}$ values (ca. -45‰ , Freeman et al., 1990). Methanotrophic bacteria provide even more ^{13}C -depleted compositions (ca. -90‰ ; Whiticar et al., 1986; Summons et al., 1994). These assumptions are supported by oxic–anoxic incubation decay experiments of marine phytoplankton (Harvey and Macko, 1997b) or by a comparative study of sediments from locations with oxic–anoxic bottom waters (Gong and Hollander, 1997) that both describe enhanced incorporation of microbial biomass to total POC under anoxic conditions.

The redox conditions displayed near lake bottom apparently extend to the first cm of sediments as shown by low $\delta^{13}\text{C}$ values ($\delta^{13}\text{C} = -27.2\text{‰}$ and $-29.9\text{‰} < \delta^{13}\text{C} < -31.0\text{‰}$ for Boconó and Tucupido reservoirs, respectively) and POC:PN ratios similar to those obtained for suspended matter (Fig. 6). The ca. 1‰ diagenetic offset, with respect to suspended matter of the overlying water column (e.g.: Lehmann et al., 2002), is also shown by sediment $\delta^{13}\text{C}$ values. However, this trend should still be validated by sediment core studies.

5. Conclusions

The combination of water cycle budgets, high resolution monitoring of water environmental parameters, chemical and isotopic measurements on water and suspended organic matter in a tropical freshwater reservoir (Peña Larga dam) located at the outlet of the Boconó watershed (Andes, NW Venezuela) allows several assessments on the redox conditions prevailing in the water column, their relationship with water and organic matter supplies and the extent of suspended organic matter mineralization. Composed of two sub-reservoirs with contrasted water inputs, the Peña Larga dam provides the opportunity to better constrain C budgets and source – composition of suspended organic matter

within two parts of a unique freshwater system with different redox and ventilation conditions.

The redox status of the water column in the Peña Larga reservoir is mainly linked to mixing and renewal of water (i.e.: the water residence time). In the part of the reservoir directly connected to the main river discharge, a seasonal water turnover induces regular water supply and mixing during the year and subsequent dissolved O₂ reload below the thermocline. Despite important riverine suspended matter inputs (sediment yield: 6×10^6 t a⁻¹, POC input: 32×10^3 t C a⁻¹), organic matter degradation is mainly driven by mineralization under oxic conditions (estimated rate: ca. 80–440 $\mu\text{mol C L}^{-1} \text{ a}^{-1}$) with limited dissolution of suspended mineral phases. Surface planktonic production can be discriminated from soil-derived organic matter supply using $\delta^{13}\text{C}$ values (^{13}C -depleted vs. ^{13}C -enriched values, respectively). The oxic reservoir of Peña Larga dam mainly acts as a sink for sediments and organic matter and thus, reduces suspended matter export downriver.

Limited water mixing and “long-term” water residence time (average: 6.2 a) lead to apparently persistent thermal stratification in the isolated parts of the Peña Larga dam. Reduced surface - bottom water mixing induces hypoxic to anoxic conditions in the water column and in lake bottom sediments. Limited organic matter mineralization occurs in waters strongly depleted in dissolved O₂ (estimated mineralization rate: ca. 40 $\mu\text{mol C L}^{-1} \text{ a}^{-1}$). Below the thermocline, bacterially mediated reduction releases important amounts of dissolved metals and trace elements (i.e.: Fe, Mn, Co, Ba), induces NH₄ accumulation and limited SO₄ reduction. Below 20 m, residual organic matter displays high organic C concentrations (in mg C g⁻¹) and ^{13}C -depleted compositions that both either reflect high contribution of microbial biomass (chemoautotrophic and/or methanotrophic bacteria) or selective loss of ^{13}C -enriched compounds. The hypoxic to anoxic conditions observed in the isolated part of this tropical reservoir throughout the year are comparable to the anoxic conditions prevailing in the deep part of the water column in temperate freshwater reservoirs undergoing eutrophication (e.g.: Lake Lugano, Lake Michigan). However, enhanced primary productivity due to excess supply of nutrients and organic matter by runoff or soil erosion on the watershed is apparently not the main process driving the evolution of water column and sediment to hypoxic to anoxic conditions, that are more likely linked to limited O₂ supply due to restricted water circulation and renewal.

Acknowledgements

This work is dedicated to the memory of late Professor Bernard Kübler (Université de Neuchâtel) who

initiated our collaboration. It was supported by the French INSU (Program 97 PROSE 53) and by the MARNR (Ministerio del Ambiente y de los Recursos Naturales Renovables, Caracas, Venezuela). The authors are grateful to M. Cornières-Vallès, A. Moreau, and Colonel R. Mena Nava (Instituto Geografico de Venezuela Simón Bolívar) for their hospitality and support. Bathymetric and hypsometric data for the Peña Larga water dam were kindly provided by A. Montilva, M.J. Guerrero, H. Briceño and M. Alvarado (DESURCA-CADAFE and MARNR, Venezuela). We are also grateful to M. Grably (BIOMCO – Paris), P. Richard (BIOMCO – Paris), J. Samuel (CGS – Strasbourg), R. Rouault (CGS – Strasbourg), and D. Million (CGS – Strasbourg) for their analytical assistance. Dr. P.-P. Zuddas (IPGP – Paris) and Dr T. Bariac (BIOMCO – Paris) helped us with their comments and suggestions to improve a former draft of this manuscript. Two anonymous reviewers are gratefully acknowledged for their extensive reviews.

References

- Achterberg, E.P., Van Den Berg, C.M.G., Boussemart, M., Davison, W., 1997. Speciation and cycling of trace metals in Esthwaite water: a productive English lake with seasonal deep-water anoxia. *Geochim. Cosmochim. Acta* 61, 5233–5253.
- Anderson, R.F., Fleisher, M.Q., LeHuray, A.P., 1989. Concentration, oxidation state and particulate flux of uranium in the black sea. *Geochim. Cosmochim. Acta* 53, 2215–2224.
- Balistrieri, L.S., Murray, J.W., Paul, B., 1992a. The cycling of iron and manganese in the water column of Lake Sammamish, Washington. *Limnol. Oceanog.* 37, 510–528.
- Balistrieri, L.S., Murray, J.W., Paul, B., 1992b. The biochemical cycling of trace metals in the water column of Lake Sammamish, Washington: response to seasonally anoxic conditions. *Limnol. Oceanog.* 37 (3), 529–548.
- Balistrieri, L.S., Murray, J.W., Paul, B., 1994. The geochemical cycling of trace elements in a biogenic meromictic lake. *Geochim. Cosmochim. Acta* 58, 3993–4008.
- Benson, B.B., Krause, D., 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnol. Oceanog.* 29, 620–632.
- Bigeleisen, J., Perlman, M.L., Prosser, H.C., 1952. Conversion of hydrogenic materials to hydrogen for isotopic analysis. *Anal. Chem.* 24, 1356–1357.
- Brock, T.D., 1985. A eutrophic lake: Lake Mendota, Wisconsin. In: *Ecological Studies*, vol. 55. Springer, Berlin.
- Chapra, S.C., Dobson, H.F.H., 1981. Quantification of the lake trophic typologies of Naumann (surface quality) and the Thienemann (oxygen) with special reference to Great Lakes. *J. Great Lakes Res.* 7, 182–193.
- Cornières, M., 1998. Etude et modélisation des transferts deau, déléments dissous et particulaires dans un bassin versant torrentiel. Cas du Rio Boconó dans les Andes vénézuéliennes. Unpubl. Doct. Thesis, Univ. Avignon (France).
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Davison, W., 1993. Iron and manganese in lakes. *Earth. Sci. Rev.* 34, 119–163.
- Davison, W., Woof, C., 1984. A study of the cycling of manganese and other elements in a seasonally anoxic lake, Rostherne Mere, UK. *Wat. Res.* 18, 139–146.
- Degens, E.T., 1969. Biogeochemistry of stable carbon isotopes. In: Eglinton, G., Murphy, M.T.J. (Eds.), *Organic Geochemistry: Methods and results*. Springer, Berlin, pp. 304–356.
- Demaison, G.J., Moore, G.T., 1980. Anoxic environments and oil source bed genesis. *Am. Assoc. Petrol. Geol. Bull.* 64, 1179–1209.
- De Vitre, R.R., Buffle, J., Perret, D., Baudat, R., 1988. A study of iron and manganese transformations at the O₂/S (–II) transition layer in a eutrophic lake (Lake Bret, Switzerland): a multimethod approach. *Geochim. Cosmochim. Acta* 52, 1601–1613.
- Edmond, J.M., Palmer, M.R., Measures, C.I., Brown, E.T., Huh, Y., 1996. Fluvial geochemistry of the eastern slope of the North-eastern Andes and its foredeep in the drainage of the Orinoco in Colombia and Venezuela. *Geochim. Cosmochim. Acta* 60, 2949–2976.
- Einsele, G., Yan, J., Hinderer, M., 2001. Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. *Global Planet. Change* 30, 167–195.
- Epstein, S., Mayeda, T., 1953. Variation of ¹⁸O content of waters from natural sources. *Geochim. Cosmochim. Acta* 4, 224–231.
- Fogel, M., Cifuentes, L., 1993. Isotope fractionation during primary production. In: Engel, H., Macko, S. (Eds.), *Organic Geochemistry*. Plenum Press, New York, pp. 73–97.
- Froelich, P.N., Klinghammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Pacific: suboxic diagenesis. *Geochim. Cosmochim. Acta* 43, 1075–1088.
- Freeman, K.H., Hayes, J.M., Trendal, J.M., Albrecht, P., 1990. Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons. *Nature* 343, 254–256.
- Gat, J.R., 1995. Stable isotopes of fresh and saline lakes. In: Lerman, A., Imboden, D., Gat, J.R. (Eds.), *Physics and Chemistry of Lakes*. Springer, Berlin, pp. 139–165.
- GNIP (Global Network for Isotopes in Precipitation), 1996. Internal Report IAEA. PAGES, WMO, IAHS.
- Gong, C., Hollander, D.J., 1997. Differential contribution of bacteria to sedimentary organic matter in oxic and anoxic environments, Santa Monica Basin, California. *Org. Geochem.* 26, 545–563.
- Gonzales de Juana, C., Ithurralde, A., Picart-Cadillat, X., 1980. Geología de Venezuela y de sus cuencas petroleras. FONINVEST, Caracas.
- Hamilton-Taylor, J., Davison, W., 1995. Redox-driven cycling of trace elements in lake. In: Lerman, A., Imboden, D., Gat, J.R. (Eds.), *Physics and Chemistry of Lakes*. Springer, Berlin, pp. 217–236.
- Hamilton-Taylor, J., Davison, W., Morfett, K., 1996. The biogeochemical cycling of Zn, Cu, Fe, Mn, and dissolved organic C in a seasonally anoxic lake. *Limnol. Oceanog.* 41, 408–418.

- Harvey, H.R., Tuttle, J.H., Bell, J.T., 1995. Kinetics of phytoplankton decay during simulated sedimentation: changes in biochemical composition and microbial activity under oxic and anoxic conditions. *Geochim. Cosmochim. Acta* 59, 3367–3377.
- Harvey, H.R., Macko, S.A., 1997a. Kinetics of phytoplankton decay during simulated sedimentation: changes in lipids under oxic and anoxic conditions. *Org. Geochem.* 27, 129–140.
- Harvey, H.R., Macko, S.A., 1997b. Catalysts or contributors. Tracking bacterial mediation of early diagenesis in the marine water column. *Org. Geochem.* 26, 531–544.
- Hollander, D.J., Smith, M.A., 2001. Microbially mediated carbon cycling as a control on the $\delta^{13}\text{C}$ of sedimentary carbon in eutrophic Lake Mendota (USA): new models for interpreting isotopic excursions in the sedimentary record. *Geochim. Cosmochim. Acta* 65, 4321–4337.
- Hongve, D., 1997. Cycling of iron, manganese, and phosphate in a meromictic lake. *Limnol. Oceanog.* 42, 635–647.
- Huon, S., Grousset, F.E., Burdloff, D., Bardoux, G., Mariotti, A., 2002. Sources of fine-sized organic matter in North Atlantic Heinrich layers: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ tracers. *Geochim. Cosmochim. Acta* 66, 223–239.
- IAEA, 2001. Global Network in Precipitation, the GNIP database. Available <<http://isohis.iaea.org>>.
- Jorgensen, B.B., 2000. Bacteria and Marine Biogeochemistry. In: Schulz, H.D., Zabel, M. (Eds.), *Marine Geochemistry*. Springer, Berlin, pp. 173–208.
- Kristensen, E., Holmer, M., 2001. Decomposition of plant materials in marine sediment exposed to different electron acceptors (O_2 , NO_3^- , SO_4^{2-}), with emphasis on substrate origin, degradation kinetics, and the role of bioturbation. *Geochim. Cosmochim. Acta* 65, 419–433.
- Lal, R., 1990. *Soil Erosion in the Tropics: Principles and Management*. McGraw-Hill, New York.
- Lal, R., 1995. Global soil erosion by water and carbon dynamics. In: Lal, R., Kimble, J., Levine, E., Stewart, B.A. (Eds.), *Soils and Global Change*. Advances in Soil Science. Lewis Pub., Boca Raton, pp. 131–142.
- Lee, C., 1992. Controls on organic carbon preservation: the use of stratified bodies to compare intrinsic rates of decomposition in oxic and anoxic systems. *Geochim. Cosmochim. Acta* 56, 3323–3335.
- Lehmann, M.F., Bernasconi, S.M., Barbieri, A., McKenzie, J.A., 2002. Preservation of organic matter and alteration of its carbon and nitrogen isotope composition during simulated and in situ early diagenesis. *Geochim. Cosmochim. Acta* 66, 3573–3584.
- Lerman, A., Stumm, W., 1989. CO_2 storage and alkalinity trends in lakes. *Wat. Res.* 23, 139–146.
- Lewis, W.M., 1984. Eutrophication and land use, lake Dillon, Colorado. In: *Ecological Studies*, vol. 46. Springer, Berlin.
- Likens, G.E., 1972. Eutrophication and aquatic ecosystems. In: Likens, G.E. (Ed.), *Nutrients and Eutrophication*. Am. Soc. Limnol. Oceanog. Spec. Symp., vol. 1, pp. 3–13.
- McConnaughey, T.A., Labaugh, J.W., Rosenberry, D.O., Striegl, R.G., Reddy, M.M., Schuster, P.F., Carter, V., 1994. Carbon budget for a groundwater-fed lake: Calcification supports summer photosynthesis. *Limnol. Oceanog.* 39, 1319–1332.
- McConnaughey, T.A., Whelan, J.F., 1997. Calcification generates protons for nutrient and bicarbonate uptake. *Earth Sci. Rev.* 42, 95–117.
- Meybeck, M., 1982. Carbon, nitrogen, phosphorous transport by world rivers. *Am. J. Sci.* 282, 401–450.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.* 114, 289–302.
- Meyers, P.A., Eadie, B.J., 1993. Sources, degradation and recycling of organic matter associated with sinking particles in Lake Michigan. *Org. Geochem.* 20, 47–56.
- Ostrom, N.E., Long, D.T., Bell, E.M., Beals, T., 1998a. The origin of particulate and sedimentary organic matter and nitrate in Lake Superior. *Chem. Geol.* 152, 13–28.
- Payne, B.R., 1991. On the statistical treatment of environmental isotope data in hydrology. In: *Isotope Techniques in Water Resources Development*. Proceeding Series, IAEA, Vienna.
- Pouyllau, M., 1989. Géomorphologie du Venezuela: carte au 1/4000000 et bibliographie sélective. Venezuela, environnements et changements. Unpublished report Univ., Toulouse (France).
- Sigg, L., Johnson, A., Kuhn, A., 1991. Redox conditions and alkalinity generation in a seasonally anoxic lake (Lake Greifen). *Mar. Chem.* 36, 9–26.
- Sternbeck, J., 1996. Manganese cycling in a eutrophic lake – Rates and pathways. *Aquat. Geochem.* 1, 399–426.
- Stumm, W., Morgan, J.J., 1996. Oxidation and reduction; equilibria and microbial mediation. In: Stumm, W., Morgan, J.J. (Eds.), *Aquatic Chemistry*, third ed. Wiley-Interscience, New York, pp. 425–515.
- Summons, R.E., Jahnke, L.L., Roksandic, Z., 1994. Carbon isotope fractionation in lipids from methanotrophic bacteria: relevance for interpretations of the geochemical record of biomarkers. *Geochim. Cosmochim. Acta* 58, 2853–2863.
- Taillefert, M., Gaillard, J.F., 2002. Reactive transport modeling of trace elements in the water column of a stratified lake: iron cycling and metal scavenging. *J. Hydrol.* 256, 16–34.
- Viollier, E., Jézéquel, D., Michard, G., Pèpe, M., Sarazin, G., Albéric, P., 1995. Geochemical study of a crater lake (Pavin Lake, France): trace-element behaviour in the monimolimnion. *Chem. Geol.* 125, 61–72.
- Wann, J.K., Chen, C.T.A., Wang, B.J., 1997. A seasonally anoxic mountain lake with an active Fe cycle in tropical Taiwan. *Aquat. Geochem.* 3, 21–42.
- Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation – Isotopic evidence. *Geochim. Cosmochim. Acta* 50, 693–709.
- Yao, W., Millero, F.J., 1995. The chemistry of the anoxic waters in the Framvaren fjord, Norway. *Aquat. Geochem.* 1, 53–88.
- Zaw, M., Chiswell, B., 1999. Iron and manganese dynamics in lake water. *Wat. Res.* 33, 1900–1910.