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CALCIUM AND MAGNESIUM CONTENTS IN THE RIVER AND SEA WATERS OF TROPICAL AREA *

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ABSTRACT

In order to investigate the following factors, the contents of calcium and magnesium in 171 water samples collected from Rio Unare, Laguna Unare, the Cariaco Trench, the Gulf of Cariaco in Venezuela, and the Barra das Jangadas and Rio Capibaribe in Brazil were analyzed.

(1) The relation of the concentration of calcium and magnesium in the river water to their chorisity factors in sea water near the river mouth.

(2) The chlorosity factors of calcium and magnesium in the extremely high saline water that occurs by evaporation in the dry season in Laguna Unare.

(3) A relation between the seasonal variation of chlorosity and of the chorosity factors of calcium and magnesium.

From the results obtained, it was found that a relation between chlorosity and the concentration of calcium showed a wide difference among the different rivers in the initial stage of mixing of fresh and saline waters, but such a difference was not found in that of magnesium.

In the water having a high chlorosity in the range of 25 - 50 g/L, the concentrations of calcium and magnesium were somewhat lower than those expected from the chlorosity. This may be considered a result of the precipitation of these elements as carbonates or hydroxides under conditions of heating, high pH, excessive evaporation, and biological action.

There was a clear inverse relation between the seasonal variation of chlorosity and of the chlorosity factors of calcium and magnesium in Laguna Unare.

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RESUMEN

Sobre el contenido de calcio y magnesio fueron analizadas 171 muestras colectadas del río y laguna Unare, Fosa y Golfo de Cariaco en Venezuela y de la Barra das Jangadas y río Capibaribe en Brasil, para discutir sobre los siguientes puntos:

1 — El efecto de la concentración del calcio y magnesio en el agua de río sobre el factor clorosidad del agua de mar cercana a la boca de río.

2 — Los factores clorosidad del calcio y el magnesio en el agua extremadamente salina que ocurre por la evaporación durante estación seca en la laguna Unare.

3 — Una relación entre la variación estacional de la clorosidad y los foctores clorosidad del calcio y magnesio.

De los resultados obtenidos se encontró que una relación entre la clorosidad y la concentración de calcio mostró una gran diferencia entre los diversos ríos en estado inicial de la mezcla de agua dulce con agua salada, pero tal diferencia no se encontró en el magnesio.

En el agua de alta clorosidad en el rango de 25 - 50 g/L las concentraciones de calcio y magnesio fueron algo más bajas que aquellas esperadas debido a la clorosidad. Se puede considerar que hay una precipitación de aquellos elementos como carbonatos e hidróxidos bajo condiciones de calor, alto pH, excesiva evaporación y acción biológica.

Hubo una clara relación inversa entre las variaciones estacionales de clorosidad y el factor clorosidad del calcio y magnesio en la laguna de Unare.

INTRODUCTION

It is well known that the chlorosity factors of calcium and magnesium in sea water are almost uniform. Since the concentrations of calcium and magnesium in river water are higher than those in sea water, the change of the chlorosity factors of these elements in the sea water near the mouth of a river is of interest in considering the process of the mixing of sea and river waters.

Yamamoto (1958) found a significant difference in the

chlorosity factor of calcium between high tide and low tide in Urado Bay, with no change in the chlorosity factor of magnesium. In the Baltic Sea and in the Gulfs of Finland and Bothnia adjoining the Baltic, Gripenberg (1937) attempted an analyses of the process of the mixing of sea water and river water from the concentration of calcium and chlorinity.

The present paper deals with the effect of the concentrations of calcium and magnesium in river water on the chlorosity factors of these elements in the sea water near the mouth of a river; and the chorosity factors of calcium and magnesium in the extremely saline water that occurs by evaporation in the dry season in Laguna Unare.

DESCRIPTION OF AREA AND SAMPLES

The present material comprises analyses of 171 samples of fresh water and sea water collected from Rio Unare, Laguna Unare, the Cariaco Trench, the Gulf of Cariaco in Venezuela, and the Barra das Jangadas and Rio Capibaribe in Brazil. (Fig. 1, 2 and Table 1)

Rio Unare and Laguna Unare

The hydrographic conditions of Rio Unare and Laguna Unare will be published in another report (6).

Rio Unare is connected with Laguna Unare through canals, and is the principal source of supply of fresh water to Laguna Unare. In addition, Rio Unare drains into the Cariaco Trench. However, the river mouth is closed during the dry season because of the remarkable fall in the river water and its shallow mouth. Rio Unare has several depth meters in the central part. In the dry season, the water of Laguna Unare flows back into Rio Unare because of the reduction of water supply, thus increasing the salinity of the river water. The salinity of the river water is also significantly increased by evaporation once the mouth has been closed.

Laguna Unare is very shallow, the depth being about 0.6 m at the central part in the dry season, and not reaching 1.4 m

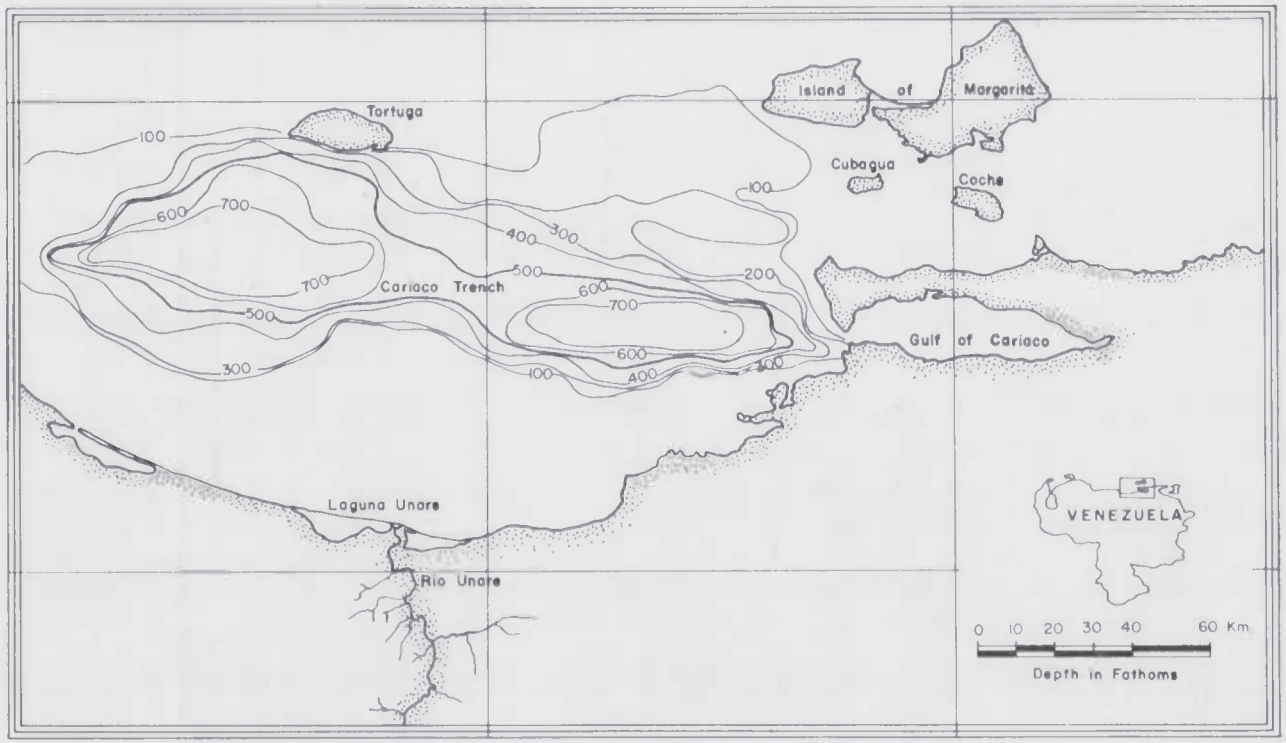

Fig. 1. Map of Rio Unare, Laguna Unare, the Gulf of Cariaco and the Cariaco Trench.

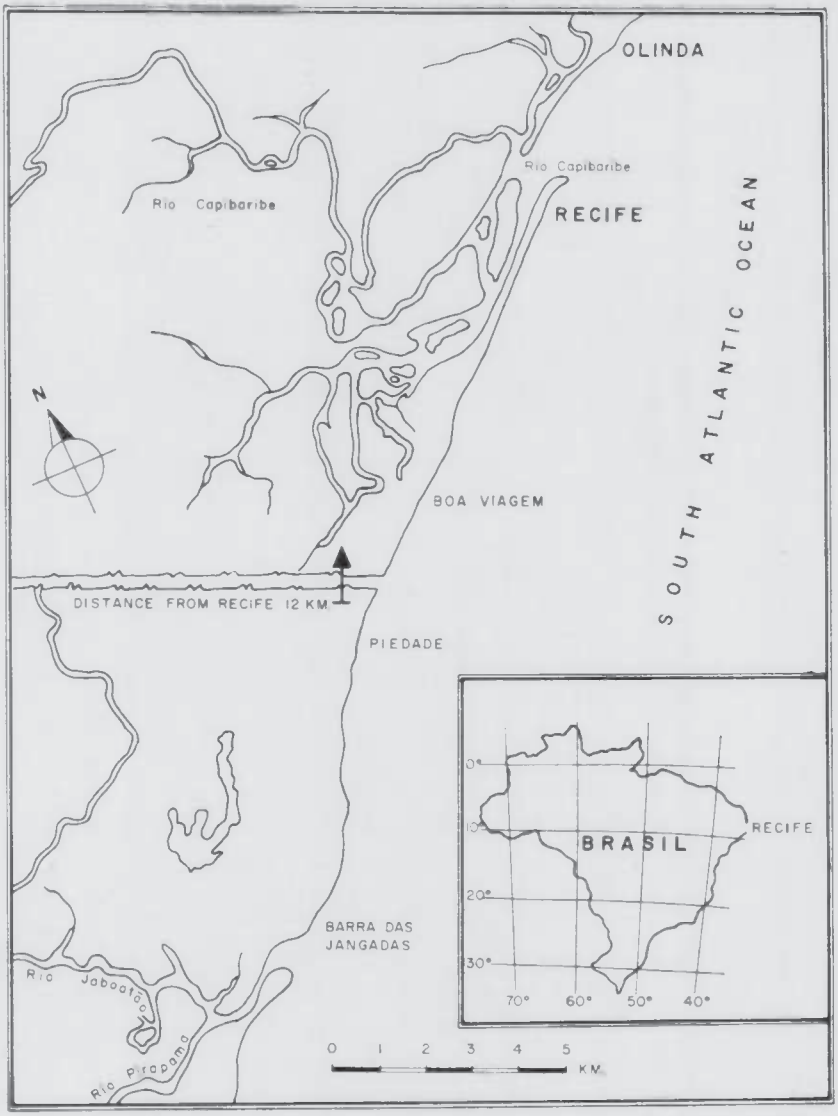

Fig. 2. Map of the Barra das Jangadas and Rio Capibaribe.

Table 1. List of used samples

Date	Number of sample	Location
March 7, 1960	44	Barra das Jangadas (Brazil)
March 10, 1960	16	Three miles off the Recife Coast (Brazil)
March 17, 1960	6	Rio Capibaribe (Brazil)
May 21, 1962-Feb. 23, 1963	36	Río Unare (Venezuela)
May 22, 1962 - Feb. 22, 1963	51	Laguna Unare (Venezuela)
December 7, 1962	12	Cariaco Trench (Venezuela)
December 7, 1962	6	Gulf of Cariaco (Venezuela)

even in the rainy season. Laguna Unare has no direct communication with the open sea, and one of the remarkable characteristics of this Laguna is a great difference of salinity between the dry and rainy seasons: that is, 20‰ in the rainy season and about 80‰ in the dry season. This characteristic is an affect of the supply and short supply of fresh water and of the high evaporation in the both seasons.

Cariaco Trench and Gulf of Cariaco

The hydrographic and chemical conditions in the Cariaco Trench and the Gulf of Cariaco have been reported by some workers (1, 2, 4, 8, 9 and 10).

The Cariaco Trench has an anaerobic characteristic and a maximum depth of about 1,400 m. The Gulf of Cariaco is an embayment having a maximum depth of about 80 m at the central part, and its mouth opens to the Cariaco Trench.

Barra das Jangadas and Rio Capibaribe.

The hydrographic and chemical conditions in the Barra das Jangadas and Rio Capibaribe have also been reported by the author (5).

The Barra das Jangadas covers the distance between the junction of two rivers (Rio Pirapama and Rio Jaboatao) and the sea, a distance of about 2 Km. with an average depth of about 3 - 5 m. With the exception of the rainy season, sea water during a high tide penetrates up to several km from the river mouth, but is completely replaced by fresh water to the river mouth at low tide.

The Rio Capibaribe runs through Recife city and drains into the sea.

Analytical Method

For the determination of calcium and magnesium in the water, the following procedure was used.

Calcium

Two to 50 ml. of a sample were pipetted into the Erlenmeyer flask according to the calcium content of the sample, and an amount of EDTA (Ethylendiamine tetraacetic acid) in excess the equivalent amount of calcium in the sample was added. The pH of this solution was controlled at pH=12 with the 8 N NaOH solution. After the settling of the precipitation of Mg $(OH)_2$, 2.5 ml of 0.01 M $CaCO_3$ solution were added to the above solution in order to complete the separation of the magnesium chelate as the Mg $(OH)_2$ formed by the addition of E D T A, and the titration of the solution was completed with E D T A using Murexide as the indicator.

Magnesium

Using 1 to 25 ml sample, a sum of calcium and magnesium was obtained by the titration with EDTA using EBT (Eriochrome Black T) as the indicator after the pH of the solution was controlled at pH=10 with the buffer solution (ammonium chloride and ammonia). Then, the amount of magnesium was obtained by the subtraction of the amount of calcium from the sum of the both elements.

RESULTS

1. — *Chlorosity factors of calcium and magnesium in the sea water.*

In order to compare the chlorosity factors of calcium and magnesium in the river water, the concentration of these elements in sea water were determined. The results obtained are shown in Table 2 and their chlorosity factors showed approximately uniform value.

2. — *Calcium and magnesium concentrations and their chlorosity factors.*
In water with a chlorosity of less than 1 g/L.

In the initial stage of the mixing of river water and sea water, it will be supposed that the concentrations of calcium and magnesium in the river water will be effective on their respective chlorosity factors in the mixed water. In this ex-

Table 2. Chlorosity factors of calcium and magnesium in the sea water.

Location		Ca/Cl	Mg/Cl
Recife Coast	Max.	0.02247	0.06664
(Brazil)	Min.	0.02197	0.06509
	Mean	0.02217	0.06580
Cariaco Trench	Max.	0.02140	0.06719
(Venezuela)	Min.	0.02100	0.06598
	Mean	0.02115	0.06648
Gulf of Cariaco	Max.	0.02118	0.06694
(Venezuela)	Min.	0.02086	0.06620
	Mean	0.02105	0.06651

pectation, the calcium and magnesium contents were plotted as ordinates against the chlorosity as abscissae (Fig. 3, 4). Although the content of magnesium and chlorosity in the water of three rivers formed a straight line, but there was no fixed relationship between the three rivers for calcium content and chlorosity. However, the points formed a straight line for each river (with the exception of one value obtained in Rio Unare). Thus, it can be considered that while the original waters of the three rivers have different concentrations of calcium, then have almost the same concentration of magnesium. It is of interest, too, to compare the calcium values at the points of intersection with the lines for the three rivers at Cl=O g/L. These values can be considered as the calcium content of the original river water, with Rio Unare having the lowest calcium content, the Barra das Jangadas and Rio Capibaribe the highest. The inclination of these lines (that is, the increasing rate of calcium against the increase chlorosity), decreased in the order of Rio Unare, Rio Capibaribe, and Barra das Jangadas. This may be considered the result of the difference of calcium content (lime) in the primitive rock in and around these rivers.

The chlorosity factors of calcium and magnesium decreased rapidly with the decrease of chlorosity, and showed an almost constant value in a chlorosity of more than 0.4 g/L.

In water with a chlorosity of more than 1 g/L

Fig. 5 shows the relationship between the chlorosity and the calcium and magnesium concentrations in water having a chlorosity of more than 1 g/L in samples, which were collected from the three rivers, Laguna Unare and the open sea. It was found that the points formed straight lines up to a chlorosity of about 25 g/L. In the higher chlorosity of more than about 25 g/L, the points were plotted somewhat below the extension of the lines described above. That is, the actual concentrations of calcium and magnesium were somewhat lower than the expected concentrations. These higher chlorosity waters were collected from Laguna Unare in the dry season.

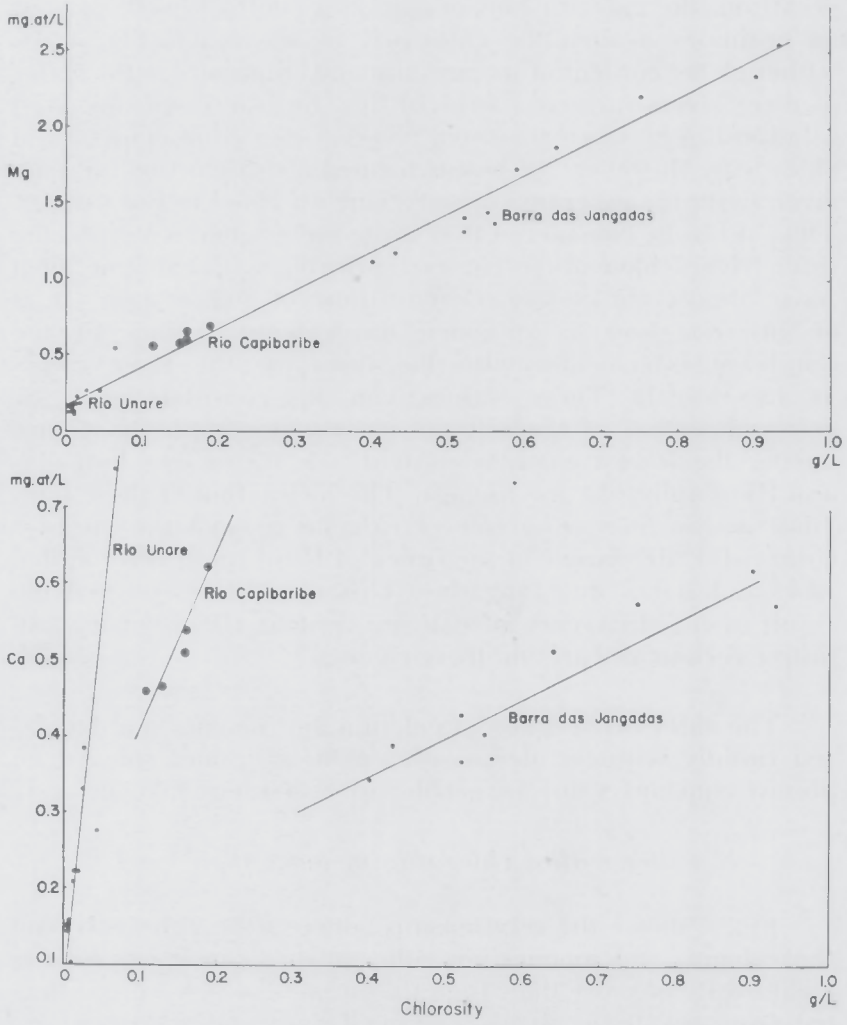

Fig. 3. Relation between calcium and magnesium contents and chlorosity in the river water.

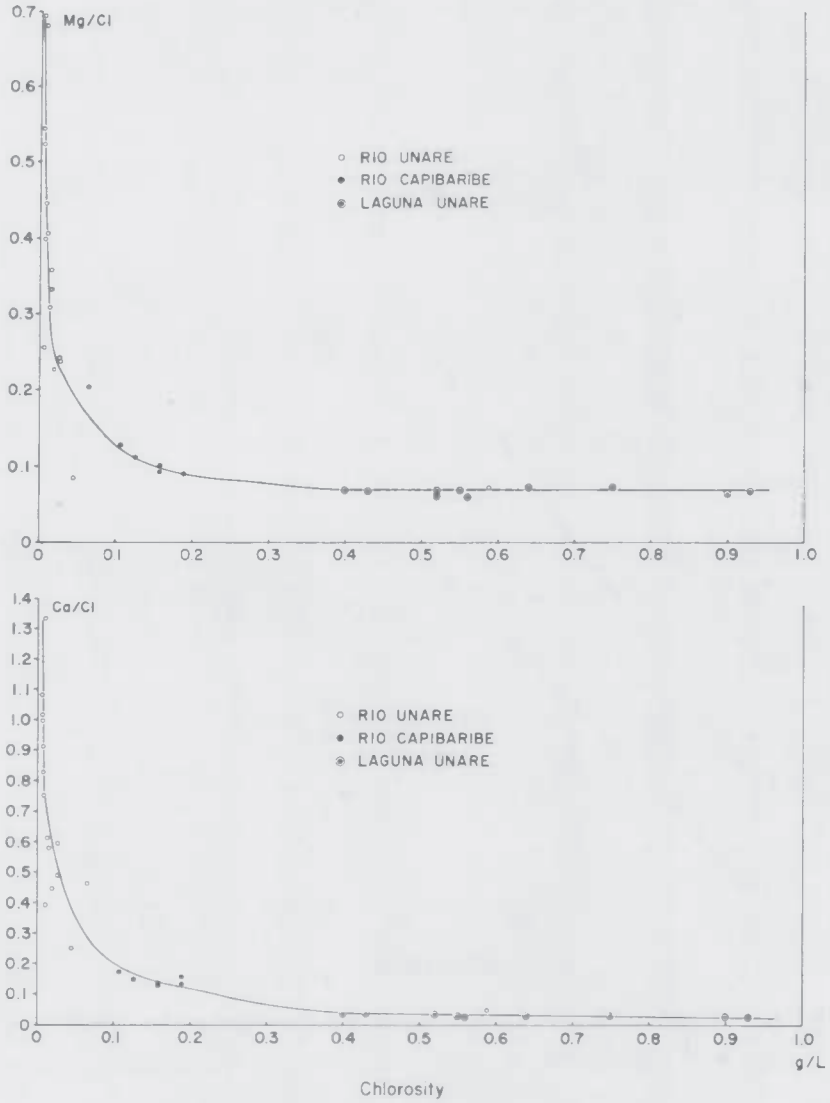

Fig. 4. Relation between chlorosity factors of calcium and magnesium and chlorosity in the river water.

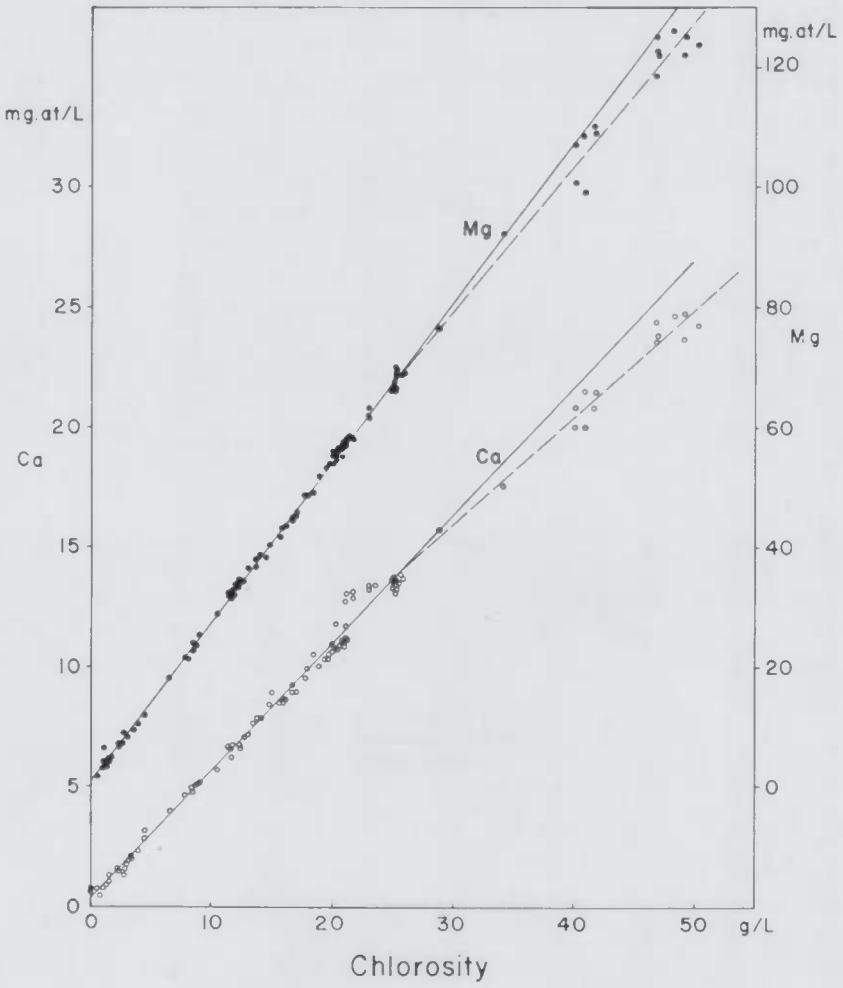

Fig. 5. Relation between calcium and magnesium contents and chlorosity.

As Smith (1940) has found in his study on the precipitation of $CaCO_3$ over the Great Bahama Bank, a difference between the concentrations of calcium and magnesium and those expected from the chlorosity may be attributed to the precipitation of these elements as carbonates or hydroxides under conditions of heating, high pH and excessive evaporation.

The relationship between the chlorosity factors of calcium and magnesium and the chlorosity was shown in Fig. 6 and 7. The points of the chlorosity factors of calcium decreased rapidly to a chlorosity of 10 g/L and then decreased more slowly with the increase of chlorosity. The chlorosity factors of magnesium decreased gradually with the increase of chlorosity but these points were more widely dispersed. It was noted that the chlorosity factors of calcium in the water of Rio Unare showed generally high values. Furthermore, in the range of a chlorosity of less than 10 g/L, the points for Rio Unare and the Barra das Jangadas, clearly formed separate branches even though the chlorosity factors of magnesium did not show a clear difference between them. This may be related to the above-mentioned difference of inclination toward the x-axis between Rio Unare and the Barra das Jangadas, (Fig. 6 and 7).

Seasonal Variation of the Chlorosity Factors of Calcium and Magnesium.

As mentioned above, in Laguna Unare the chlorosity showed a remarkably high seasonal variation. The relation between the seasonal variation of chlorosity and of the chlorosity factors of calcium and magnesium was shown in Fig. 8. The values in Fig. 8 are shown as average values. There is a close inverse relationship between the chlorosity and the chlorosity factors of these elements, and it is notable that the chlorosity factors of calcium and magnesium decrease considerably in May and June, when there is a extremely high chlorosity. Since a high production of phytoplankton and extremely high oxygen concentration were observed in these months, the low chlorosity factors of these elements might be caused not only by chemical precipitation but also by a biological precipitation of these elements.

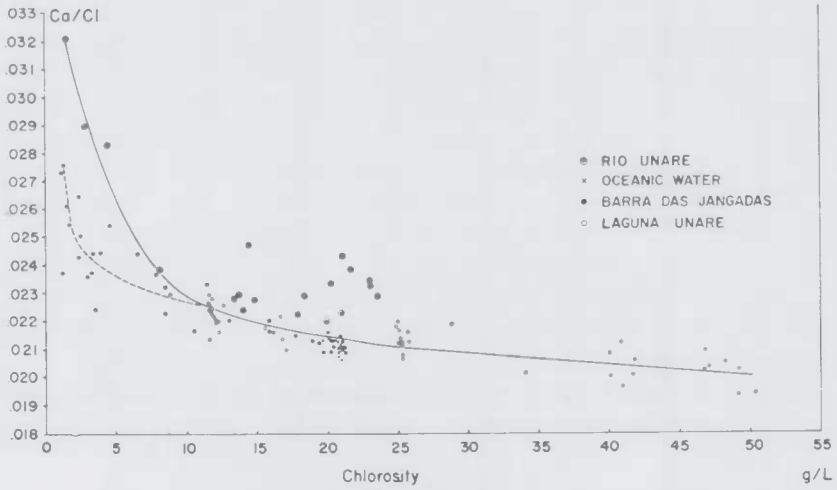

Fig. 6. Relation between chlorosity factor of calcium and chlorosity.

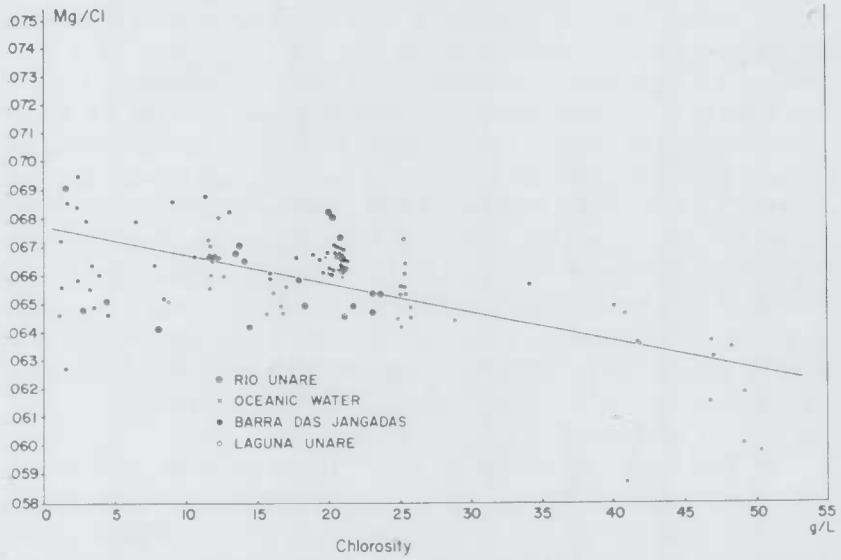

Fig. 7. Relation between chlorosity factor of magnesium and chlorosity.

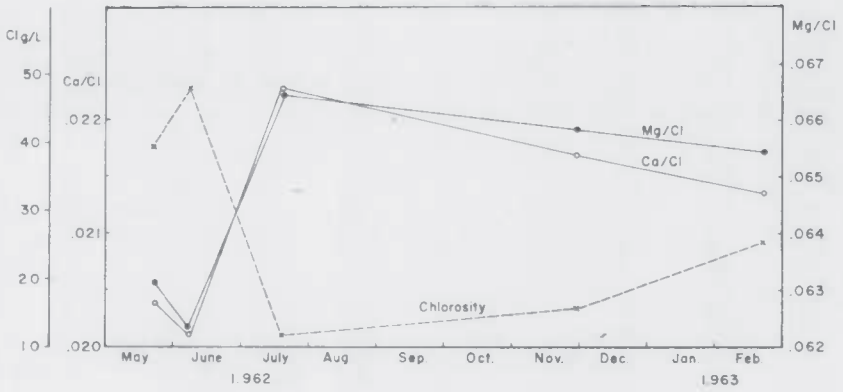

Fig. 8. Seasonal variation of chlorosity factors of calcium and megnesium.

CONCLUSIONS

In the initial stage of the mixing of fresh water with saline water, the following differences in the relation between chlorosity and the concentrations of calcium and magnesium were found: (1) Although the points of calcium concentration plotted against chlorosity in the water of each river formed a straight line for each river, the inclination of lines toward the x - axis showed a wide difference among the different rivers; (2) On the other hand, almost all of the points of magnesium concentrations plotted in the same way lay on a straight line independent of the different rivers; (3) Furthermore, the chlrosity factors of calcium in the water having chlorosity in the range of about 1 - 10 g/L, showed a clear difference between Rio Unare and the Barra das Jangadas, but such a difference was not found in the chlorosity factors of magnesium. This may be attributed to the difference in calcium content (lime) of the primitive rock in and around the different rivers.

In the hyperchlorosity water of more than 25 g/L collected from Laguna Unare in the dry season, it was noted that the concentrations of calcium and of magnesium were somewhat lower than the concentrations expected from the chlorosity. This might be due to the precipitation of these

elements as carbonates or hydroxides under conditions of heating, high pH, excessive evaporation, and biological action. Finally a clearly inverse relationship between the seasonal variation of chlorosity and the chlorosity factors of calcium and magnesium was observed in Laguna Unare.

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