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CHEMICAL AND PHYSICAL OBSERVATIONS IN GOLFO DULCE, AN ANOXIC BASIN ON THE PACIFIC COAST OF COSTA RICA[1]

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ABSTRACT

Golfo Dulce is an embayment containing small concentrations of hydrogen sulfide near the bottom due to sulfate reduction. The processes of denitrification, nitrate reduction, and organic decomposition are also evident. Hydrographic data taken 8 days apart indicated an influx of ocean water into the basin. It appears from past observations in the eastern tropical Pacific that the basin erratically receives ocean water during winter and spring.

INTRODUCTION

Golfo Dulce (Fig. 1) is an embayment on the Pacific coast of Costa Rica lying between 8° 27′ and 8° 45′ N lat. The bathymetry of the gulf (H.O. Chart 1037) suggests that the deeper inside water might be stagnant, so chemical, physical, and geological observations were made in the system on 1–2 and 10 March 1969 during cruise 35 of the RV *Thomas G. Thompson.*

Our echo soundings on 1 March generally agreed with those on H.O. Chart 1037. The gulf is about 20 km long and has maximum depths of a little more than 200 m; the effective sill depth is around 60 m. In these respects, it is similar to Saanich Inlet on Vancouver Island, British Columbia, a sometimes anoxic system that has been studied by Herlinveaux (1962) and by Richards (1965) and colleagues.

Three stations inside the gulf, one on the sill, and one just outside the sill, were occupied on each of the two visits. The water column was sampled at close vertical intervals (Table 1); and salinity, temperature, dissolved oxygen, ammonia, nitrate, nitrite, phosphate, silicate, and hydrogen sulfide were measured. Alkalinity and *p*H were also observed, but they displayed no unusual distributions. The phosphate, silicate, nitrate, nitrite, and ammonia determinations were carried out automatically on a Technicon AutoAnalyzer. Short gravity cores were obtained at the three stations and at two other positions inside the sill.

ANALYTICAL METHODS

Salinity was determined from conductivity measurements.

Temperature was measured, using standard deep-sea reversing thermometers.

Dissolved oxygen was determined by a modified Winkler technique, using reagent concentrations recommended by Carpenter (1966) and by the colorimetric procedure of Broenkow and Cline (1969).

Inorganic phosphate was determined by a stannous chloride procedure modified from Barnes (1959).

Nitrite ions were estimated according to the procedure of Bendschneider and Robinson (1952).

Nitrate ions were determined by the cadmium column reduction method of Wood et al. (1967).

Ammonia was determined by the rubazoic acid procedure of Procházková (1964) as modified for use in seawater by Johnson (1966).

Reactive silicate was estimated by the method of Mullin and Riley (1955) using sodium silico-fluoride as a primary standard.

Using a Corning model 12 expanded scale *p*H meter and Corning electrodes,

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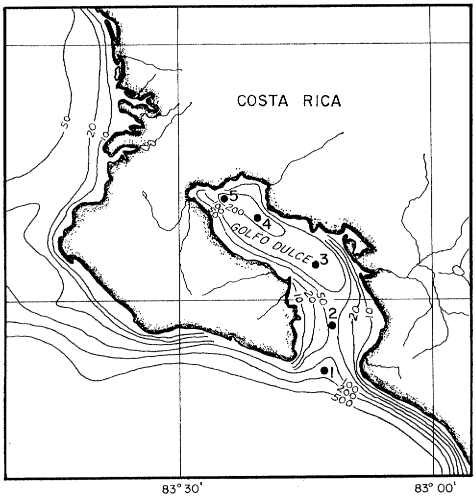

FIG. 1. Golfo Dulce, Costa Rica. Approximate bathymetry and station locations. From map prepared by el Instituto Geografico de Costa Rica, Ministerio de Transportes, Edicion Provisional, 1966.

*p*H was determined after the sample was brought to 10C in a closed, thermostated cell. Beckman *p*H 7 buffer was used as the standard. Reported *p*H values were corrected to *in situ* temperatures and pressures (Strickland and Parsons 1965).

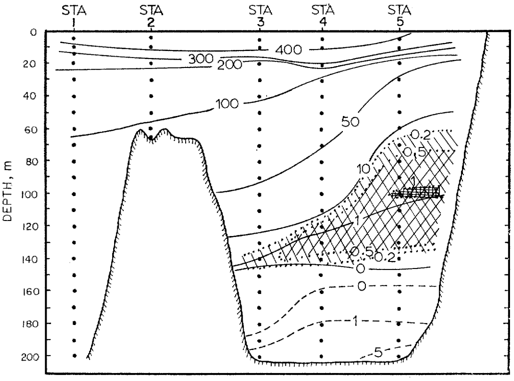

FIG. 2. Golfo Dulce, 10 March 1969. O_2, μg-atom/liter (solid isopleths); H_2S, μg-atom/liter, with observed values shown using the sampling depth dot as the decimal point (dashed isopleths) and NO_2^--N, μg-atom/liter (dotted isopleths). NO_2^--N values between 0.2 and 0.5 μg-atom/liter shown by the least dense shading, 0.5 to 1.0 μg-atom/liter by the denser, and one value > 1.0 μg-atom/liter is indicated by the densest shading.

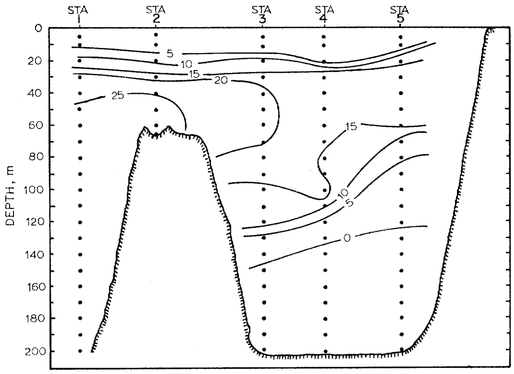

FIG. 3. Distribution of NO_3^--N, μg-atom/liter, in Golfo Dulce, 10 March 1969.

Alkalinity was determined by the *p*H method of Anderson and Robinson (1946) in a thermostated cell (25C). Liberated CO_2 was purged from solution with tank nitrogen.

Total carbon dioxide was estimated by gas chromatography according to the method of Swinnerton et al. (1962), using a Fisher gas partitioner and aqueous gas stripper. Samples were taken from the water samplers with a 5-ml Hamilton gas-tight syringe.

Hydrogen sulfide was determined colorimetrically by the method of Cline (1969). Sodium sulfide ($Na_2S \cdot 9H_2O$) was used as the standard.

OBSERVATIONS

On both occasions, small concentrations of hydrogen sulfide were observed in the bottom waters of the inner gulf. The innermost station was the most oxygen deficient and had the highest concentrations of sulfide (Fig. 2). The inner gulf was characterized by the rapid vertical decrease in dissolved oxygen to less than 10% of saturation at 30- to 40-m depths. Denitrification and nitrate reduction were apparent from the decrease in and disappearance of nitrate with increasing depth (Fig. 3) and the appearance of a secondary nitrite maximum at 100 m (Fig. 2).

Both reactive silicates and phosphates increased markedly with depth inside the gulf (Fig. 4, Table 1). Bottom concentra-

TABLE 1. *Observations in Golfo Dulce, Costa Rica, 10 March 1969. Sta. 1: 8° 20′ 30″ N, 83° 13′ 58″ W; Sta. 2: 8° 27′ 10″ N, 83° 12′ 58″ W; Sta. 3: 8° 34′ 55″ N, 83° 15′ 57″ W; Sta. 4: 8° 38′ 20″ N, 83° 19′ 55″ W; Sta. 5: 8° 41′ 15″ N, 83° 24′ 10″ W*

	Station 1				Station 2				Station 4				Station 5				Station 3				
Nominal depth (m)	S (‰)	Temp (°C)	σ_t	Si (μg-at./liter)	S (‰)	Temp (°C)	σ_t	Si (μg-at./liter)	S (‰)	(°C) Temp	σ_t	Si (μg-at./liter)	S (‰)	Temp (°C)	σ_t	Si (μg-at./liter)	ΔZ* (m)	S (‰)	Temp (°C)	σ_t	Si (μg-at./liter)
0	33.34	30.00	20.50	1.19	32.59	29.92	19.97	1.04	31.82	30.24	19.28	0.49	31.69	32.26	18.49	6.48	0	32.12	29.94	19.61	2.34
5	33.60	28.29	21.27	1.56	32.87	29.37	20.36	1.95	31.84	30.05	19.37	0.28	32.29	28.77	20.13	1.54	0	32.18	29.80	19.70	2.83
10	34.03	24.45	22.79	3.88	33.38	27.58	21.33	2.33	32.04	29.56	19.68	0.02	32.51	27.54	20.69	0.88	0	32.72	28.14	20.66	0.63
20	34.09	22.46	23.42	11.14	33.72	24.67	22.49	7.35	32.84	26.27	21.34	0.05	33.92	21.67	23.51	18.95	0	33.43	22.26	22.97	14.65
30	34.52	19.07	24.66	15.60	34.23	20.67	24.02	16.11	34.13	20.66	23.94	20.40	34.43	18.78	24.66	27.61	0	34.46	19.07	24.61	21.52
40	34.66	18.01	25.03	16.52	34.58	18.34	24.88	19.58	34.49	18.44	24.79	26.49	34.60	17.56	25.09	32.85	0	34.61	18.29	24.92	19.21
50	34.82	16.45	25.52	18.09	34.81	16.74	25.55	19.12	34.58	17.72	25.04	29.54	34.65	17.13	25.23	36.80	0	34.70	17.21	25.25	25.26
60	34.83	16.29	25.56	18.14	34.86	15.74	25.72	19.31	34.62	17.28	25.18	36.10	34.69	16.71	25.36	40.20	0	34.73	16.91	25.35	25.25
65					32.58?	15.71	23.98?	19.29													
70	34.85	15.94	25.67	19.04					34.72	16.78	25.37	31.25	34.74	16.35	25.48	47.84	0	34.76	16.73	25.41	26.56
80	34.87	15.69	25.74	19.38					34.74	16.38	25.48	41.92	34.75	16.21	25.52	51.01	0	34.76	16.53	25.46	28.41
90	34.88	15.53	25.78	19.79					34.76	16.31	25.51	41.43	34.75	16.13	25.54	51.57	0	34.79	16.41	25.51	31.32
100	34.88	15.47	25.80	19.69					34.79	16.29	25.54	30.74	34.75	15.96	25.58	54.55	0	34.79	16.12	25.58	40.07
110	34.88	15.42	25.81	19.96					34.79	16.12	25.57	39.35	34.77	15.93	25.60	56.43	−2	34.80	16.01	25.61	43.79
120	34.90	15.41	25.82	19.78					34.77	15.86	25.62	57.92	34.77	15.80	25.64	59.75	−2	34.80	16.00	25.61	41.98
130	34.90	15.39	25.82	19.61					34.79	15.82	25.64	58.40	34.79	15.78	25.65	60.08	−2	34.80	15.84	25.65	57.78
140	34.89	15.27	25.85	19.65					34.79	15.71	25.67	61.84	34.79	15.72	25.67	63.12	−2	34.79	15.76	25.66	61.50
150	34.90	15.23	25.86	19.77					34.79	15.67	25.68	65.55	34.80	15.67	25.68	64.04	−2	34.79	15.73	25.66	64.02
160	34.90	15.17	25.88	20.19					34.79	15.62	25.69	67.32	34.80	15.65	25.72	65.56	−2	34.79	15.68	25.68	63.63
170	34.90	14.96	25.92	20.61					34.79	15.61	25.69	67.50	34.80	15.61	25.70	67.95	−3	34.79	15.65	25.68	65.12
180	34.92	14.94	25.94	20.81					34.80	15.60	25.70	69.13	34.79	15.60	25.72	68.98	−3	34.79	15.64	25.68	69.08
190	34.92	14.77	25.98	21.24					34.80	15.58	25.71	75.38	34.81	15.58	25.72	75.49	−3	34.81	15.61	25.71	71.84
200	34.92	14.33	26.07	21.91					34.81	15.57	25.72	78.83	34.82	15.56	25.72	81.93	−3	34.81	15.59	25.71	77.43

* True depth correction, station 3 only. At all other stations the true depth was the same as the nominal depth.

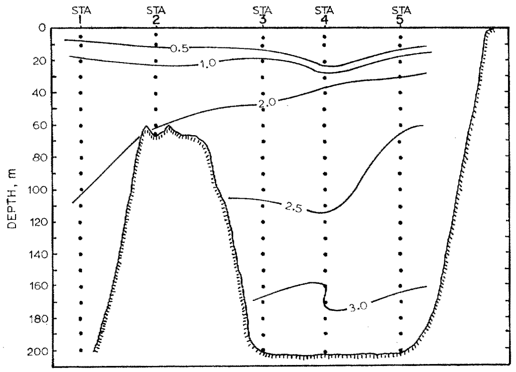

FIG. 4. Distribution of PO_4^{3-}-P, μg-atom/liter, in Golfo Dulce, 10 March 1969.

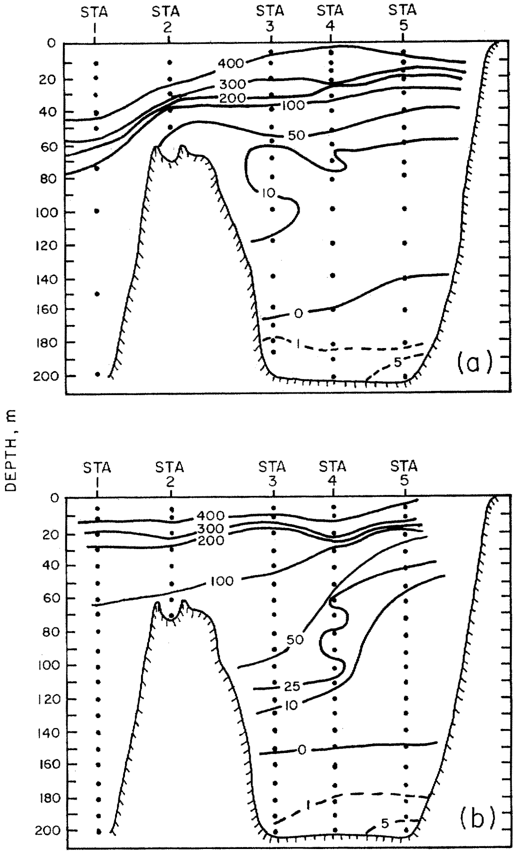

FIG. 5. Distributions of dissolved oxygen, μg-atom/liter (solid isopleths), and H_2S, μg-atom/liter (dashed isopleths), on (a) 2 March and (b) 10 March 1969.

tions of silicates were about 77 μg-atom/liter inside the gulf, whereas at the same depth (200 m) outside, the silicate concentration was only 21.9 μg-atom/liter. The phosphate concentration at 200-m depth inside the gulf was 3.63 μg atom/liter, compared with 1.17 at the same depth outside. These comparisons suggest a greater than 3-fold accumulation of the products of organic decomposition in the deep water of the inner gulf.

On 10 March, the salinity at the bottom inside the gulf was close to that observed on the sill, and the densities on the sill and of the inside bottom waters were nearly the same; but their greatly different identities are clearly shown by the differences in silicate and phosphate.

During both visits, ammonia and the alkalinity tended to increase slightly with depth, and *p*H decreased from around 8.4 at the surface to 7.9 at the bottom. The increase in ammonia from about 0.15 μmole at the surface to 0.4–0.7 μmole at the bottom could be accounted for by a modest accumulation during sulfate reduction and denitrification. The surface water had a somewhat low specific alkalinity of 0.098 [meq/liter (‰)], but the values in the deeper water were close to the "normal" 0.123.

The chemical distributions on 2 and 10 March differed slightly but significantly. The changes in oxygen distribution (Fig. 5a, b) are typical. The 400-μg-atom/liter isopleth on 2 March was at 45-m depth outside the basin and at 10-m depth inside. By 10 March, the isopleth was approximately level at 15 m. Between the two samplings, the 50-μg-atom/liter and lower concentration isopleths deepened markedly at station 3. Outside the gulf, the thermocline was at 70-m depth on 2 March, but on 10 March it had risen to 35 m. Inside the gulf, the thermocline rose from about 40 to 30 m between the two visits. At stations 3 and 4, there were significant decreases in silicate concentrations between 70- and 160-m depth between the two sampling dates (Fig. 6a, b). The decreases in silicates were accompanied by decreases

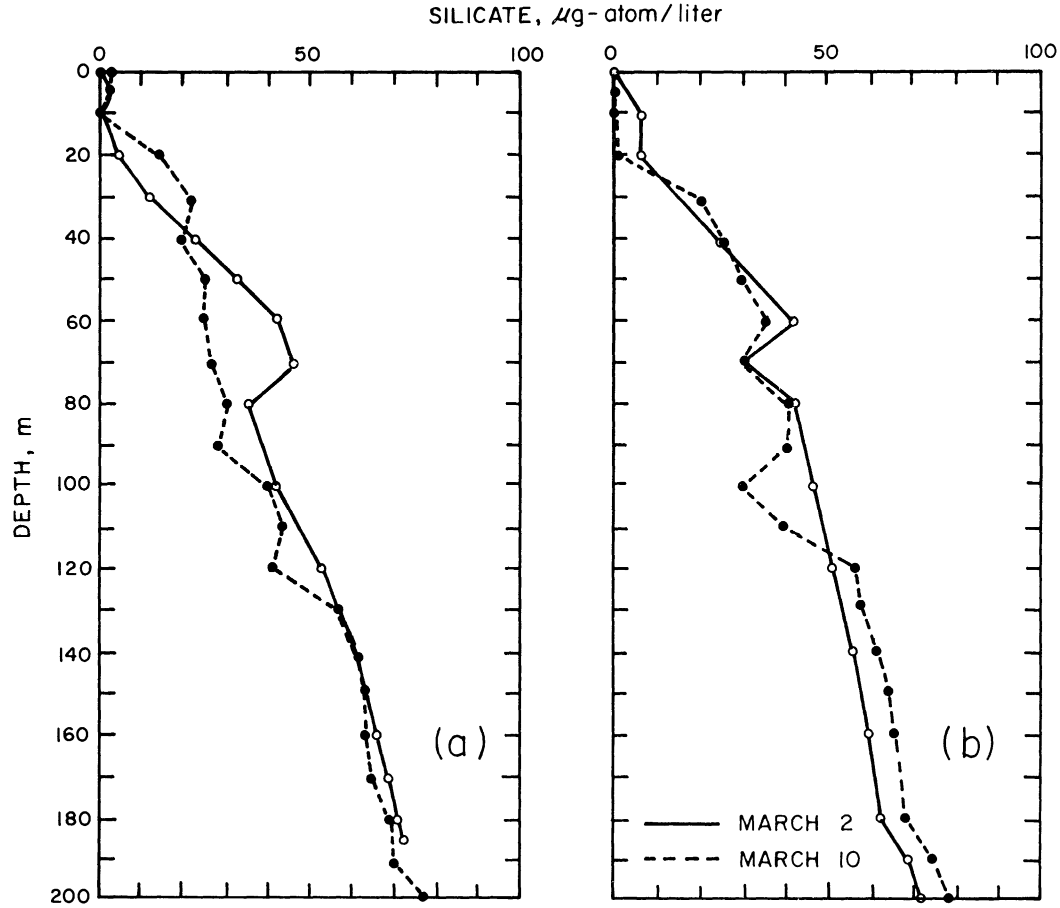

FIG. 6. Vertical distributions of reactive silicates (µg-atom/liter) at (a) station 3 and (b) station 4 on 2 March (solid lines) and 10 March (dashed lines) 1969.

in phosphates and increases in oxygen and nitrate concentrations.

DISCUSSION

Nutrient-oxygen relationships

Golfo Dulce, like other anoxic basins we have studied, demonstrates the systematic oxidation of organic matter in which first oxygen, then nitrate, and finally sulfate are used as terminal proton acceptors. In this basin at depths below approximately 120 m, all the nitrate had been reduced, presumably to free nitrogen, since little ammonia or nitrite was observed. An approximate calculation of the amount of nitrate lost from the water column can be made, using the oxidation relationships that exist between apparent oxygen utilization (AOU), nitrate, and phosphate. These ratios, AOU : NO_3^- : PO_4^{3-} have been calculated for the coastal waters of Costa Rica (Broenkow 1965; Department of Oceanography, University of Washington, unpublished) and they were not found to deviate significantly from the predicted ratios of 276 : 16 : 1, by atoms, in the upper 150 m. The actual oxidative ratios cannot be readily evaluated in Golfo Dulce because of complications arising from 1) denitrification, 2) sulfate reduction, 3) photosynthesis and oxygen exchange at the sea surface, and 4) the apparent preferential remineralization of phosphate in and just below the pycnocline (10–40 m).

TABLE 2. *Estimate of denitrification. TT-035,* Sta. 36, Z = 140 m*

	μg-at./liter
$(PO_4^{3-})_{obs}$	2.85
$(PO_4^{3-})_p$	-0.57
$(PO_4^{3-})_{den}$	-0.35
$(PO_4^{3-})_{ox}$	1.93
$(NO_3^-)_{ox} = 16 \times 1.93 =$	30.88
$(NO_3^-)_p$	2.3
$(NO_3^-)_{obs}$	0.0
Nitrate deficiency	33.28

* RV *Thomas G. Thompson,* cruise No. TT-035. University of Washington, Department of Oceanography, unpublished data report.

The maximum amount of nitrate lost from the deeper waters of the basin (>140 m) is about 33 μg-atom/liter NO_3^--N. This estimate was calculated from the observed nutrient concentrations, $(PO_4^{3-})_{obs}$ and $(NO_3^-)_{obs}$, and the assumptions that the oxidative nitrate-phosphate ratio $(NO_3^- : PO_4^{3-})_{ox} = 16 : 1$, preformed phosphate $(PO_4^{3-})_p = 0.57$ μg-atom/liter, preformed nitrate $(NO_3^-)_p = 2.3$ μg-atom/liter, and the release of oxidative phosphate during denitrification, $(PO_4^{3-})_{den}$, is approximated by the equation of Richards et al. (1965):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 94.4\,HNO_3 = 106\,CO_2 + 55.2\,N_2 + 177.2\,H_2O + H_3PO_4. \qquad (1)$$

The amounts of preformed phosphate and nitrate were estimated from the intercepts of AOU vs. NO_3, and AOU vs. PO_4 diagrams, compiled from data obtained during two cruises to the eastern tropical North Pacific Ocean (unpublished). The slopes and intercepts of these diagrams were determined from linear regression analysis. A sample calculation is shown in Table 2. Phosphate liberated during denitrification $(PO_4^{3-})_{den}$ was estimated from equation (1).

In the application of equation (1), we assumed that all the ammonia released was simultaneously oxidized to nitrate. Observations in the oxygen minimum zone of the eastern tropical Pacific indicate that nitrate reduction is occurring in nearly anoxic water ($O_2 < 1$ μg-atom/liter) and no ammonia is accumulating. If ammonia were not being oxidized (Richards 1965), the reduction of 33 μg-atom/liter of nitrate should have released about 6 μg-atom/liter of ammonia—an amount easily measured. The absence of ammonia may result from assimilation or some oxidative process not involving free oxygen.

Short-term changes

The chemical changes that occurred in the 8 days between samplings indicate that a bolus of new water entered the basin during the period. The temperature distributions outside the gulf indicated an upward displacement of 20C water from 70 to 35 m between the two visits. This was apparently sufficient to introduce water denser than that at intermediate depths inside the basin. This denser water flowed northward toward the head, sinking as it moved. The depth of the new water can be identified by its chemical characteristics—low silicate, low phosphate, high oxygen, and relatively high nitrate concentrations. Low silicate concentrations indicated that station 3 had new water at 90, 120, and 160 m, and station 2 had new water at 100 m. It is possible that the 90-m anomaly at station 3 was continuous with the 100-m anomaly 11 km farther up the gulf at station 4. None of the new water was observed at station 5.

As the new water moved to the deeper waters of the basin, a compensating flow had to occur from the deeper to the shallower layers and eventually out at the mouth. It appears from the oxygen isopleths that the outward flow occurred near the surface and the vertical exchange from the deep to shallow layers occurred at the head of the basin. At station 2 in the center of the basin, the oxygen isopleths remained at the same depths over the 8 days. The isopleths in the upper 60 m at the head rose about 10 m. In contrast, the 50-μg-atom/liter isopleth near the sill sank

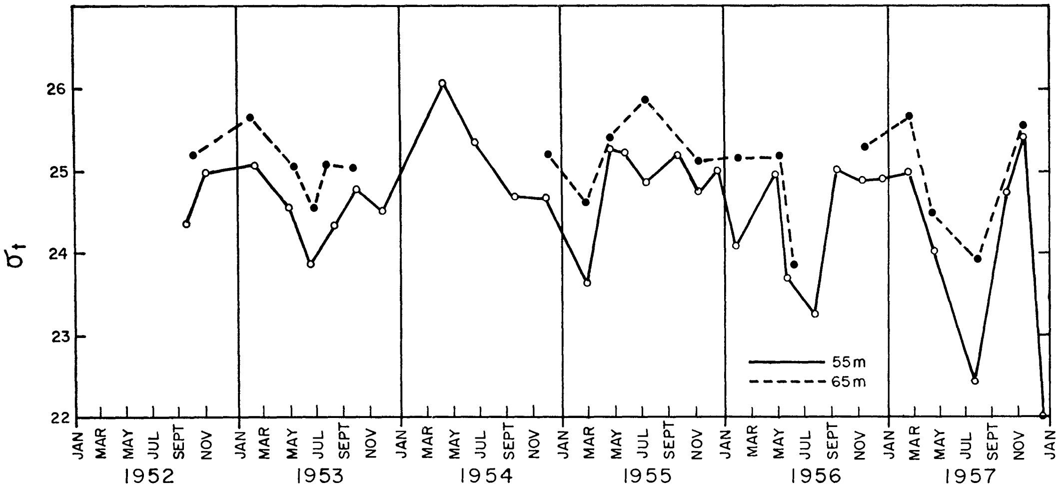

FIG. 7. Seasonal variations in σ_t at 55 and 65 m in the Gulf of Nicoya, Costa Rica, 1952–1957. Data from Peterson (1960).

40 m in response to the new higher oxygen water entering over the sill.

The entrance of new water appears to occur at intermittent times. This is deduced from the vertical and horizontal separation of the low silicate boluses. The mechanism might be a combination of upwelling due to coastal winds and an internal wave activity.

Seasonal cycle

The seasonal period of coastal upwelling at Golfo Dulce can be postulated from hydrographic data taken during a 1952–1957 study of the Gulf of Nicoya 120 nautical miles north of Golfo Dulce (Peterson 1960). The seasonal variations in sigma-*t* at 55 and 65 m are plotted in Fig. 7. The station is off the mouth of the Gulf of Nicoya in 70 m of water. The data indicate that there is an approximate 12-month cycle in the depth of the pycnocline. This corresponds to the seasonal wind structure, which is southerly in the summer because of the Azores high pressure cell and northerly in the winter when the cell moves farther south and is replaced by the northeast trades and the coastal northerly Papagayo winds. The Papagayo winds are the dominant winds in the winter in the Gulf of Nicoya, blowing from 0.5 to 4 or 5 days at a time, often reaching gale force (Peterson 1960). In the Gulf of Panama, 120 nautical miles east of Golfo Dulce, northerly winter winds are closely correlated with upwelling (Schaefer et al. 1958). Thus it appears that the local wind regime is the predominant factor controlling the renewal of water in Golfo Dulce.

Three small tropical embayments that contain anoxic, sulfide-bearing waters have now been reported—Kaoe Bay in Indonesia (van Riel 1943), Golfo de Cariaco, Venezuela (Richards 1960; Gade 1961), and Golfo Dulce. General physical similarities between Golfo Dulce and Saanich Inlet suggest that Golfo Dulce may occasionally (or perhaps regularly) flush, as Saanich Inlet appears to flush annually. March 1969 was preceded by a period of unusually low rainfall for this region of normally high rainfall. Although the principal rivers entering the inner gulf, Rio Esquinas and Rio Rencon, are not long, their possible effect on flushing the gulf during torrents cannot be estimated.

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