GEOCHEMICAL STUDIES ON THE MANGROVE REGION OF CANANÉIA, BRAZIL.
I. TIDAL VARIATIONS OF WATER PROPERTIES

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SYNOPSIS

This paper refers to the contribution of the small "rivers" called "marigots" to the nutrients biochemical cycle in the mangrove region of Cananéia, State of São Paulo, Brazil.

INTRODUCTION

The mangrove region of Cananéia (Lat. 25°01',0 S — Long. 47°55',5 W) is drained by small "rivers" called "marigots" in French (BESNARD, 1950), which contain chiefly marine tidal waters. They flow into a lagoon sheltered from the sea by Comprida Island (Fig. 1). The water, which is dark brown probably due to dissolved tannic acid from the mangrove bark, characteristic of the "marigot", has some peculiar properties (MACHADO, 1950) from the geochemical point of view.

The tidal oscillation of the lagoon water brings about similar oscillations in the "marigot" with the result that the lagoon water moves up and down the "marigots", and is mixed with "marigot" water. Due to the mixture of sea water with water drained from land the geochemical properties of the lagoon water are more or less changed secondarily.

METHODS

The variation of the properties of the "marigot" water with the tide was observed at the mouth of river Nóbrega (Fig. 1; Fig. 2), one of the "marigots" in the lagoon region, where depth is about 2 meters. Seven observations were made at intervals of two hours, from 6:00 to 18:00 on the 18th January, 1958. During each observation period water samples were collected from three or four different depths with a Pettersen-Nansen insulated water bottle. Immediately after sampling, measurements of temperature and pH as well as fixation of dissolved oxygen were carried out on board. On the following day, the dissolved oxygen was titrated and colorimetric determinations of nutrients were carried out. These include phosphate, nitrate, nitrite and ammonia. Because of the abundance of reduced materials in the water these were also measured iodometrically to check the deviation of the titrated value of dissolved oxygen by WINKLER'S method. Determinations of salinity and calcium were carried out later at the Oceanographic Institute in São Paulo.

RESULTS

The results of these observations are summarized in Table I.

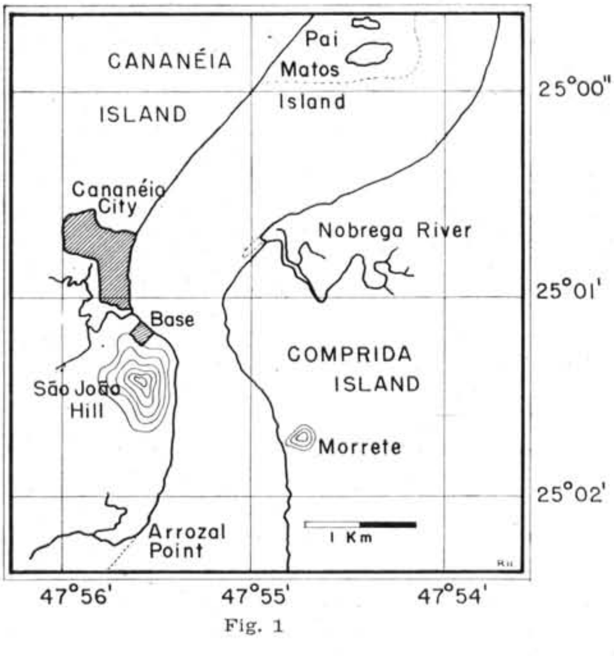

Fig. 1

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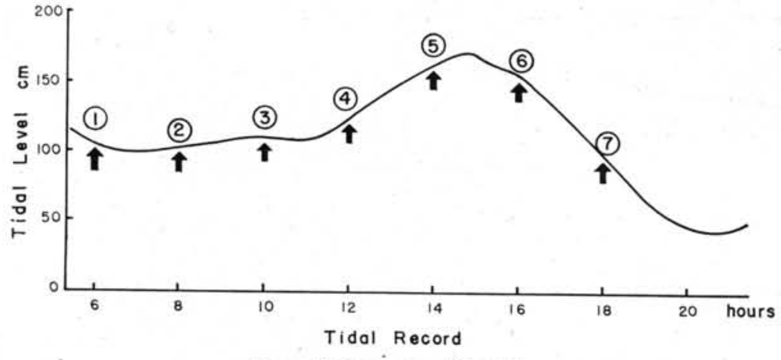
TABLE I

Sample Nº	Time (18/1/58)	Air Temp. (ºC)	Depth Obs. (m)	Water Temp. (ºC)	Chlorin-ity (°/₀₀)	Salinity (°/₀₀)	O_2 obs. (ml/l)	Dissolved Oxygen		pH	P_2O_5-P	NO_3-N	NO_2-N	NH_4-N	Reduced Matter (O_2 consumed — ml/l)
								O_2 sat. (ml/l)	Sat. Deg. (%)		µg-atoms/l				
A-1-1	06:00 — 06:30	23.8	0	26.1	10.74	19.425	2.78	5.32	52.2	7.05	< 0.1	—	< 0.1	2	—
1-2			1	26.0	10.96	19.815	2.85	5.31	53.7	7.2	< 0.1	—	< 0.1	4	—
1-3			1.5	26.1	11.40	20.61	2.94	5.29	55.6	7.4	< 0.1	—	< 0.1	6	—
A-2-1	08:00 — 08:15	25.8	0	26.6	9.98	18.04	2.27	5.32	42.7	7.1	< 0.1	3.2	< 0.1	5	—
2-2			1	26.1	12.065	21.80	3.52	5.20	67.7	7.85	< 0.1	8.2	< 0.1	1	—
2-3			2	26.0	(14.075)	(25.43)	3.81	(5.14)	(74.2)	7.85	< 0.1	3.6	< 0.1	1	—
A-3-1	10:00 — 10:15	27.4	0	25.8	9.39	16.98	2.28	5.40	42.2	7.1	< 0.1	—	< 0.1	6	—
3-2			1	26.9	12.35	22.32	4.21	5.14	81.9	7.85	< 0.1	—	< 0.1	0	—
3-4			2	27.1	11.87	21.46	3.76	5.17	72.7	7.85	< 0.1	—	< 0.1	0	—
A-4-1	12:00 — 12:20	29.6	0	28.8	9.99	18.06	3.14	5.13	61.2	7.1	< 0.1	—	< 0.1	7	0.75
4-2			1	27.8	12.71	22.965	4.24	5.09	83.3	8.1	< 0.1	—	< 0.1	1	0.437
4-3			2	27.7	13.035	23.56	4.87	5.07	96.1	8.0	< 0.1	—	< 0.1	1	0.269
A-5-1	14:00 — 14:30	28.5	0	28.3	12.315	22.26	4.65	5.03	92.4	8.0	< 0.1	1.4	< 0.1	0	0.213
5-2			1	28.1	13.14	23.755	4.73	5.01	94.4	8.1	< 0.1	4.0	< 0.1	0	0.224
5-3			2	28.2	13.205	23.86	4.66	5.01	93.0	8.1	< 0.1	3.3	< 0.1	0	0.224
5-4			2.5	28.3	13.19	23.84	4.66	4.97	93.8	8.1	< 0.1	3.7	< 0.1	0	0.251
A-6-1	16:00 — 16:15	28.4	0	29.6	13.27	23.98	4.52	4.88	92.6	7.9	< 0.1	—	< 0.1	0.2	0.230
6-2			1	28.4	13.12	24.07	4.70	4.97	94.6	8.1	< 0.1	—	< 0.1	0.4	0.168
6-3			2	28.5	13.055	23.595	4.58	4.98	92.0	8.1	< 0.1	—	< 0.1	0.2	0.241
A-7-1	18:00 — 18:15	26.5	0	28.9	11.99	21.665	3.74	4.99	74.9	7.6	< 0.1	—	< 0.1	2	0.604
7-2			1	28.6	12.705	22.96	3.61	5.00	72.2	7.7	< 0.1	—	< 0.1	2	0.624
7-3			1.5	28.6	12.025	21.735	3.52	4.98	70.7	7.4	< 0.1	—	< 0.1	3	0.655

1) Water temperature — (Fig. 3)

As the "marigot" is relatively shallow (2 m deep or less) the water temperature varies greatly with the change of the air temperature. Accordingly the change of the water temperature with the tidal fluctuation is as remarkable as that of the other chemical factors. There was a slight lowering of the temperature in the surface layer at high water (14:00), probably due to the inflowing sea water, moving towards the surface from the subsurface layer, as will be seen when dealing with the chemical properties of the water.



Tidal Record
Base at Cananéia 18-1-1958

Fig. 2

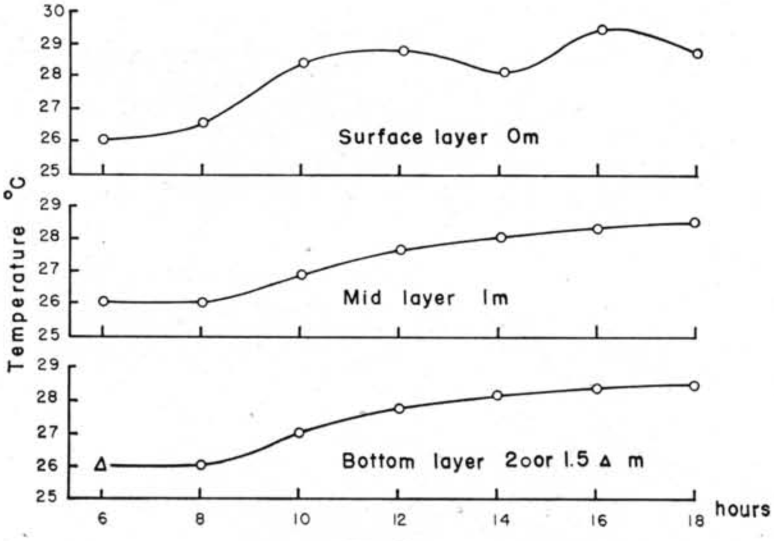


Fig. 3

2) Salinity — (Figs. 4 and 5)

The salinity of the surface water (Fig. 5) changes almost completely according to the tidal fluctuation, but the maximum salinity occurs after the high water time (cf. Fig. 2).

3) Dissolved oxygen — (Figs. 6 and 7)

The tidal variation of dissolved oxygen in the water, in particular of the surface water, showed a good parallelism to the tidal fluctuation recorded on the tidal gauge of the marine station (see Fig. 1). The water flooding through the Barra de Cananéia contained 4.8 ml/l of oxygen, and the "marigot" water only had 2.3 ml/l of dissolved oxygen. The remarkable low quantity of oxygen in the "marigot" water is caused by a characteristic state of reduction in the upper reaches of the "river" and indicates a correlation with the quantity of reduced matter in the water.

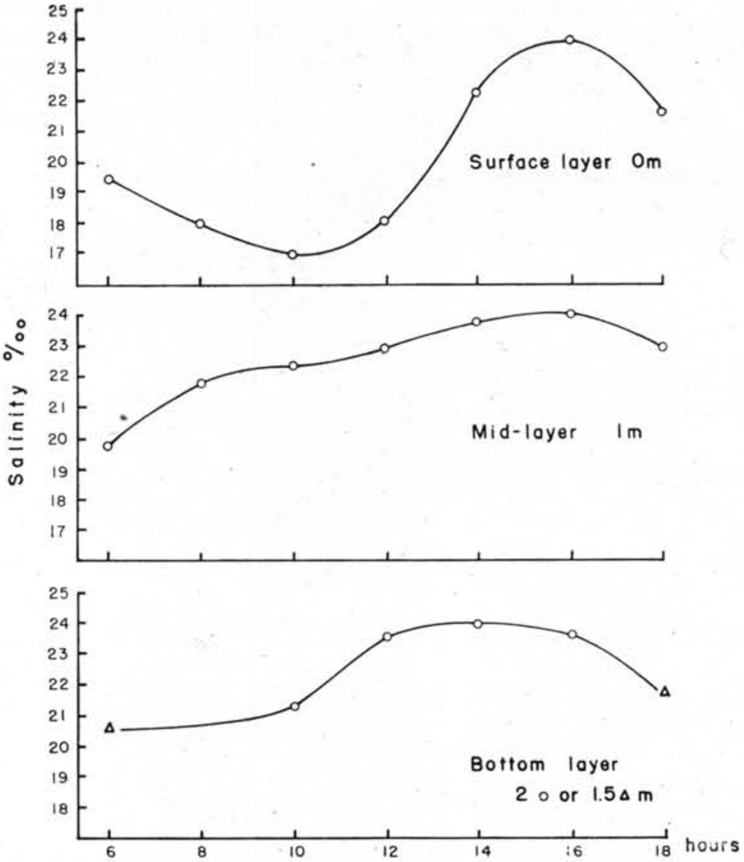


Fig. 4

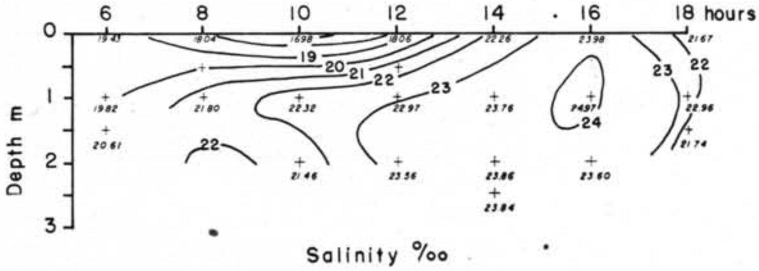


Fig. 5

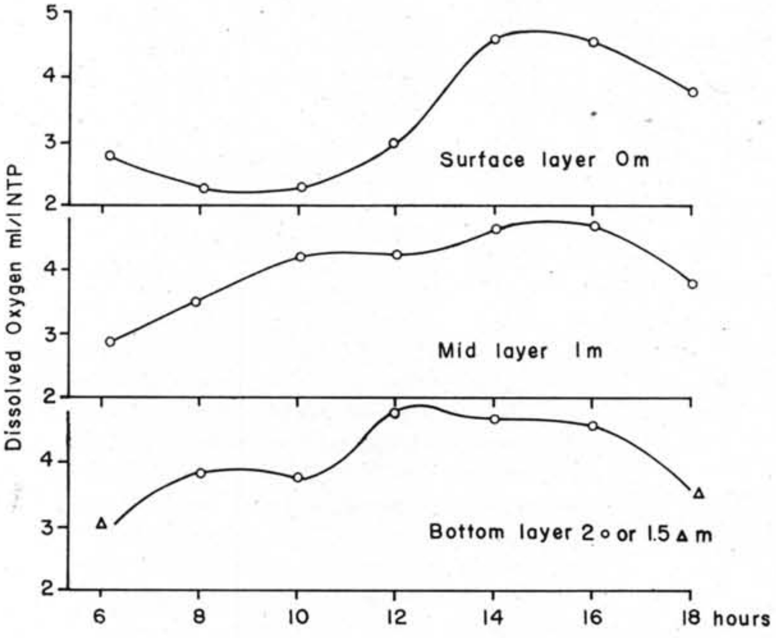
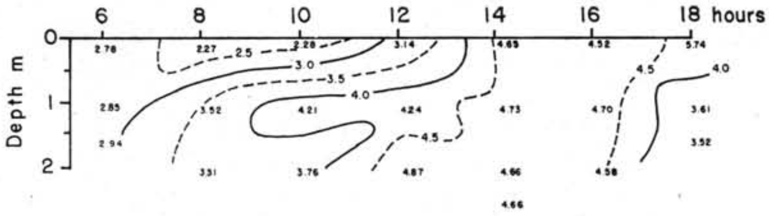


Fig. 6



Dissolved Oxigen ml/l NTP
18-1-1958

Fig. 7

4) Hydrogen-ion concentration — (Figs. 8 and 9)

At flood tide, the outer sea water, with pH 8.4 penetrates into the subsurface layer at the outlet of the "marigot". The pH of the surface water keeps nearly constant, pH 7.2 (Fig. 9-1), until the penetrating water pushes up onto the surface layer and blocks the outflow of the water of the "marigot", which has low salinity and low pH. There is a distinct discontinuity layer (Fig. 9) with pH ranging from 7.5 to 8.0 at the subsurface layer at about 50-75 cm in depth during the flood tide.

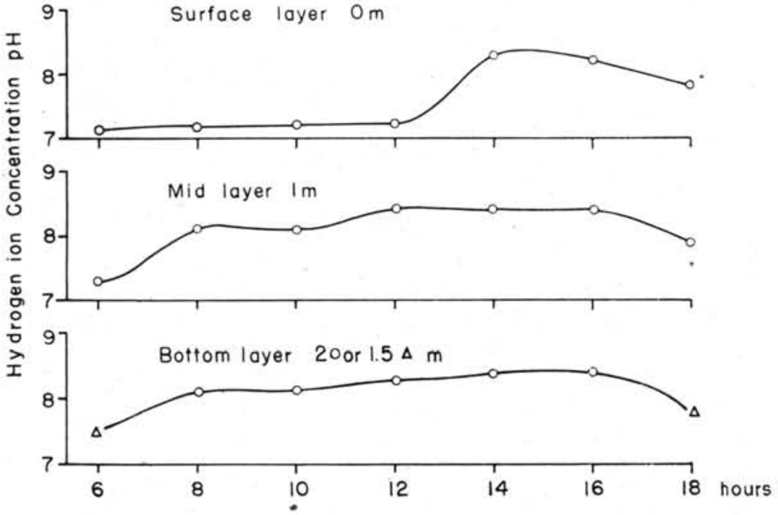
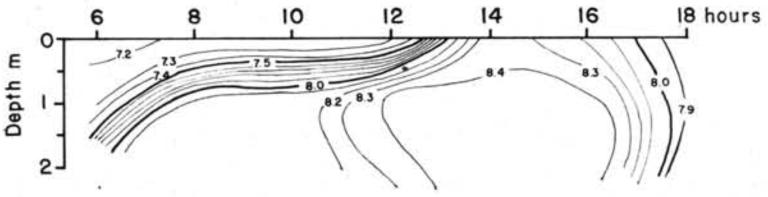


Fig. 8



Hydrogen ion Concentration pH
18-1-1958
Fig. 9

5) Nutrients — (Figs. 10 and 11)

The quantities of nutrients, i.e. phosphate, nitrate, nitrite and ammonia, of the samples were determined colorimetrically with a Dubosque colorimeter. Unfortunately, this colorimeter was not as reliable as an electric colorimeter, but it seemed enough to observe the relative variation of the nutrients with the tide in the present case.

The colorimetric determination by means of the Dubosque colorimeter makes the determination fairly difficult because of the extreme weakness of the color developed as well as by the intense turbidity of the water sample. Since the developed colors, in the present case from the determination of phosphate and nitrite, were respectively too weak to determine their quantities, both could be probably estimated as below 0.1 μg-atoms/l. Since the determination of nitrate in the water was only obtained from two series of water samples collected respectively at high and low water, it was hardly possible to observe the variation of its quantity in the water with tidal oscillation. An approximate amount of nitrate in the water would be about 3 μg-atoms-N/l.

The tidal variation of the quantity of ammonia-N as illustrated in Figure 11, was striking when examined in relation to the other properties of the water. With the rise of the flood tide, the bottom water which was low-salinity and contains ammonia as much as 6 μg-atoms-N/l or more, rises and spreads over a characteristic discontinuity layer between the two differents water masses, namely, the interior water of the "marigot" and the saline sea water. This maximum layer of ammonia spreads over the surface layer before the period of high water.

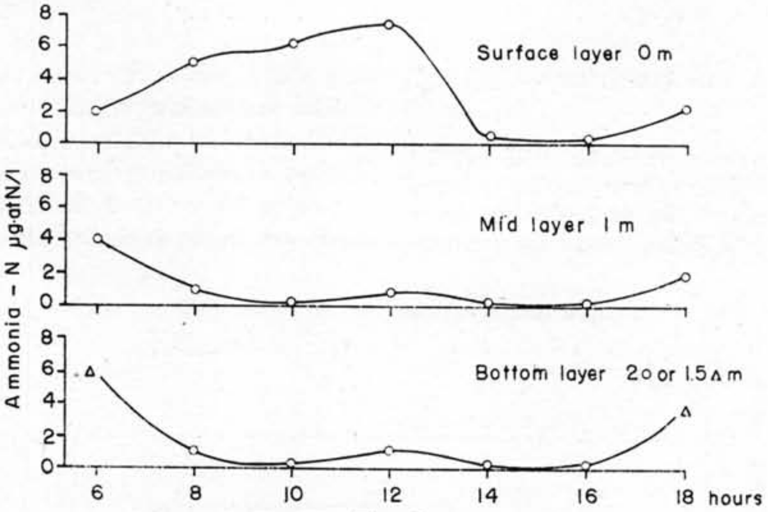
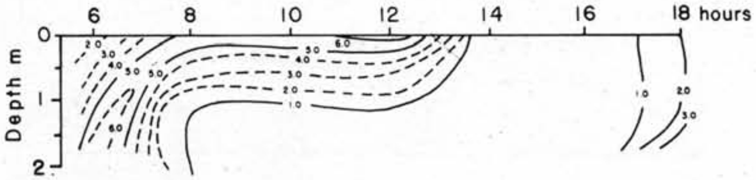


Fig. 10



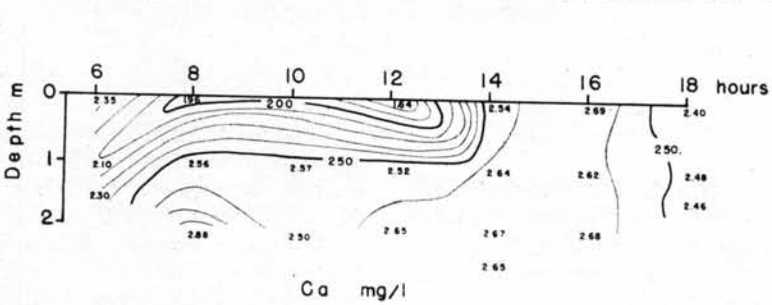
Ammonia-N μg at N/l

18-1-1958

Fig. 11

6) CALCIUM — (Fig. 12)

The amount of calcium in the water was determined by means of chelatometric titration with EDTA reagent (sodium ethylenediamine-tetraacetate) (KATO, 1966a). Since the calcium content in brackish water depends principally upon the degree of mixing of the sea water and the fresh-water, the calcium content in the "marigot" water fluctuated with the tidal movement of the lagoon water, as illustrated in Figure 12, and showed features similar to the salinity variation (of Fig. 5).



Ca mg/l

18-1-1958

Fig. 12

7) Reduced matter — (Figs. 13 and 14)

The amount of reduced materials in contaminated water generally influences the titration value of dissolved oxygen as determined with thiosulfate solution in the Winkler method. Consequently, a series of chemical determinations of reduced materials in the "marigot" water was carried out to check the analytical deviation of the oxygen value caused by reduced material. This is one of the remarkable characteristics of the "marigot" water, as will be described in other papers.

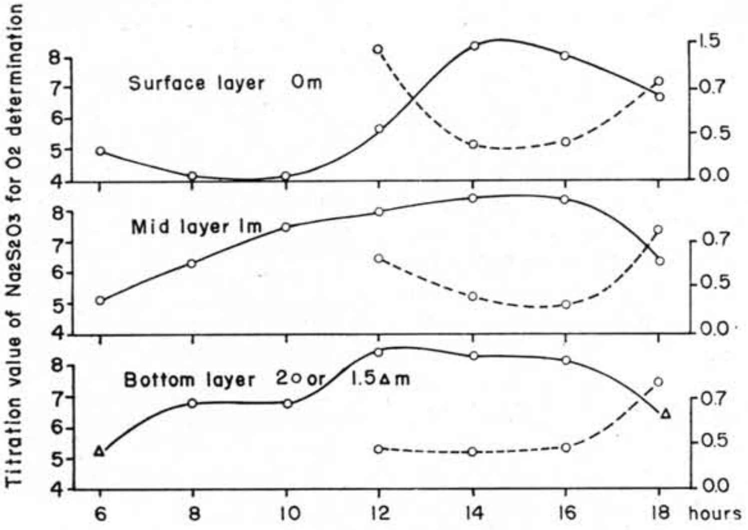


Fig. 13

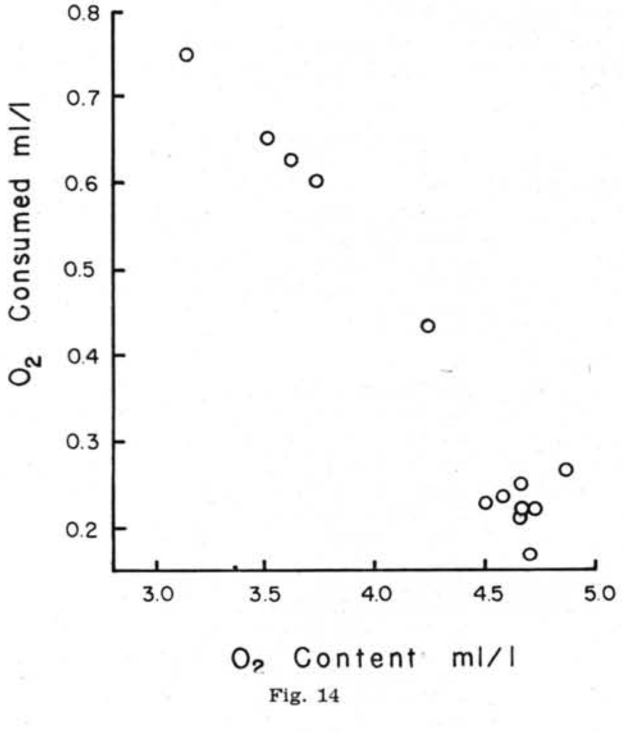


Fig. 14

The quantity of reduced matter in the water was determined as follows:

Five millimeters of N/100 iodine solution were added to the water sample in a 250 ml brown oxygen bottle immediately after collection. The iodine consumed by reduced materials in the sample was determined with N/100 sodium thiosulfate after letting the sample stand for one hour.

The tidal variation of the content of reduced matter in the water is shown in Figure 13 together with the variation of dissolved oxygen content. An interesting linear relation was observed, as illustrated in Figure 14, between the decrease of oxygen content and amount of reduced material in the sample. For example, the water which had 3 ml of oxygen per liter contained an abundant quantity of reduced materials corresponding to 0.75 ml/l of oxygen. Consequently, the oxygen value of contaminated water like the "marigot" water determined iodometrically by Winkler's method requires correction for the content of reducing material. The values of dissolved oxygen given in Table 1 are uncorrected however.

CONCLUSION

Characteristic dark brown-colored water occurs in peculiar "rivers" of the watersheds of mangrove areas. Chemical properties of the water are very characteristic because of the geochemical influence of the peculiar environment occurring in the watershed. It proved interesting to observe the tidal variation of the water properties, to check the geochemical influences of the "marigot" water upon the lagoon water, and to learn about the hydrographic flooding of the "marigot" water in connection with the tidal fluctuation of the lagoon water.

At flood tide, the outer oceanic water penetrates at the bottom layer of the entrance of the "marigot" and lifts the upper layer of the "marigot" water while mixing vertically with it. During the process, a chemically discontinuous layer is formed over the intermediate layer of 0.5-1.0 meter in depth, where two characteristic masses of water, of the "marigot" and of the lagoon come into contact with gradual vertical mixing. It should be also noted that a zone of high ammonia concentration covers the upper part of the discontinuity layer as mentioned above. A considerable amount of organic nitrogenous materials of the "marigot" probably accumulates in the discontinuous layer. There they are actively decomposed by bacteria liberating ammonia.

On flood tide water with higher salinity penetrates into the subsurface layer and appears at the surface one hour before high water blocking the outflow at the mouth of the "marigot" for two hours.

On ebb tide the blocked "marigot" water begins flowing out, recovering its lost characteristics, i.e, a high reduction state, lower pH value, and a dense suspension of organic matter.

A strong solar radiation in summer will raise the temperature of the "marigot" water and accelerate bacterial decomposition of organic material, dissolved, suspended or deposited in the "marigot". Most of the ammonia liberated owing to active decomposition of organic materials will escape into the air on account of the remarkably high temperature of the water as well as of a high reduction state, which occurs in the water and in the sediment of the "marigot". A part of the liberated ammonia will of course be oxidized to nitrite and nitrate by dissolved oxygen, while an increased growth of phytoplankton will cause an active consumption of the oxidized nitrogen compounds as well as of the phosphates. The nitrate content, 3-8 μg-atoms-N/l, observed is rather large compared with its absence in the outer lagoon water (Kato, 1966b), as observed in February of the same year. Thus the outflow of these "marigots" have a very important role in the biochemical cycle of nutrients occurring in the whole lagoon region.

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RESUMO

A região de mangue de Cananéia (Lat. 25°01',0S — Long. 47°55',5W) é drenada por pequenos "rios" ("marigots") e contém, principalmente, águas provenientes das oscilações das marés.

Na área de junção, as águas do mangue são de côr acastanhada; suas propriedades são características devido à influência geoquímica na área de junção.

A comprovação da influência das águas dos "marigots" sôbre as da lagoa depende da observação acêrca da variação das propriedades das águas com a oscilação da maré; a essa observação associa-se aquela referente ao processo hidrográfico de vazão dos "marigots" em relação com a flutuação da maré na lagoa.

Durante a enchente, a água oceânica penetra na entrada do "marigot", pelo fundo, e desloca as águas superficiais dêste, misturando-se com elas verticalmente. Durante o processo, forma-se uma camada quìmicamente descontínua sôbre a camada intermediária (0,5 a 1,0 m de altura), com gradual mistura vertical de duas massas características de águas.

Sôbre a camada superior descontínua surge uma zona de alta concentração de amônia, provàvelmente devido à grande quantidade de matéria orgânica nitrogenada, que se acumula na camada descontínua e sofre ativa decomposição bacteriana.

Na enchente, a água salgada aparece na superfície uma hora antes das águas altas bloquearem por duas horas a bôca dos "marigots".

Na vazante, as águas bloqueadas do "marigot" começam a fluir, recobrando as características perdidas, isto é, alto estado de redução, pH baixo, e densa suspensão de matéria orgânica.

Forte radiação solar, durante o verão, aumenta a temperatura do "marigot", acelerando a decomposição bacteriana da matéria orgânica; amônia é produzida e parte dela é liberada para o ar devido à alta temperatura e ao alto estado de redução, tanto da água como do sedimento do "marigot"; parte da amônia é oxidada pelo oxigênio dissolvido, transformando-se em nitrito e nitrato.

O aumento constante do fitoplâncton provoca ativo consumo de compostos oxidados de nitrogênio e dos fosfatos.

O conteúdo de nitrato, 3-8 μg-atoms-N/l, é mais alto do que nas águas externas da lagoa, como foi observado em fevereiro.

É grande a influência dos "marigots" no ciclo bioquímico dos nutrientes na região lagunar em estudo.

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