

Dissolved organic matter in Chascomús Pond (Argentina). Influence of calcium carbonate on humic acid concentration *

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Abstract

Water chemistry of the Chascomús Pond (Province of Buenos Aires, Argentina) was studied during a year characterized by low precipitation. Supersaturation of calcium carbonate up to a calcite saturation index of about 20 in spring and summer was observed, together with a diminution of the concentration of dissolved organic matter, in particular humic substances (HS). These results suggested an adsorption between organic matter and calcium carbonate which should influence the growth of calcium carbonate crystals. A preferential removal of higher molecular weight HS was observed by gel permeation chromatography experiments.

Introduction

Chascomús Pond (35 °, 36'S, 58 ° W, Fig. 1) lies in a geomorphological unit called 'Pampa deprimida' in the Province of Buenos Aires (Argentina). This pond belongs to the Río Salado drainage basin, whose soils are rich in nutrients and organic matter. In the basin intensive rural and agricultural activities take place. Chascomús Pond is a shallow eutrophic ecosystem (Tot-P = 0.25 mg l⁻¹; Tot-N = 1.56 mg l⁻¹, Ca²⁺ = 0.52 mM; Mg Ca⁻¹ molar ratio = 1.1, chlorophyll *a* = 25.3 µg l⁻¹, phytoplankton primary production 121.0 g m⁻² y⁻¹ of C), with a nearly continuous vertical mixing. The mixing promotes a high concentration of suspended particulate matter (112.8 mg l⁻¹) and low water transparency (Secchi disc reading 0.19 m). The water column is almost always thermally homogeneous and saturated with dissolved oxygen (Conzonno & Claverie, 1987/8, 1990).

In previous studies (Conzonno & Fernández Cirelli, 1987, 1988), we have reported on the presence of high concentration of dissolved organic matter in this pond,

mainly being humic substances (HS). Chemical characteristics and properties of HS were determined, as well as the factors influencing their distribution and dynamics. In this paper we describe the fluctuations of dissolved organic matter in a year characterized by low precipitation. As a result of evaporation an increase of dissolved solids, diminution of the pond's depth and a high degree of calcium carbonate supersaturation were detected.

Materials and methods

Surface samples were collected monthly from April 1988 to May 1989 in the centre of the pond by means of a 2 liter nonmetallic Van Dorn sampler. Water temperature was measured *in situ*, the pH (Orion 701 A) and Ca²⁺, Mg²⁺, CO₃²⁻, HCO₃⁻ and Cl⁻ (volumetric titration according to Golterman, 1971) were determined in aliquots of unfiltered water. Samples were immediately filtered (0.45 µm pore size, Millipore) previous to analyses of chemical oxygen demand (COD) (Golterman, 1971), absorbance at 250 nm (1 cm path length Jasco 7850 spectrophotometer), colour units by visual

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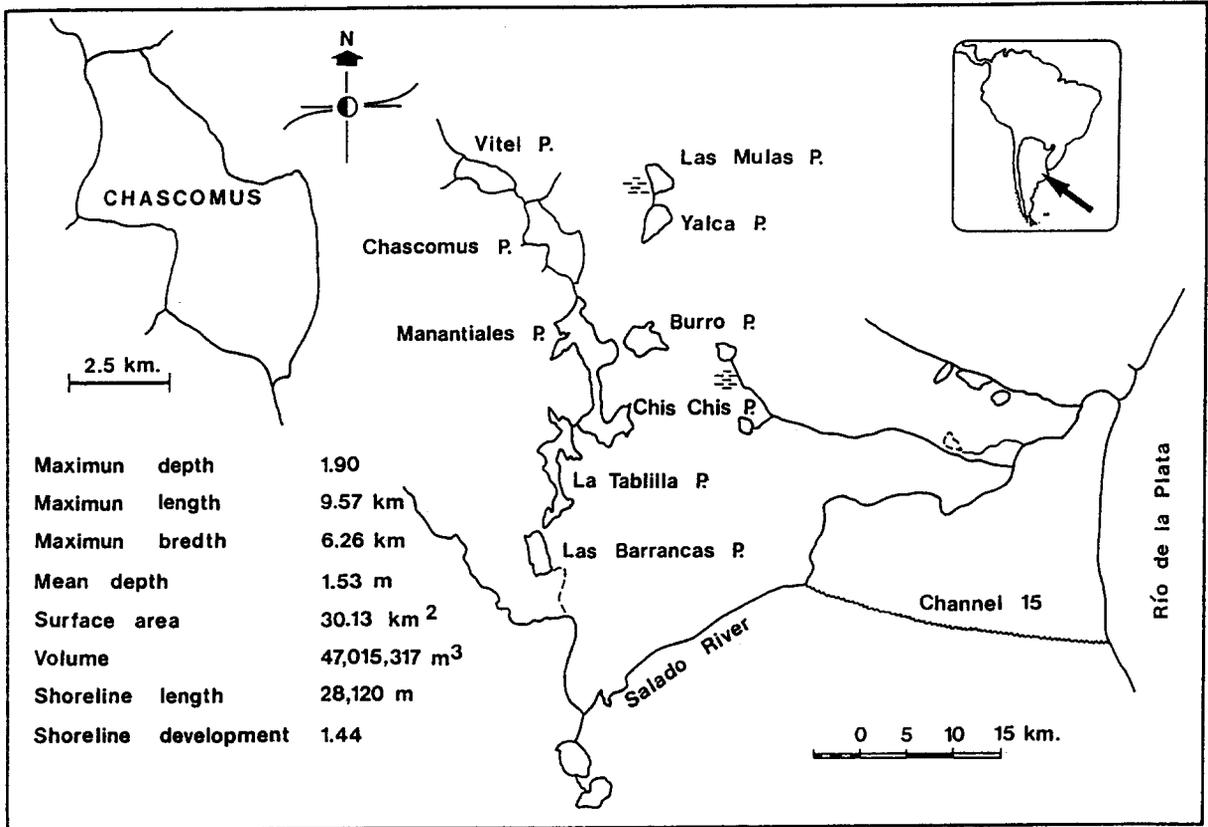


Fig. 1. Chascomús Pond, morphometric parameters and its location in the Río Salado drainage basin.

comparison (APHA, 1985), sulphate by turbidimetry, sodium and potassium by flame emission photometry (Golterman, 1971). Total dissolved solids were taken as the sum of the major ions. Calcite saturation index (SI) was calculated considering calcium and carbonate concentrations, activity coefficients (using Davies approximation) and equilibrium constant at each temperature (Stumm & Morgan, 1970). The filtered samples without further treatment were chromatographed on a Sephadex G-100 (Pharmacia Fine Chemicals) column (2.5 × 25 cm) eluted with phosphate buffer of the same ionic strength and pH of the water sample. Fractions (3 ml) were recorded at 250 nm and the void volume (V_0) was determined with Blue Dextran 2000 (Pharmacia Fine Chemicals). Evaporation was evaluated by the method of Thornthwaite (1948).

Results and discussion

We studied dissolved organic matter in Chascomús Pond during a period (April 1988–May 1989) charac-

terized as dry, since the registered precipitation was 616 mm (mean value 1982–1987: 1311 mm) and the precipitation – evaporation balance was negative (Fig. 2A). As a consequence, diminution of the depth, from 3.5 m (April 1988) to 1.6 m (May 1989) and a significant increment of total dissolved solids, from 0.5 to 0.9 g l⁻¹ (Fig. 2B) were observed. The rise in water temperature in spring and summer time (25 °C in January compared to 8.8 °C in July) promoted the decrease in CO₂ as well as an increase in photosynthetic activity, which was evidenced in higher values of pH and CO₃²⁻ concentration, up to 8.89 and 0.59 mM respectively (Fig. 2C). Taking into account the values of calcium concentration (up to 0.67 mM, Fig. 2C), calcite saturation index (SI) was determined. The high values obtained from 2.3 to 23.0 (Fig. 2C) are in accordance with those reported for eutrophic and hypertrophic lakes (Effler & Driscoll, 1985; Murphy *et al.*, 1983).

On the other hand Golterman & Kouwe (1980) and Golterman & Meyer (1985) have reported that supersaturation of CaCO₃ strongly depends on the pH in

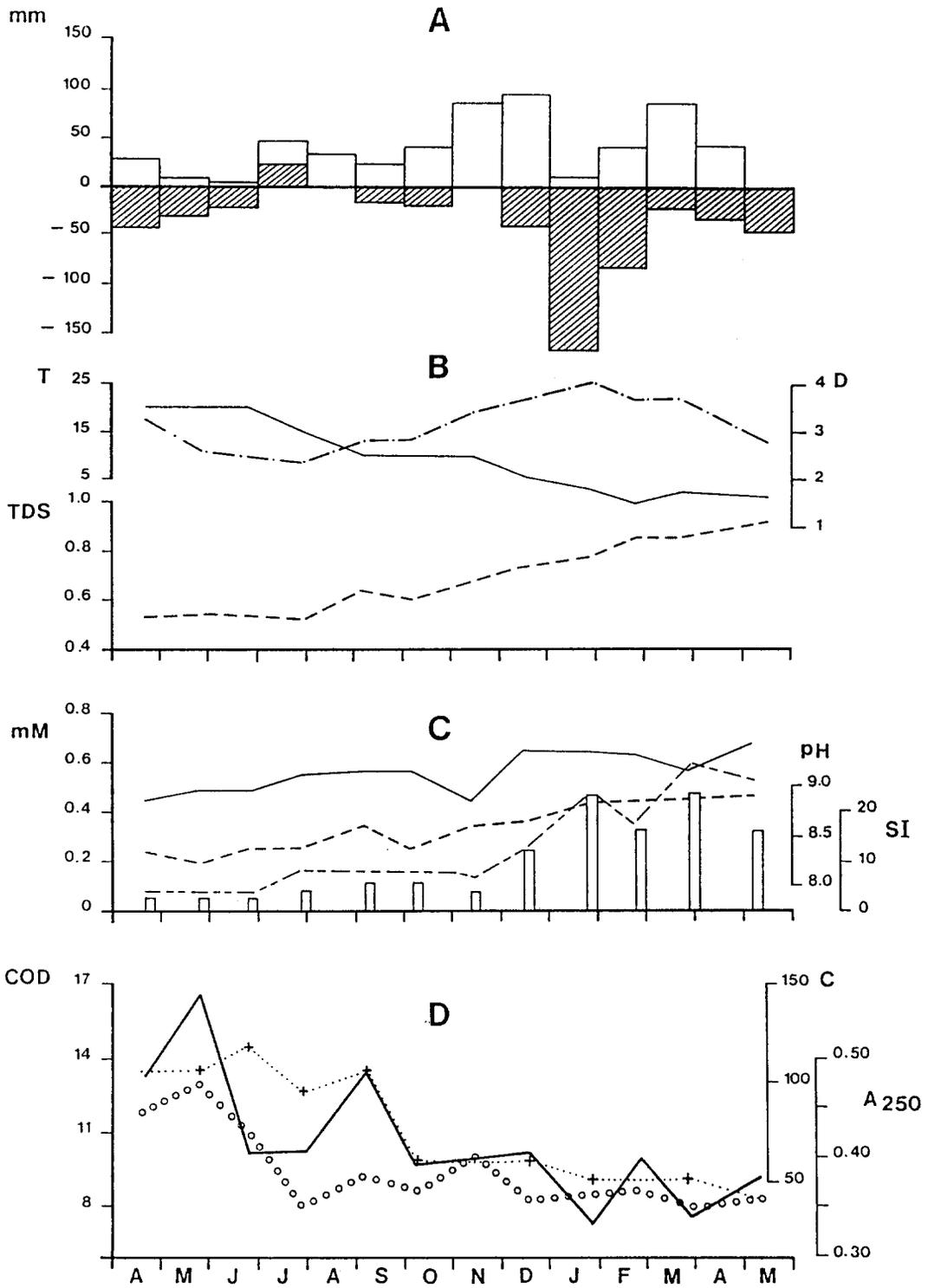


Fig. 2. A: Precipitation (mm) □ and precipitation-evaporation ▨ B: T, Water temperature (°C) —; TDS, total dissolved solids (g l⁻¹) - - - and D, depth (m) — C: Carbonate (mM) - - - -; calcium (mM) —; pH - - - - and SI, saturation index □ . D: COD, chemical oxygen demand (mg l⁻¹ O₂) —; A₂₅₀ absorbance at 250 nm oooo and C, colour units (mg l⁻¹ Pt) ·····

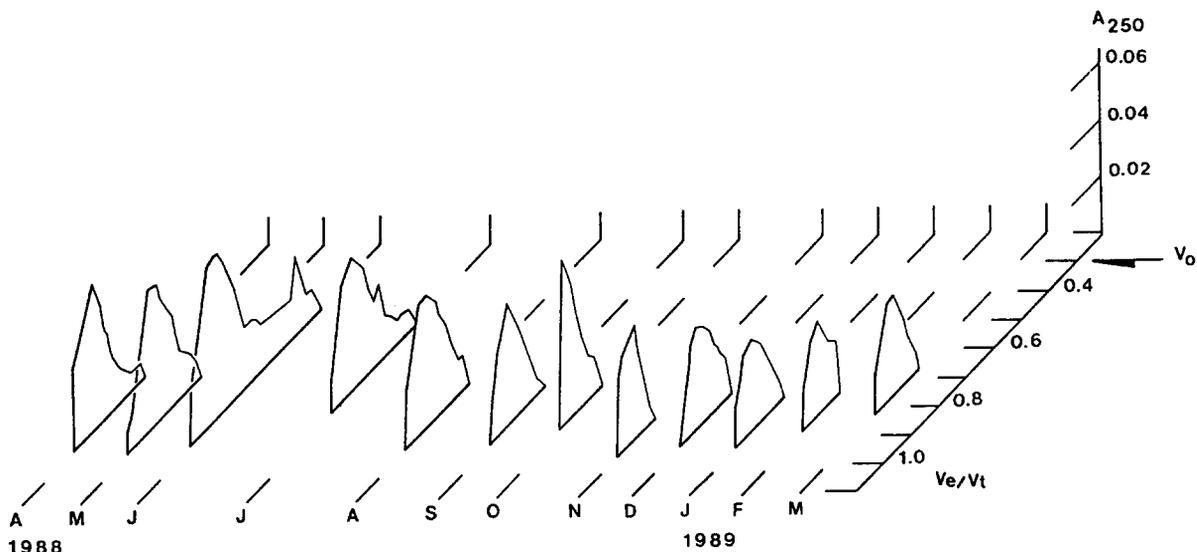


Fig. 3. Gel permeation chromatography (Sephadex G-100) of samples all over the period of study. V_e = elution volume, V_t = total gel volume, V_o = void volume.

lakes and rivers. They have formulated the following relation between the ionic product for CaCO_3 (IPc) and pH: $\text{IPc} = A \text{pH}^B$. With A ranging from $6.8 \text{ E-}05$ to $3.8 \text{ E-}22$ and B from 4.5 to 23.8. In view of these considerations, we try to relate IPc and pH for Chascomús Pond in the study period. In spite of the low number of determinations ($n = 12$), we found the following correlation: $\text{IPc} = 1.7 \text{ E-}31 \text{ pH}^{25.5}$ ($r^2 = 0.87$). Differences with reported data can be explained on the basis of the physical and chemical composition of the aquatic systems. Further determinations should be necessary for definitive conclusions.

In July, a decrease of dissolved organic matter was observed from 16.4 to $7.5 \text{ mg l}^{-1} \text{ O}_2$ (Fig. 2D). Such diminution coincided with a lower concentration of HS in solution, as evidenced by the observed decreases in colour units, from 120 to $40 \text{ mg l}^{-1} \text{ Pt}$ and in A_{250} , from 0.48 to 0.34 (Fig. 2D). These decreases may be attributed to an association between CaCO_3 and organic matter as has been observed by other authors (Otsuki & Wetzel, 1973; 1974; Stewart & Wetzel, 1981a). The growth of the carbonate nuclei should be inactivated by the adsorption of dissolved organic substances onto the carbonate surfaces. The mineral surface may be physically isolated from its environment inhibiting free inorganic equilibration between CaCO_3 and the surrounding water (Chave, 1965; Suess, 1970; Reynolds, 1978; Stewart & Wetzel, 1981a), which could explain the high SI values observed. Since the association of organic matter with calcium carbonate takes place with

small calcite crystals as reported by Pantin (1965), it is likely that HS do not actually precipitate but remain in suspension favoured by the vertical mixing in the natural ecosystem. HS should have been retained by the membranes used to filter the samples prior to analysis, thus explaining the observed decrease of dissolved organic matter.

In order to investigate if there is a preferential interaction of high or low molecular weight species with calcium carbonate, gel permeation chromatography experiments of samples all over the study period were performed (Fig. 3). The importance of molecular shape and size in the behaviour of natural aquatic humic substances has been often emphasized (Stewart & Wetzel, 1982; De Haan & De Boer, 1986; Jones *et al.*, 1988). Sephadex G-100 was selected for gel chromatography to cover a wide range of molecular weight. As expected in accordance with the results of COD, colour and A_{250} measurements, the peak area decreased with time (Fig. 3). It can also be observed that along the period studied elution takes place with increasing elution volumes, suggesting a preferential removal of high molecular weight fractions, normally referred to as humic acids. Similar observations were reported by Stewart & Wetzel (1981b) for water samples collected from 55 lakes in southwestern Michigan. Fractions with molecular weight less than $10\,000$ (V_e/V_t 0.7 – 0.9), should remain in solution in spring and summer when association with calcium carbonate is more significant.

The above described phenomena, under these climatological conditions, underline the importance of calcium carbonate in the cycle of dissolved organic substances which influences not only their concentration in solution but also their physico chemical characteristics.

Calcium carbonate precipitation in water bodies is a phenomenon of special interest (Küchler-Krischun & Kleiner, 1990). The formation of small calcite crystals offers a large surface for the concentration of various dissolved substances for adsorption and co-crystallization. Since studies performed in 25 ponds of this area (Ringuelet *et al.*, 1967) showed the presence of carbonate (ranging from 3 to 400 mg l⁻¹) and calcium (from 8.2–231.8 mg l⁻¹), the interaction between dissolved organic matter, in particular HS, and calcium carbonate observed in Chascomús Pond may be common in other Pampasic ponds. Since this may influence the metabolism and evolution of these aquatic ecosystems, systematic studies from a limnological point of view are required.

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