UNA INTERPRETACION DE LOS FACTORES QUE INFLUYEN SOBRE LA VARIABILIDAD DE LA ALCALINIDAD EN EL RÍO PARANÁ MEDIO (ARGENTINA)

AN INTERPRETATION OF THE FACTORS INFLUENCING ALKALINITY VARIABILITY IN THE MIDDLE PARANÁ RIVER (ARGENTINA)

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Abstract

The multinational Paraná River (drainage basin, ~2.6 10^6 km^2; annual discharge, ~500 km^3 y^{-1}) has a long (~900 km) and wide (~30 – 50 km) flood valley, which occupies its middle and lower stretches. Most of the valley's area (estimated area of ~50000 km^2) holds a myriad of ponds, ox-bows, and channels which, following the seasonal variation of the prevailing discharge regime, exchanges water, dissolved species, sediment, and biological materials with the Paraná's main stem. Exceptional hydrological events (e.g., ENSO-triggered) flood almost totally the expanse of the flood valley. A ten year-long (1965 – 1975) continuous series of alkalinity measurements allowed probing into the mechanisms that determine the observed alkalinity variability -controlled by several biogeochemical processes (e.g., photosynthesis/respiration, nitrification/denitrification, etc.) occurring in the riparian environment-, which are associated with the Paraná's hydrological stage.

Key words: *alkalinity, flood regime, ENSO effect, biogeochemistry*.

Introduction

Properly defined, total alkalinity is "the equivalent sum of the bases that are titratable with a strong acid" (Stumm and Morgan, 1996). In terms of molar concentrations, total alkalinity (A_T) is equal to,

$$A_T = m\,(HCO_3^-) + 2m\,(CO_3^{2-}) + m\,(B(OH)^{4-}) + m\,[H_3(SiO)^{4-}] + m\,(HS^-) + m\,(\text{organic anions})$$

$$+\, m\,(OH^-) - m\,(H^+),$$

where *m* is the molar concentration. In most natural waters only carbonate and bicarbonate ions are of significance, because, in comparison, the other ions exhibit very low concentrations. Accordingly, the previous equation shortens to:

$$A_T \approx m\,(HCO_3^-) + 2m\,(CO_3^{2-})$$

Therefore, in most natural waters, total alkalinity is approximately equal to carbonate alkalinity (Drever, 1997).

A_T is largely dependent on the lithology dominating the headwaters of streams and rivers (e.g., weathered carbonate rocks or hydrolyzed silicates are main sources). Therefore, it is frequent to find in certain rivers a significant correlation between A_T concentration and river discharge. This is not usually the case in large fluvial systems, where hydrological seasonality rules a dynamic water exchange between the lentic environments prevailing in the flood valley – partly mantled with riparian vegetation-, and the lotic conditions of the main river stem. The result of this scenario is a markedly low –or not significant- correlation between the two considered variables.

The objective of this communication is to consider the processes which, associated with different hydrologic stages, may affect A_T concentrations in a large river with an extended flood plain, such as the middle and lower Paraná.

Materials and Methods

An uncommon ten-year-long data series (1965 – 1975), involving A_T and discharge determined in the middle Paraná River (about 600 km upstream from the mouth) was used in this exercise (Lenardón, 1979). The employed analytical technique involved a titration with a H_2SO_4 standard solution and phenolphthalein (8.3-pH titration endpoint) and methyl orange, as indicators. Argentina's waterways authority supplied the daily river discharge series at the city of Paraná (~600 km upstream from mouth) for the indicated period. Other determined parameters were pH, TDS, color, turbidity, total hardness, Cl^-, and SO_4^{2-} (Lenardón, 1979). Commercially available statistical software allowed data processing.

Results

Given the lithology and climate dominating Paraná's western upper catchments (i.e., Bermejo and Pilcomayo rivers), it is likely that the prevailing reaction controlling A_T production in the Andean headwaters might be the dissolution of carbonates, which results in an A_T increase:

$$CaCO_3\ (s) + CO^2\ (g) + H_2O\ (l) \leftrightarrow Ca^{2+}\ (aq) + 2\ HCO_3^-\ (aq)$$

Likewise, in the Brazilian and Paraguayan tropical headwaters, rock weathering (i.e., hydrolysis of silicates) is surely important, in reactions like the weathering of plagioclase, which also increases A_T:

$$2\ NaAlSi_3O_8\ (s) + 9\ H_2O\ (l) + 2\ H_2CO_3\ (aq) \leftrightarrow Al_2Si_2O_5(OH)_4\ (s) + 2\ Na^+\ (aq) + 4\ Si(OH)_4\ (aq) +2\ HCO_3^-\ (aq)$$

This well-known reaction produces kaolinite as the only solid product. Other reactions, such as nitrification and denitrification, photosynthesis and respiration -among others- contribute to increase or decrease A_T in the Paraná's main stem.

The geomorphological scenario changes drastically when the upper Paraná joins the Paraguay River. The relatively narrow and well-defined river valley characterizing the upper Paraná River becomes an ample flood plain (~30 - 50 km wide) and ~900 km-long. Countless channels, ponds, and ox-bows – in the riparian ecosystems-, often partially mantled with floating vegetation, dissect this singular wetland (Iriondo et al., 2007). This very complex ecosystem is largely dependent on the river's hydrological stage, significantly affecting the chemical variables.

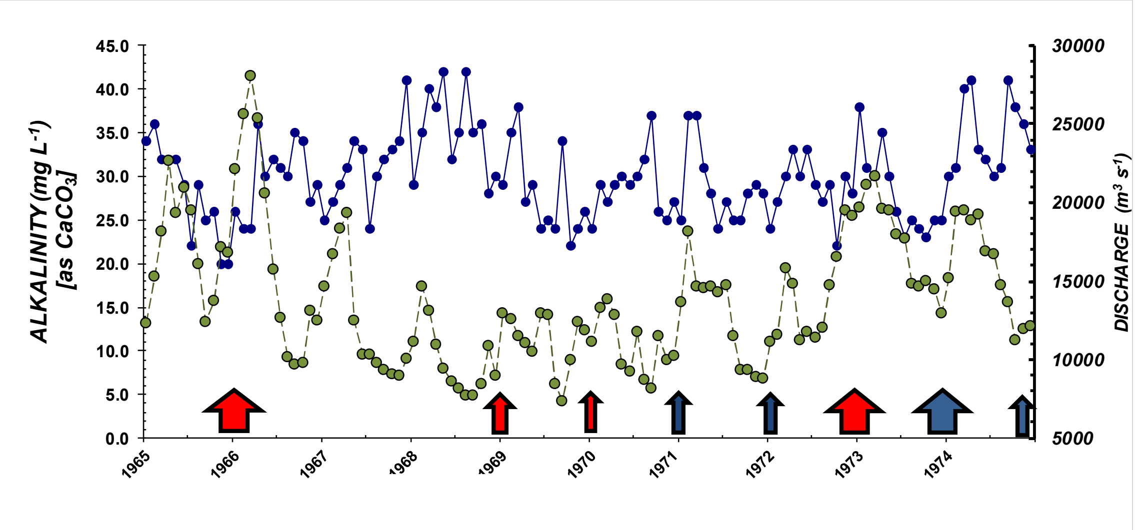

Fig. 1. Variability of alkalinity (blue dots) and discharge (green dots) in the middle Paraná River, ~600 km upstream the mouth. Wide arrows indicate the occurrence of strong El Niño (red) and La Niña (blue) events. Remaining narrower arrows correspond to moderate events. Data from Lenardón (1979). Blue symbols: alkalinity; green: discharge.

Although difficult to interpret, Fig. 1 shows that high, over-the-bank river discharges (i.e., Q > ~17000 $m^3\ s^{-1}$, for example, during strong El Niño events), are associated with increased A_T.

While stalled or interrupted during low river stages, the connections between the flood plain and the main stem remain almost permanently operative. High A_T concentrations are also discernible associated with some low discharge periods (e.g., during La Niña events). During such phases, the relative importance of the Bermejo and Pilcomayo rivers as discharge suppliers to the middle Paraná increases, as also does carbonate alkalinity.

Fig. 1 suggests that the correlation between both, A_T and discharge, is not significant ($p > 0.01$). Correlations were low between discharge and other variables routinely used in water analysis, like TDS ($r = -0.166$, $p < 0.05$), turbidity ($r = -0.148$, $p < 0.05$), and filtered color ($r = 0.471$, $p < 0.001$) (Lenardón, 1979).

In order to ease interpretation, the following graph (Fig. 2) was constructed with A_T geometric means and discharge values for an average year. (i.e., of the studied period, 1965 – 1975).

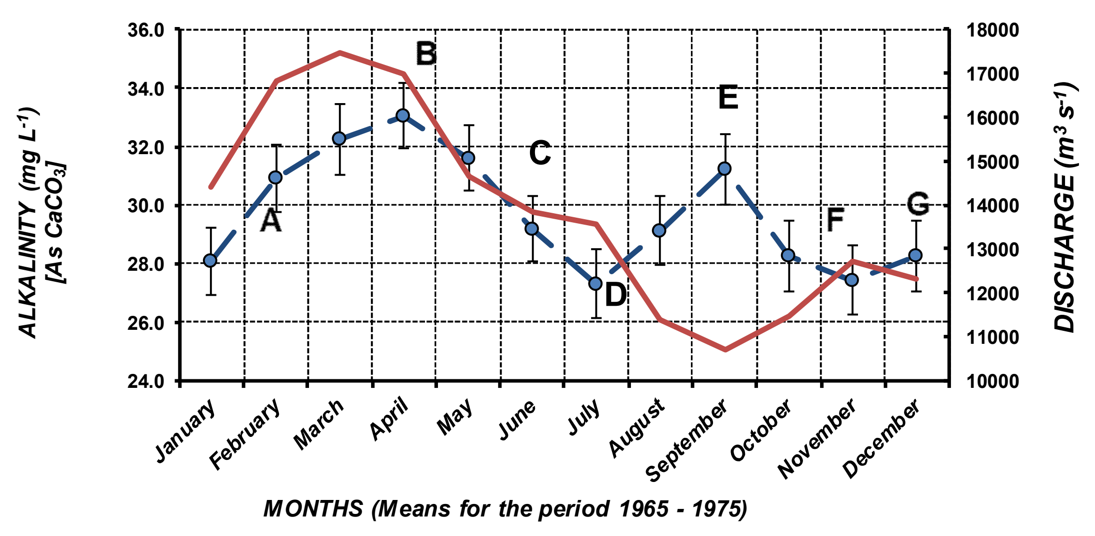

Fig.2. Middle Paraná hydrograph (arithmetic means, red line) and A_T (geometric means, blue line) for the 1965 – 75 period. Letters correspond to processes explained in the text. Error bars for A_T are ± one (geometric) standard deviation.

A significant covariance is observable in Fig. 2 for the period January – July. Summer rains mobilize the products of mineral weathering which are, most likely, the main factors increasing A_T. Several other processes may participate increasing A_T, such as denitrification, (A):

$$5\ CH_2O\ (s) + 4\ NO_3^-\ (aq) + 4\ H+\ (aq) \rightarrow 5\ CO_2\ (aq) + 2\ N^0_2\ (g) + 7\ H_2O\ (l)$$

Over-the-bank flooding flushes out water accumulated in the wetland (i.e., notice the one-month lag between both variables in Fig. 2) for months (or even years). Due to the consumption of H^+, A_T increases through denitrification and by means of the assimilation of nitrate ions into photosynthesis (B):

$$106\ CO_2\ (aq) + 16\ NO_3^-\ (aq) + HPO_4^{2-}\ (aq) + 122\ H_2O\ (l) + 18\ H^+ \leftrightarrow C_{106}H_{263}O_{110}N_{16}P\ (s) + 138\ O_2\ (g)$$

Another mechanism likely to participate in A_T increase is the reduction of sulfate:

$$SO_4^{2-} + 2\ CH_2O\ (s) + H^+\ (aq) \rightarrow 2\ CO^2\ (aq) + HS^-\ (aq) + H2O\ (l)$$

The water and nutrients exchange between the flood plain and the main channel decreases as discharge decreases. Ponds and channels become partially disengaged from the river's main stem; nitrification increases, lowering A_T (C and D):

$$NH_4^+\ (aq) + 2\ O_2\ (g) + CH_2O\ (s) \leftrightarrow NO_3^-\ (aq) + H_2O\ (l) + 2\ H^+\ (aq)$$

In deeper ponds, the oxidation of sulfide may also contribute to the A_T decrease (D):

$$HS^{-} (aq) + 2\ O_2 (g) \rightarrow SO_4^{2-} (aq) + H^{+} (aq)$$

Decreasing discharges cause a decrease in the mobilization of weathering products, lowering A_T concentration.

Starting in August, the scenario changes and both variables become significantly opposed (Fig. 2). Soon, austral spring restarts the assimilation of nitrate ions into the photosynthesis processes, causing an A_T increase due to H^+ consumption (E); A_T-rich waters due to the promoted photosynthetic activity in ponds and ox-bows flow back towards the Paraná's main stem. Reduced discharge also contributes to increase the concentration of the nutrient pool supplied by the river's upper drainage basins.

However, the processes of photosynthesis and respiration are coupled by assimilation of NO^{3-}, and HPO_4^{2-}. The assimilation of NH_4^+ during photosynthesis causes the production of H^+, which leads to a decrease of A_T (F). In November-December, discharge stars a swelling rate and A_T begins the austral summer increasing trend (G).

Conclusions

Several biogeochemical reactions occurring mostly in the Paraná's lentic realm -closely linked to the river's hydrological stage- appear to be significant factors in controlling the variability of A_T concentrations determined in the middle Paraná main stem or lotic system. Although it is not possible to establish the relative significance of each mechanism (e.g., photosynthesis/respiration, nitrification/denitrification, etc.), this exercise should be seen as an approach to understand the association between the river's hydrological stage and the resulting biogeochemical processes.

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