VARIATIONS SAISONNIERES DES COMPOSANTES DE L'ALCALINITÉ DES EAUX DANS LE HAUT-ESTUAIRE DU FLEUVE SAINT-LAURENT (QUEBEC)

(Composantes de l'alcalinité du fleuve Saint-Laurent)

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(Received August 11, 1982; revised December 27, 1982)

Abstract. Measurements of the total alkalinity and its components have been made on waters collected from the St. Lawrence River during the year 1980-1981. Analyses of the total inorganic carbon, the borates, the phosphates and the silicates along with the pH and the total alkalinity permitted an evaluation of each component. In all seasons, the carbonate system was the major component (96%) of the total alkalinity. The residual alkalinity accounting for only 2 to 3% and obtained by the difference between the total alkalinity and the sum of the components appears attributable to weak organic acids. The saturation state of calcite coincided with a river saturated by dissolved calcium carbonate during the summer season and only 45% saturated during the winter season.

1. Introduction

The natural buffering ability of freshwater media to counteract the increasing influence of acid rains (Oden, 1976) is its total alkalinity. This comprehensive measurement includes the contributions of the carbonates, phosphates, borates, silicates, hydroxylate ions and a residual amount whose origin is less clear. As we have previously reported various chemical and hydrodynamic parameters of the St-Lawrence River (Dumas et al., 1977, 1980a), we now wish to quantify the factors which contribute to its total alkalinity and to identify their sources from their seasonal variations.

2. Dosage

The carbonate alkalinity was calculated from Equation (5) using the initial pH, the total inorganic carbon (Σ CO₂) and the related equilibrium constants. Each water sample (100.0 cc) was titrated in a covered beaker with 0.02NH₂SO₄ from an automatic Metrohm titrator to pH 3.5. The equivalence point measured geometrically gave the same results, within ±0.1%, as that obtained with a Gran plot (1952).

The borates were analyzed by mannitol according to the modified method of Pelletier and Lebel (1978). Their contribution to the total alkalinity of St-Lawrence River was too small to be significant, as opposed to salt water systems (Pelletier and Lebel, 1978).

The phosphates and silicates, determined by the method of Strickland and Parsons
(1965), were calculated by Equations (7) and (8). In these calculations, the contribution of the \( \text{PO}_4^{2-} \) species in the pH range 7.2 to 8.1 was excluded due to its small contribution (less than 0.1 \( \mu \text{mol} \)) as well as the alkalinity due to all the silicates (\( \approx 1 \mu \text{eq l}^{-1} \)).

The precision of each method used was verified at different times by ten analyses on the same sample, thus giving the following coefficients of variation: pH = 0.6%; \( \Sigma \text{CO}_2 = 0.5\% \); total alkalinity = 0.8%; phosphate = 5.0%; Ca = 0.7%; Mg = 0.9%.

3. Results and Discussion

The water passing stations #1 and #4 is primarily characteristic of their upstream tributaries, St-Maurice River and Becancour River, respectively. Stations #2 and #3 appear to have good vertical mixing as their surface values are the same as the deepwater ones, except in winter where the surface water at station #2 is more acidic and contains less bicarbonate. This appears due to either some localized horizontal stratification or its contact with the acidic ice cover (meltwater values: pH = 5.70; alkalinity = 140 \( \mu \text{eq l}^{-1} \)).

The calculation of the dissolved \( \text{CO}_2 \), using \( p\text{CO}_2 = K_1 (\text{H}^+)(\text{HCO}_3^-) \) for each season, gives \( 10^{-3.0} \text{ atm} \) in Summer and Fall 1980 to \( 10^{-2.7} \text{ atm} \) in Winter 1981 compared to \( 10^{-3.5} \text{ atm} \) for the equilibrium value of atmospheric \( \text{CO}_2 \) in pure water. Considering that the solubility of \( \text{CO}_2 \) doubles from 20\(^\circ\) to 0\(^\circ\), then these samples contained 3 times the theoretical value. Although this supersaturation is less than that reported by Garrels and MacKenzie (1971), such results pose a serious question to the accuracy and interpretation of \( \text{CO}_2 \) measurements.

The carbonate system exhibits a progressive decrease from Summer 1980 to Spring 1981 as shown in Table II. The two principal factors which can modify to such an extent the carbonate concentration are geophysical: temperature and dilution. A decrease in temperature should increase the calcium carbonate content due to its exothermic enthalpy of solubilization and also should increase the amount of \( \text{CO}_2 \) dissolved in the water. Dilution, caused by rains and spring run off, should cause a decrease in the carbonate concentration. It appears that dilution is more important than temperature although there is no assurance that equilibrium was reached in either case. However, in all seasons, the carbonate system is responsible for at least 96\% of the total alkalinity.

The alkalinity due to phosphates (0.2\%) was of minimal significance. The residual alkalinity calculated by the difference of total alkalinity and the sum of the other forms, represents from 2 to 3\% of the total alkalinity. This residual alkalinity is considered due to organic material resulting from biological activity since this residual value decreases by half in the winter period. Taking the June and October residual average as 45 \( \mu \text{eq l}^{-1} \) and the concentration of organic material measured at stations #2 and #3 for June, July and October 1976 and 1977 (Dumas et al., 1977, 1980a) as 3 \( \mu \text{g C l}^{-1} \), then our residual alkalinity corresponds to 15 \( \mu \text{eq mg}^{-1} \) of organic carbon. This is well situated between the 20 \( \mu \text{eq mg}^{-1} \) of Schnitzer and Khan (1978) for an 'average fulvic acid' and the 5.5 \( \mu \text{eq mg}^{-1} \) of organic C found by Henriksen and Seip (1980) for lake water in Norway.