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Diurnal pH Variation in Texas Bays, and Its Application to Primary Production Estimation[1]

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Introduction

The diurnal pH variation in marine waters is of considerable interest because it is closely related to the buffer mechanism of sea water, primary production, and some other physico-chemical processes; such as daily water temperature variation.

pH measurements in the marine environment have been relatively few. Measurement difficulties are encountered, since sea water is a relatively strong buffer solution; and the instrumentation necessary for accurate hydrogen ion concentration measurement has not been available in many cases. Sargent and Hindman (1943) have improved instrumentation with a pH meter which, they reported, had a sensitivity of approximately 0.002 pH unit. Recently, the Beckman Instruments Corporation Model G-S pH meter (sensitivity 0.0025) has been made commercially available.

In Table 1 some of the diurnal pH data from the literature are presented. For the open seas a daily change of approximately 0.05 pH unit change was reported by Moberg (1927) on the California coast near San Diego, and by Smith (1958) on the Texas Gulf Coast.

To obtain additional information on the dynamic nature of pH changes in aquatic environments, concurrent measurements of the diurnal variations in pH, phosphate (Bruce, 1959) and oxygen were made on some south Texas bays during the summer (July-August) and winter (December) of 1957.

ACKNOWLEDGMENT

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TABLE 1

Some Existing Diurnal pH Variation Data

Investigators	Min. pH	Max. pH	Δ pH	Location
*Powers (1920)	7.6	8.6	1.0	A small lagoon in Puget Sound
*Wells (1922)	......	......	......	Waters over tropical banks, Tortugas, Florida
*Moberg (1927)	8.34	8.40	0.06	Mission Bay, California
	8.14	8.39	0.25	Mission Bay, California
*Nicol (1935)	8.8	9.5	0.7	Salt marsh pools in Aberlady Bay, England
	8.6	9.8	1.2	Salt marsh pools in Aberlady Bay, England
*Emery (1946)	7.5	9.0	1.5	Tide pool, near La Jolla Beach, Calif.
Odum (1956, 1957a)	7.4	7.7	0.3	Silver Springs, Florida
Schütte and Elsworth (1954)	9.1	12.6	3.5	Soft water vleis near Capetown, Africa
*Smith (1958)	8.10	8.15	0.05	Gulf of Mexico
Verduin (1956)	8.35	8.85	0.6	Western Lake Erie
	7.95	8.70	0.75	Western Lake Erie
	7.9	8.8	0.9	Western Lake Erie
McQuate (1956)	7.74	9.06	1.32	Sandusky Bay
Talling (1957)	8.3	8.7	0.4	White Nile, Africa
	8.4	8.9	0.5	Gebel Aulia, Africa
	8.3	9.0	0.7	Gebel Aulia, Africa
	8.7	9.1	0.4	Lake Victoria, Africa

* Denotes salt water environments.

THEORETICAL CONSIDERATIONS

It is apparent that solar energy is the prime cause of diurnal change in pH either directly or indirectly. Both photosynthesis and respiration of marine organisms influence the carbonic acid equilibrium system in sea water. It therefore appears feasible to calculate the magnitude of both photosynthesis and respiration by observing pH change and other supporting field data, Wells (1922) measured carbon dioxide metabolism and related it to daily pH changes at Tortugas. Harvey (1955) has summarized various aspects of the correlation between the pH and carbonic acid system in the sea, and Ryther (1956) has reviewed some of the problems with measurement of primary production by pH change.

The buffer mechanism of sea water is quite complicated. However, the most significant buffering action can be said to come from carbonic and boric acids and their salts which are present in the water. The remainder of the many weak acids in sea water may be considered to be insignificant. The magnitude of the contribution of boric acid and its salts to the buffer mechanism is approximately 5 per cent for oceanic water of a pH around 8.2 and a higher per cent for higher pH values. It is therefore necessary to consider boric acid when one computes the magnitude of primary production in the sea by diurnal pH change. A brief review of the relationship between pH and carbonic acid system in the sea follows.

From the first and second dissociation equations of carbonic acid the following relations are obtained:

$$\mathrm{pH} = \mathrm{pK}_1 + \log \frac{C_{\mathrm{HCO}_3^-}}{C_{\mathrm{H}_2\mathrm{CO}_3}} \qquad (1)$$

$$\mathrm{pH} = \mathrm{pK}_2 + \log \frac{C_{\mathrm{CO}_3^{--}}}{C_{\mathrm{HCO}_3^-}} \qquad (2)$$

ere capital C denotes molar concentration, and pK_1 and pK_2 denote the negative garithm of the first and second dissociation constants of carbonic acid.

Assuming pK_1 and pK_2 are constant, the pH changes observed are due to changes in e ratio of bicarbonate and carbonate ions, and/or bicarbonate ion and carbonic acid. rrection for boric acid contribution on pH changes must be made. Therefore, any ange of the relative concentration of carbonic acid components, H_2CO_3, HCO_3^-, and $_3^{--}$, due to photosynthesis and respiration of aquatic organisms, tends to change the I of the water.

The dissociation constants of both carbonic and boric acids in sea water are given by ach (1951) and Lyman (1957) as functions of temperature and chlorinity. Lyman's nstants are used in this paper. His apparent first and second dissociation constants r carbonic acid are defined as:

$$K'_1 = \frac{A_{H^+} C_{HCO_3^-}}{A_{(H_2CO_3 + CO_2)}} \qquad (3)$$

$$K'_2 = \frac{A_{H^+} C_{CO_3^{--}}}{C_{HCO_3^-}} \qquad (4)$$

here A denotes active concentration.

Solar energy also changes the temperature of the water thus affecting pH. Buch and ynäs (1939) studied the relationship between temperature and pH in a closed system. hey found that pH falls with rising temperature at a magnitude dependent upon the H and salinity of the water. At a chlorinity of 19.5‰, a temperature range of 20–30° C, nd a pH of 8.2, the pH falls 0.01 unit per each 1° C rise in temperature.

If one could assume environmental changes are restricted to temperature changes, one would expect the minimum pH to occur at the time of highest water temperature. Hence he minimum pH would be during daylight hours when the water temperature is maximum, and maximum during night when the water temperature is lowest. This trend s opposite to the pH changes which one would expect from biological activity.

If diffusion due to changes in solubility of molecular CO_2 is unimportant, a pH change aused by temperature change does not affect the total carbon dioxide content of the water. In computations of the concentration of carbon dioxide components in the environment, temperature errors are minor since the constants used are corrected for temperature.

In an environment in which calcium carbonate precipitation and dissolution are active, pH change due to biological CO_2 removal may be obscured unless a precise knowledge of the quantity of precipitate is obtainable since calcium carbonate affects buffering action. Another complication is the diffusion exchange of carbon dioxide across the air-water interface. The diffusional problem needs much more detailed investigation.

STATIONS

Four stations were selected for this study. The productivity of these stations was studied by Odum and Hoskin (1958) by means of the diurnal oxygen method. The locations of the stations are given in Figure 1. All stations were representative of large areas of the shallow bays, ranging from 1 foot to 6 feet in depth.

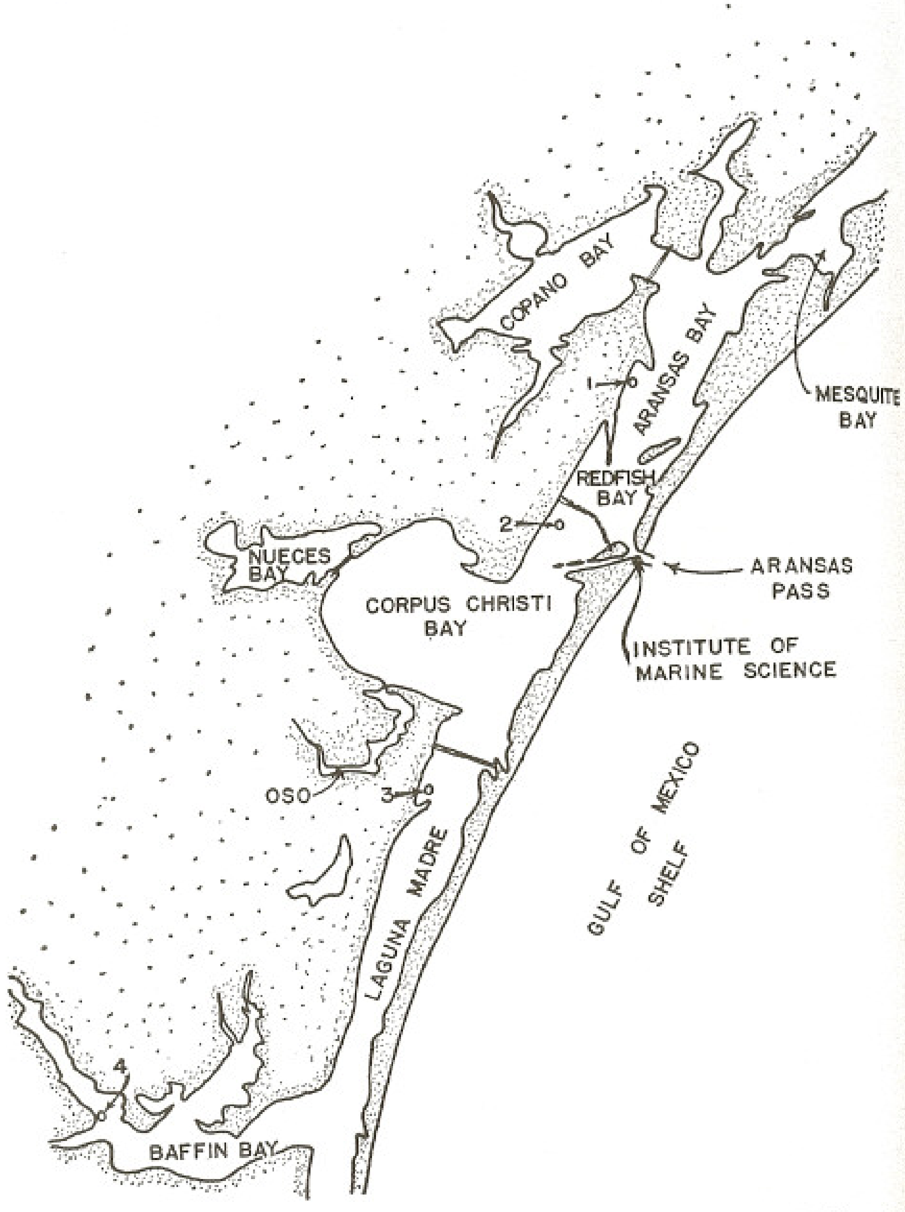


Fig. 1. Locations of stations occupied in diurnal pH measurements in Texas bays: Rockport Basin, 1; Redfish Bay station, 2; Laguna Madre station, 3; Baffin Bay station, 4.

Redfish Bay was the shallowest of the bays studied (approximately 1 foot deep) and had the heaviest growth of benthic "grasses" (*Thalassia* and *Ruppia*). The "grasses" emerged at low tide. The water mass at the station was thought to be relatively stationary.

The Laguna Madre station was midway between Pita Island and the Texas mainland in about 2 feet of water. A fairly heavy growth of *Diplanthera* "grass" existed.

The Baffin Bay area was about 5 feet in depth. The water was turbid with a visibility of not over 2 feet. The chlorinity of the water exceeded 30‰.

The Rockport station was in the Rockport Yacht Basin in water about 6 feet deep. During the investigation the water surfaces became intermittently covered with oil slicks.

METHODS

Measurements of pH were made with a Beckman Model G-S pH meter. The meter was enclosed, with desiccant, in a transparent polyethylene bag to exclude salt air. Both the glass and calomel electrodes were the general purpose extension type used with all laboratory models of Beckman Instruments. The electrodes were inserted through a No. 11 rubber stopper fitted to a glass container in which the pH of water samples was measured. Standard buffer solution of pH 7.00 was kept at the water temperature by partially immersing the container in the sea water, thus eliminating the temperature correction between the water and buffer solution.

Water samples were either taken by filling the bottles at the appropriate depth by hand or measurements were taken by inserting the electrodes directly into the water. In the former case the pH was measured as quickly as possible and without exposure to air. Although the Beckman Model G-S pH meter has been found sensitive to 0.003 pH units, with the possibility of greater field errors, the pH value was recorded to 0.01 unit.

In order to obtain carbonate alkalinity of the water samples both titration alkalinity and total inorganic boron analyses were made on samples collected at three-hour intervals. Boron samples were frozen in dry ice until the analyses were made. The titration alkalinity was determined according to the method of Wattenberg (1933) using a pH of 6.0 at the end point. The total inorganic boron was measured by the method of Noakes (1959).

Results and Discussion

The field data obtained at the four stations are presented in Figures 2 through 5 and summarized in Table 2.

TABLE 2

Observed Field Data During the Investigation of Diurnal pH Variation in Texas Coastal Waters

Location	Date (1957)	pH Range	ΔpH	Temp. Range (° C.)	Cl‰	Titration Alkalinity (Milliequivalent/1) Range	Average	Total Inorganic Boron (Millimol/1)
Baffin Bay	July 26–27	8.20–8.34	0.14	29.0–32.0	31.8	4.01–4.13	4.09	0.90
	Aug. 15–16	7.94–8.35	0.41	29.0–32.0	36.1	4.34–4.39	4.37	1.10
	Dec. 22–23	8.52–8.62	0.10	19.2–21.2	34.9	3.69–3.80	3.74	0.87
Redfish Bay	July 18–19	8.23–8.91	0.68	28.0–35.0	16.6	2.45–2.65	2.53	0.37
	Dec. 25–26	7.98–8.41	0.43	18.0–23.0	15.7	2.92–3.01	2.95	0.61
Laguna Madre	Aug. 1–2	8.15–8.42	0.27	27.4–32.0	31.6	2.83–2.95	2.86	0.92
	Dec. 28–29	8.21–8.49	0.28	14.4–17.5	17.6	2.82–2.88	2.85	0.40
Rockport	Aug. 5–6	8.37–8.44	0.07	31.0–32.0	18.9	2.82–3.02	2.88	0.64

From the analyses it was observed that titration alkalinity and inorganic boron did not show a regular diurnal cycle but were about the same throughout the 24-hour period. Chlorinity differed quite markedly from station to station ranging from approximately 16‰ at Redfish Bay to 36‰ at Baffin Bay.

In comparison with other stations Redfish Bay showed the largest diurnal variation in

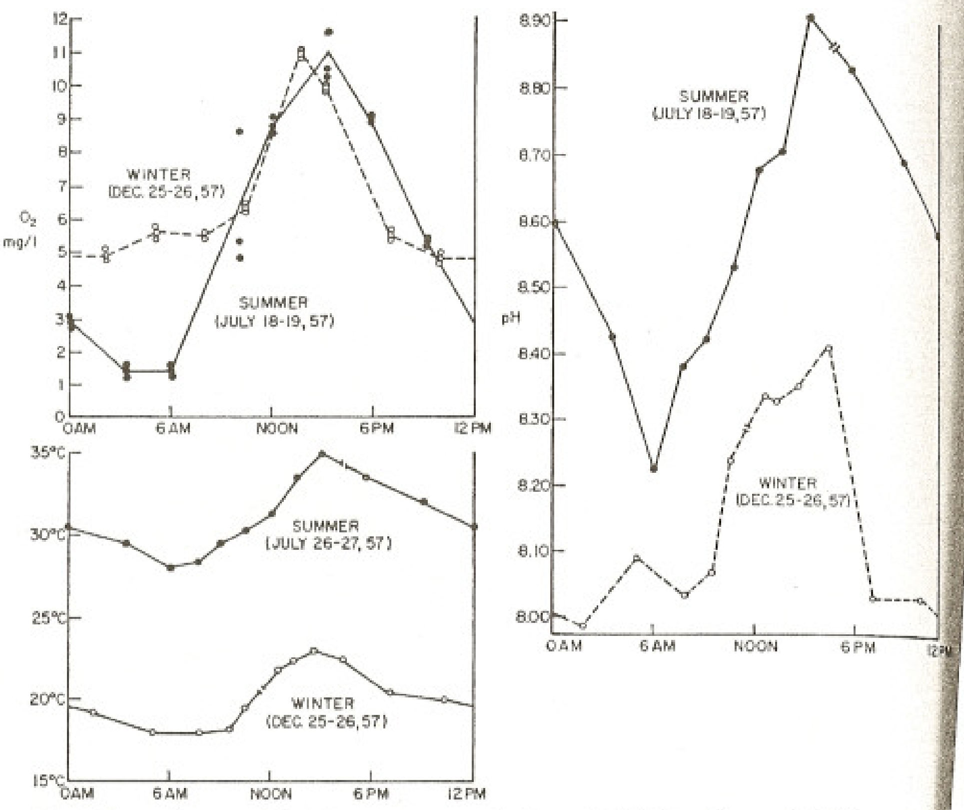


FIG. 2. Diurnal oxygen, pH, and temperature variation at Redfish Bay, Texas. Solid lines, summe data for July 18–19, 1957. Dotted lines, winter data for Dec. 25–26, 1957.

dissolved oxygen, temperature and pH (Fig. 2). The values of pH and temperatu from this station in summer were higher and showed a greater diurnal range than i the winter. However, in the Laguna Madre a higher pH was observed in the winter tha in the summer.

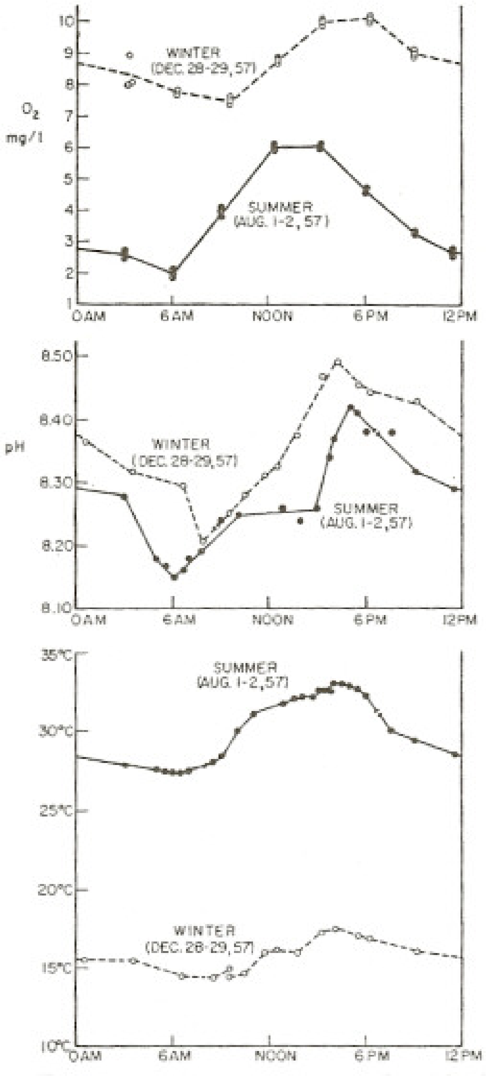
Three sets of diurnal pH values were obtained in Baffin Bay (Fig. 4). Winter p values were higher than the summer, but diurnal changes were less. The two summ stations showed a marked difference in the magnitude of diurnal pH change althou the variation of oxygen and temperature were almost the same.

The Rockport station (Fig. 5) was occupied after a dinoflagellate bloom. This stati had the least diurnal variation in dissolved oxygen, pH and temperature of the locati studied. A maximum was observed at 1800 hrs. which was quite different from that other stations. The amplitude of diurnal oxygen and pH was less in the deeper envir ments where the effects of metabolism were dispersed in a greater volume of water

DIURNAL VARIATION OF TOTAL CARBON DIOXIDE

Using the data for pH and carbonate alkalinity, the total carbon dioxide compone $C_{CO_3^{--}}$, $C_{HCO_3^-}$, $C_{H_2CO_3}$ and C_{CO_2} can be calculated at any given time of the day. The e tions for this computation are summarized as follows:

$$C_{HCO_3^-} = \text{Carbonate Alkalinity} \frac{A_{H^+}}{2\,K'_2 + A_{H^+}} \text{ gm.-ion/L} \qquad (5)$$



IG. 3. Diurnal oxygen, pH, and temperature variation near Pita Island, Laguna Madre, Texas. id lines, summer data for Aug. 1–2, 1957. Dotted lines, winter data for Dec. 28–29, 1957.

$$C_{CO_3^{--}} = \text{Carbonate Alkalinity} \frac{K'_2}{2K'_2 + A_{H^+}} \text{ gm.-ion/L} \qquad (6)$$

$$C_{(CO_2 + H_2CO_3)} = \frac{A_{H^+} C_{HCO_3^-}}{K'_1} \text{ gm.-Mole/L} \qquad (7)$$

t the total components of the carbon-dioxide system be represented by $\sum CO_2$:

$$\sum CO_2 = C_{CO_3^{--}} + C_{HCO_3^-} + C_{(CO_2 + H_2CO_3)}$$

Then:

$$\sum CO_2 = \text{Carbonate Alkalinity} \frac{A_{H^+} + K'_2 \left(1 + \frac{A_{H^+}}{K'_1}\right)}{2K'_2 + A_{H^+}} \text{ gm.-Mole/L} \qquad (8)$$

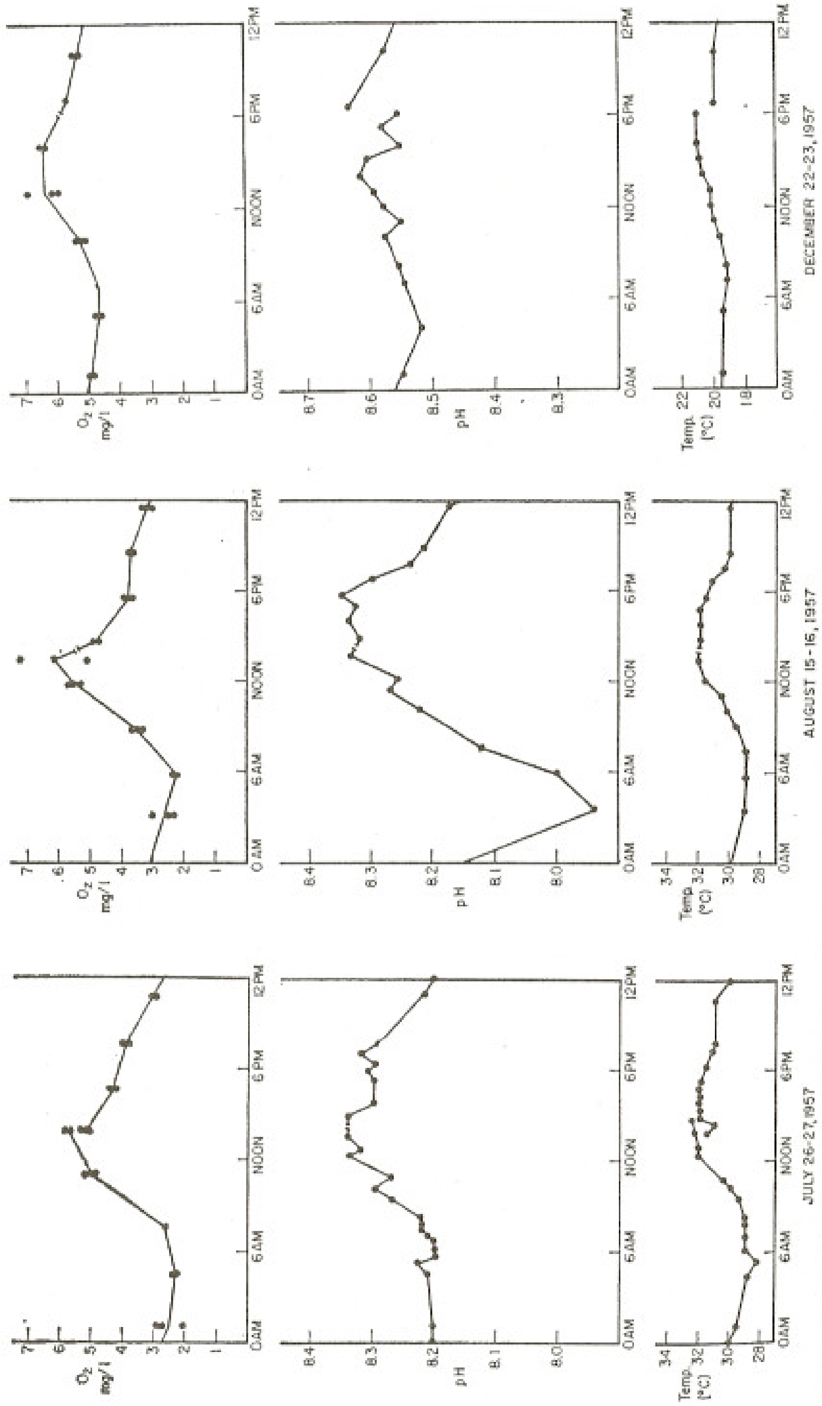
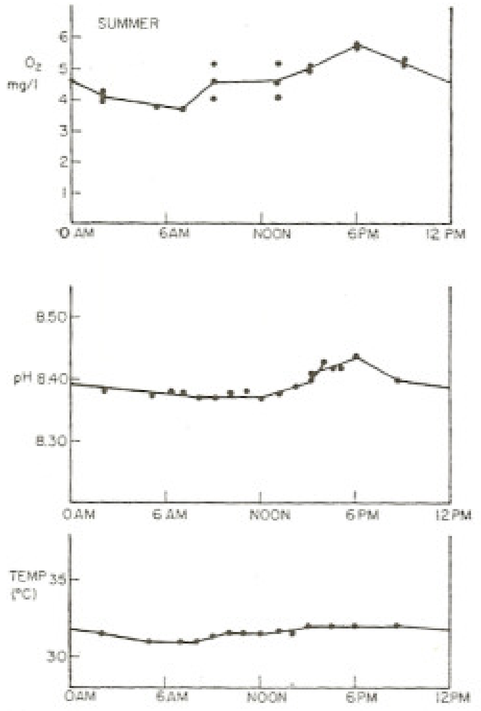


Fig. 4. Diurnal oxygen, pH, and temperature variation at Baffin Bay, Texas, July 26–27, Aug. 15–16, Dec. 22–23, 1957.

From equation 8 the average total CO_2 components were plotted by hour in Figur 6 to 13. For purposes of comparison diurnal oxygen results were also plotted. The ra of change of total CO_2 was plotted as was the per cent saturation of molecular CO calculated from Buch's data (Buch, 1951).



IG. 5. Diurnal oxygen, pH, and temperature variation at Rockport Basin, Texas, Aug. 5–6, 1957.

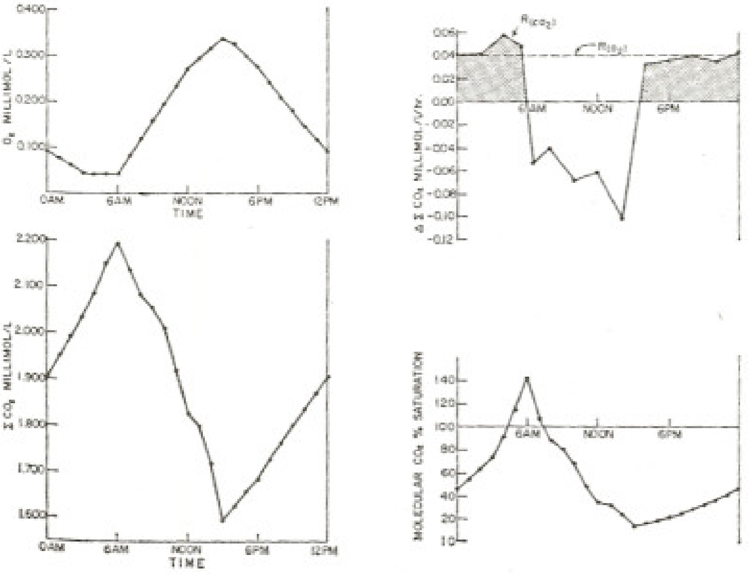


FIG. 6. Diurnal computations for Redfish Bay, July 18–19, 1957. Hourly variation of dissolved oxygen, total carbon dioxide components $[C_{CO_3^-} + C_{HCO_3^-} + C_{(CO_2 + H_2CO_3)}]$, rate of change of total carbon-dioxide, and per cent saturation of molecular carbon-dioxide. The dotted line, $R_{(O_2)}$, is the nighttime rate of respiration computed from the diurnal oxygen method (Odum, 1956). The nighttime rate of respiration was also computed from carbon dioxide by estimating the shaded area between the night rate of change, $R_{(CO_2)}$, and zero.

ESTIMATION OF PRIMARY PRODUCTION

Assuming the diurnal variation of total CO_2 was largely due to photosynthesis and respiration, the estimation of primary production can be performed by the diurnal curve method (Odum, 1956).

From oxygen studies with diurnal curves, Odum and Hoskin (1958) found the oxygen diffusion constant for these Texas bays to be about 1 gm. O_2/M^2/hr. for 0.2 atmosphere saturation gradient between atmosphere and water. A diffusion coefficient of similar order of magnitude for carbon dioxide may be expected for the same conditions of wave motion and turbulence. With no free carbon dioxide at all in the water the rate of diffusion of the carbon dioxide from the air would be about 6.7 gm. CO_2/M^2/ gradient of one atmosphere. Since the partial pressure of CO_2 in the air is only about 3×10^{-4} atmospheres, the maximum diffusion rate expected into the water during the middle of the day is about 1.5 mg./M^2/hr. and negligible compared to the respiration rates, which are 100 to 1000 times as great in these bays.

It is of considerable interest, that observations of the carbon dioxide content of the sea and air during the International Geophysical Year show that equilibrium seldom exists. In some 10,000 miles of oceanic observations in the Gulf of Mexico, Caribbean and Middle Atlantic (Ibert and Hood, 1958), only rarely was it observed that the carbon dioxide concentration of air and the sea were the same. In most cases the concentration in the air was high with respect to that of the sea. Diffusion of carbon dioxide into the sea surface is evidently slow or the conditions evidenced could not persist.

In the summer in Redfish Bay there was a change in total CO_2 content of the water of 0.6 mM/L during the period from 0600 to 1500 Central Standard Time. From sunrise to late afternoon the rate of decrease of total CO_2 was nearly constant. The rate of increase of CO_2 due to the summation of respiration and diffusion was also nearly constant throughout the dark hours.

With the low partial pressure of CO_2 gas in both air and water, diffusion was negligible. Thus the graph of night rate of change is apparently a record of the course of community respiration. In order to obtain a value for respiration, the graphical areas between the rate of change curves for CO_2 during the dark hours and the zero lines were estimated (Figs. 6–13, shaded areas). The average respiration rates found at night were used to estimate the daytime respiration. For comparison, the dotted line R is plotted in these figures to indicate the respiration correction as computed from the oxygen method (Odum and Hoskin, 1958). At the summer station in Redfish Bay (Fig. 6) the value for respiration obtained from oxygen data and that from carbon dioxide are nearly the same. The respiratory quotient for this station was, thus, found to be 1, The gross primary production was then obtained by estimation of the area of the rate curve beneath the respiration value. The gross primary production, P_G, was found to be 0.92mM/L/day. Data from the other stations were handled in the same manner and the estimated gross primary production rates are given in Table 3.

Hourly changes in the CO_2 system components (CO_2, HCO_3^-, CO_3^{--} and H_2CO_3) based on the diurnal pH variation data for the summer station at Redfish Bay are shown in Figure 14. The bicarbonate ion changes most, followed by carbonate ion and carbonic acid. Dissolved carbon dixoide (and carbonic acid) represent only a small portion, less than 1 per cent of total CO_2 content in the water. Observations of Hood, Park,

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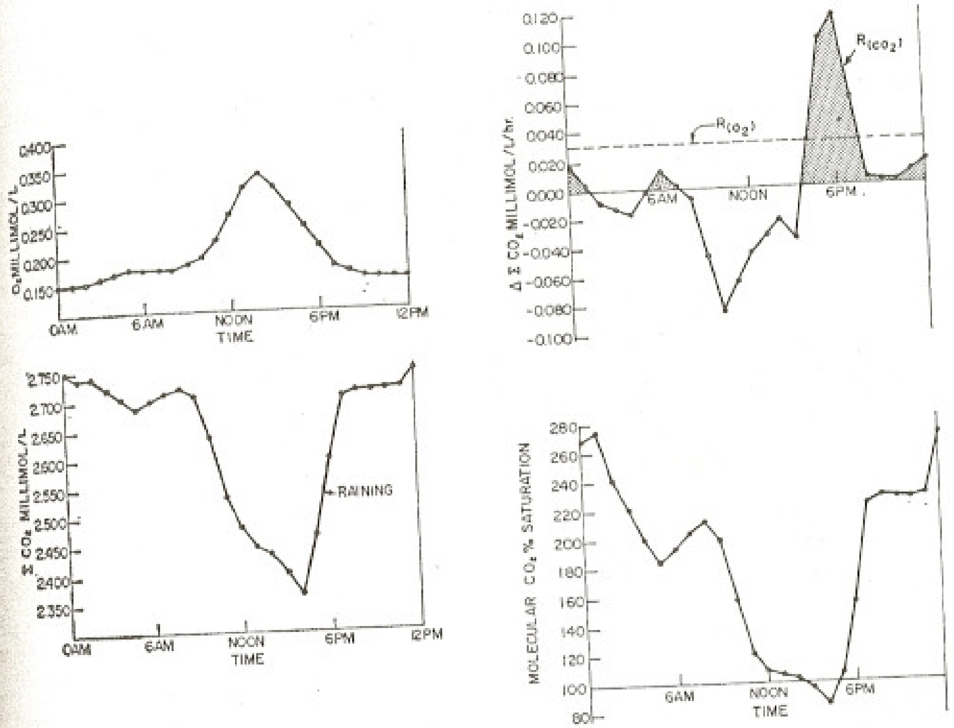

FIG. 7. Diurnal computations for Redfish Bay, Dec. 25–26, 1957. See legend for Figure 6.

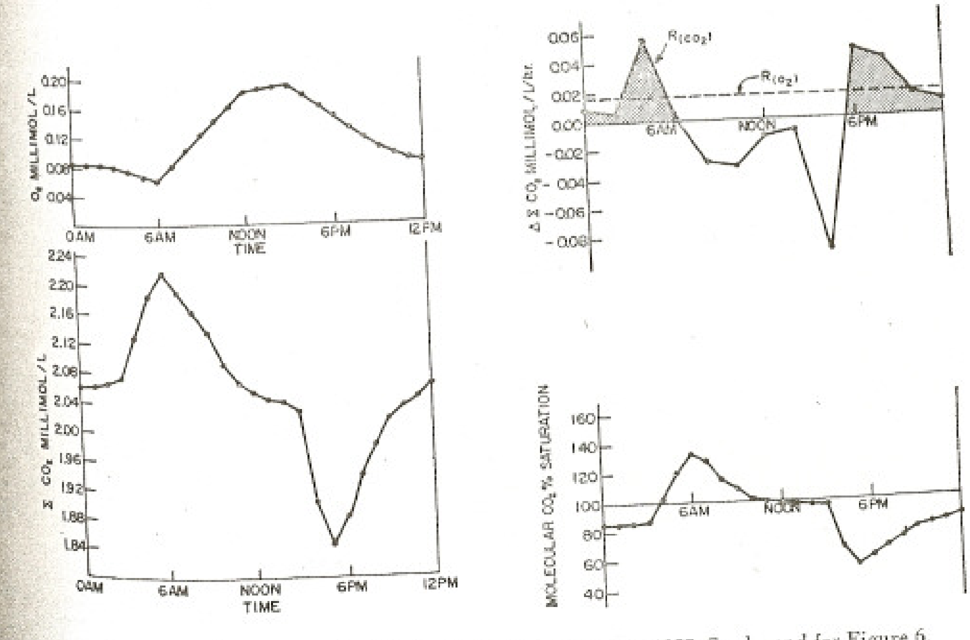

FIG. 8. Diurnal computations for Laguna Madre, Aug. 1–2, 1957. See legend for Figure 6.

TABLE 3

Comparison of Gross Primary Production and Respiration Estimations by O_2 and pH Measurement in Highly Productive Texas Coastal Bays

		Gross Primary Production			Respiration Estimation		
Location	(Date (1957)	O_2 Method mM/L/day	CO_2 Method mM/L/day	PQ O_2/CO_2	O_2 Method mM/L/day	CO_2 Method mM/L/day	RQ O_2/CO_2
Baffin Bay	July 26–27	0.27	0.31	0.9	0.48	0.31	1.5
	Aug. 15–16	0.24	0.90	0.3	0.30	0.91	0.3
	Dec. 22–23	0.16	0.19	0.8	0.23	0.29	0.8
Redfish Bay	July 18–19	0.88	0.92	1.0	0.96	1.00	1.0
	Dec. 25–26	0.43	0.68	0.6	0.75	0.49	1.5
Laguna Madre	Aug. 1–2	0.25	0.56	0.4	0.41	0.58	0.7
	Dec. 28–29	0.17	0.27	0.6	0.15	0.25	0.6
Rockport Basin	Aug. 5–6	0.13	0.12	1.0	0.24	0.12	2.0

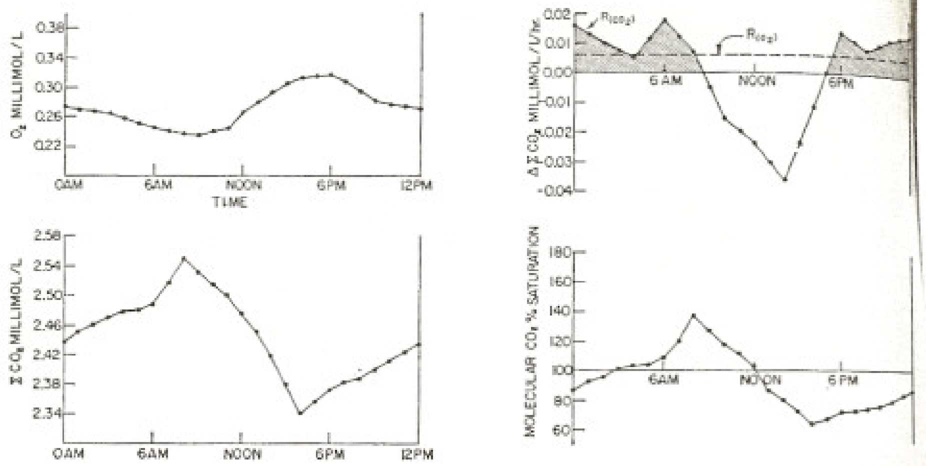

FIG. 9. Diurnal computations for Laguna Madre, Dec. 28–29, 1957. See legend for Figure 6.

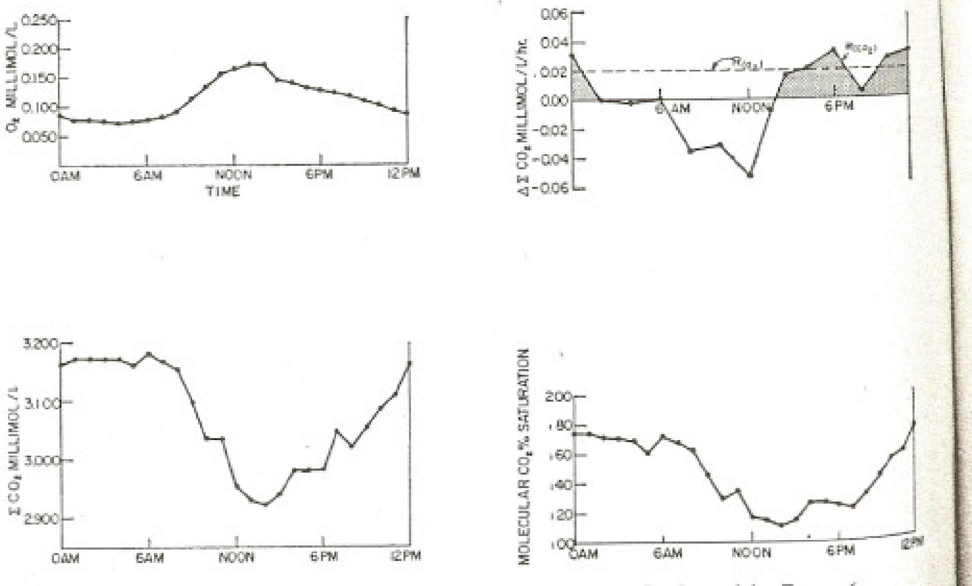

FIG. 10. Diurnal computations for Baffin Bay, July 26–27, 1957. See legend for Figure 6.

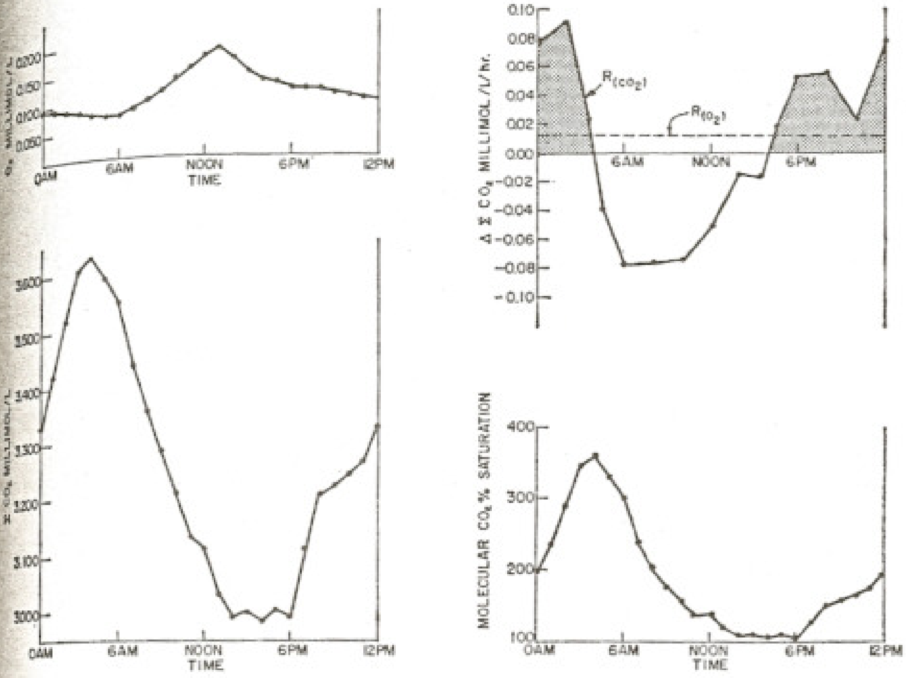

Fig. 11. Diurnal computations for Baffin Bay, Aug. 15–16, 1957. See legend for Figure 6.

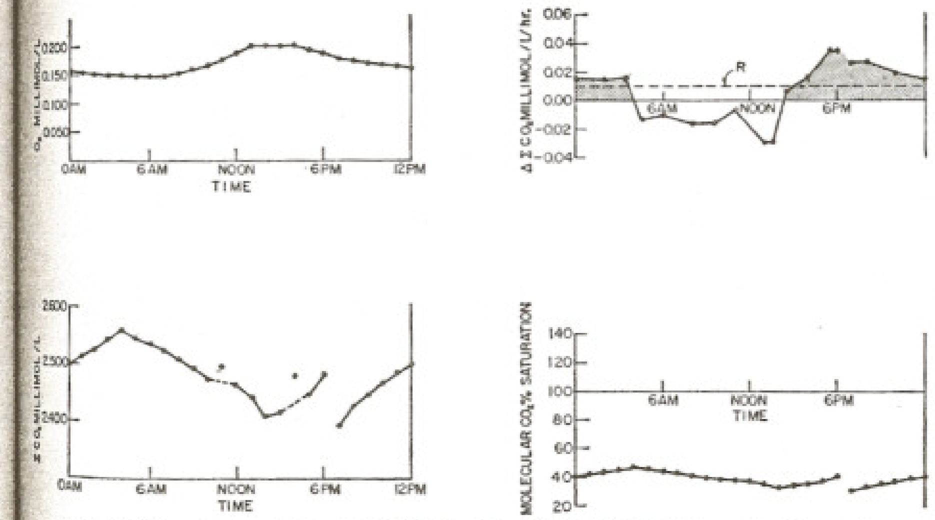

Fig. 12. Diurnal computations for Baffin Bay, Dec. 22–23, 1957. See legend for Figure 6.

nd Smith (1958) show that many marine plants tend to utilize bicarbonate ion directly s a source of carbon in photosynthesis.

Effect of Cold Front and Heavy Showers on Total Carbon Dioxide Content

At the winter station on Redfish Bay (Figs. 2 and 7) relatively heavy rainfall fell ccompanied by a cold front between 1600 and 1900 Central Standard Time Decem- er 25, 1957. During a period of 3 hours the pH of the water dropped abruptly from

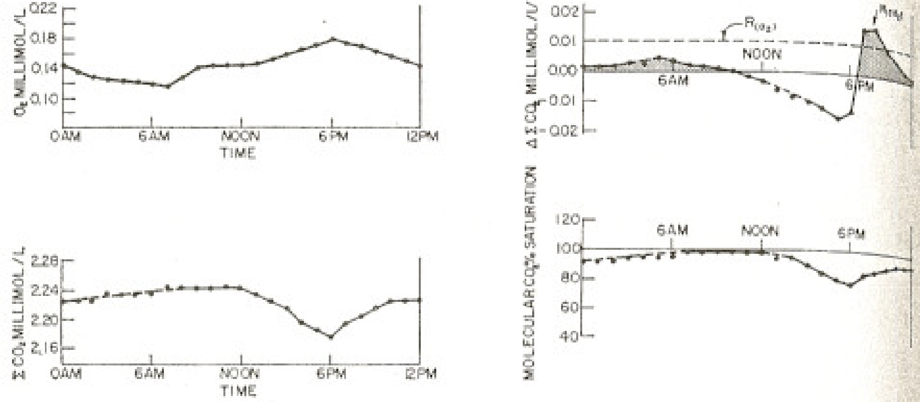

FIG. 13. Diurnal computations for Rockport Basin, Aug. 5–6, 1957. See legend for Figure 6.

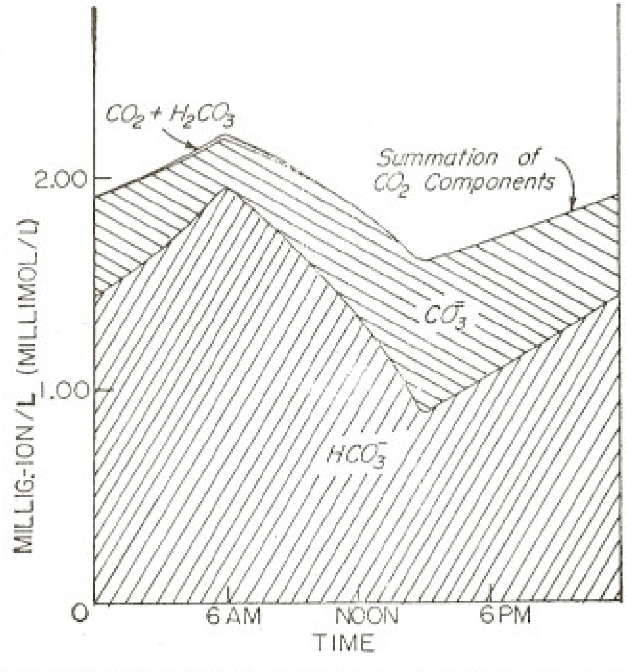

FIG. 14. Change in the components of the carbon-dioxide system based on data from Redfish Bay, Texas, July 18–19, 1957.

8.41 to 8.03 and the temperature from 22.4° C to 20.4° C. These changes are more rapid than those normally observed due to a decrease in light intensity and appear to be caused by increased diffusion rates and/or by addition of CO_2 rich fresh water through rainfall. The rain storm greatly increased surface agitation and mixing rates resulting in increased carbon dioxide invasion of the bay waters.

The over-all effect of the rain storm may be estimated from the data shown in Figure 15. The total CO_2 content of the water was increased by approximately 0.33 mM/L in 3 hours during rainfall. The photosynthesis during this period was minimal because of

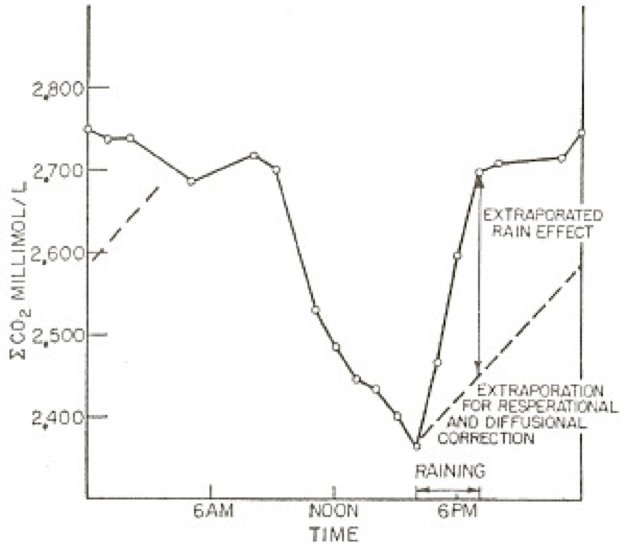

Fig. 15. Estimation of the effect of rain by extrapolation of data from Figure 7.

the low light intensity. Assuming the respiration had the similar tendency to that shown in Figures 6 and 9, it seems reasonable to draw a relatively straight line from 1600, the start of the rain, to 0600 next morning. From the extrapolation a correction value of approximately 0.08 mM CO_2 was obtained. The net change of CO_2 due to the storm was 0.25 mM/L/3 hours or 0.08 mM/L/hr. It is interesting that similar changes have been observed with respect to dissolved molecular carbon dioxide in the Caribbean during the summer of 1958 (Ibert and Hood, 1958).

Photosynthetic and Respiratory Quotients

Both photosynthetic ($PQ = O_2/CO_2$ by molecules and respiratory quotients ($RQ = O_2/CO_2$ by molecules), based on the field data obtained, cover a wide range of values. PQ, from 0.3 to 1.0, and RQ, of 0.3 to 2.0, were observed (Table 3).

Ryther (1956) reviewed and summarized the existing measurements of PQ in plankton reporting values which are rather close to unity, as expected for the synthesis of carbohydrates. Calculations of PQ can be made from the chemical compositions of aquatic plants (by the relative ratio to carbon, oxygen, and hydrogen). The calculated PQ values range from 1.09 to 1.48 with an average of about 1.20. When the plants use ammonia as their nitrogen source, the PQ is calculated to be about 1.10 and experimentally was found to be 1.06; with nitrate-nitrogen the PQ values calculated and measured were 1.45 and 1.47 respectively (Cramer and Myers, 1948).

Contrary to the above expectations for single populations, the field data obtained in this study showed much lower PQ values. The reason for this anomaly is not clear. Low values were also found in some Florida springs by Odum (1957b). Apart from unavoidable experimental errors in the field a number of explanations are possible. The role of bacteria may significantly affect the PQ ratio since 10^7 bacteria/ml. were found by Carl Oppenheimer in the waters of the bays studied. The bacteria may be consuming CO_2 without releasing oxygen. For example, photosynthetic anaerobic bacteria, growing at the sunlit interface between mud and water, consume hydrogen sulfide and CO_2

during their photosynthetic activities and produce water instead of oxygen. There also may be diurnal changes in the kind of metabolism which may produce odd overall quotients. The correction of daytime photosynthesis with nighttime respiration may be less correct for one gas than for the other.

Another possible source of the PQ discrepancy may be the alkalinity difference between the shallow bay environments and oceanic waters; in some cases the chlorinity of the bay waters exceeded 30‰. In Figure 16 the correlation between chlorinity and titration alkalinity may be observed. The ratio of alkalinity to chloride in the waters of the bays studied did not follow the pattern in oceanic waters (dotted line). Other data have indicated the variance in ion ratios of the waters of these bays as compared to that of sea water (Hood, 1952). Because of these observations, it is unlikely that the constants used in computation of the carbon dioxide components are directly applicable. The extent of this variance is indeterminable at the present time.

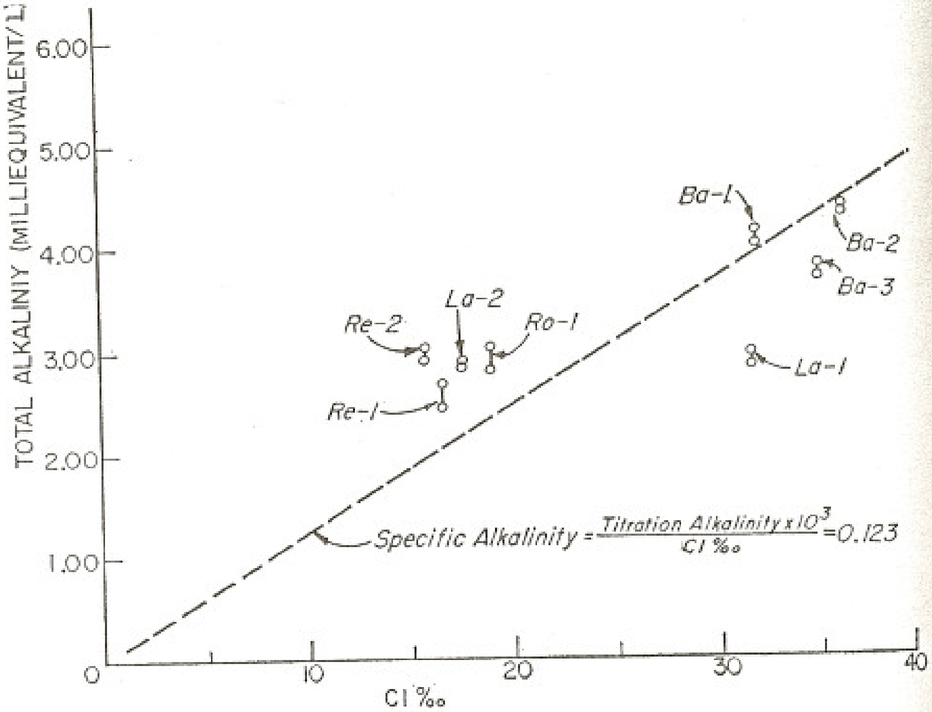

FIG. 16. Titration alkalinity as a function of chlorinity in Texas bays during summer and winter of 1957: Ba-1, Baffin Bay, July 26–27, 1957; Ba-2, Baffin Bay, Aug. 15–16, 1957; Ba-3, Baffin Bay, Dec. 22–23, 1957; Re-1, Redfish Bay, July 18–19, 1957; Re-2, Redfish Bay, Dec. 25–26, 1957; La-1, Laguna Madre, Aug. 1–2, 1957; La-2, Laguna Madre, Dec. 28–29, 1957; Ro-1 Rockport Basin, Aug. 5–6, 1957.

Calcium carbonate precipitation and dissolution from the bays would cause a marked diurnal fluctuation in alkalinity due to carbon dioxide components. Should precipitation occur, the PQ obtained should be greater than unity. Since the bays show PQ of less than unity and relatively constant titration alkalinity, it is not likely that active calcium carbonate precipitation was responsible for the odd photosynthetic quotient.

In the calculations presented above, with respect to the carbon dioxide components, it was assumed that the effect of diffusion processes was negligible for a very low partial pressure gas involved in a dynamic biological system. It should, however, be clearly indicated that the method for detection of carbon dioxide; i.e., measurement of pH and carbonate alkalinity followed by the necessary calculations to give carbon dioxide components, does not include molecular CO_2 or that part of the system involved in direct transfer across the sea surface. If respired CO_2 is molecular carbon dioxide, then in order for this to be measured by the analytical method used, it would be necessary for equilibrium to be established. Whether this occurs in the bays is not certain. Also, it is possible for organic complexes to form such as carbamino carboxylic acids (Hood, Smith, and Jeffery, 1958) which would tend to tie up the carbon dioxide in a form not measured by the method employed. However, in the case of the carbamino carboxylic acids, it would be expected that growing plants would utilize these acids as a source of carbon in preference to the inorganic forms.

The data presented for respiratory quotient (Table 3) is as difficult to interpret as the data for photosynthetic quotients. In general, the same reasoning used for photosynthetic quotient may be applied. Additional studies of the type conducted in this study but in different environments may lead to information which would help to explain the differences observed between oxygen and carbon dioxide metabolism.

Summary

1. Diurnal measurements of pH, alkalinity, boron and oxygen were made in four contrasting Texas bays in summer and winter. The oxygen curves were corrected for diffusion and the pH data computed as total carbon dioxide. From the rate of change graphs community photosynthesis and respiration were computed for carbon dioxide changes and compared to computations based on oxygen changes.

2. In situ pH and alkalinity measurements for estimation of primary production yield values of similar order of magnitude to oxygen methods, but the difference in productivity values measured with this method and with the diurnal oxygen method needs to be explained. Photosynthetic quotients (O_2/CO_2) of 0.3–1 were observed. A better understanding of the metabolism of organisms and the physical chemistry of both carbon dioxide and oxygen in the environment will be necessary before the differences between the two methods can be resolved.

3. It is evident that calcium carbonate precipitation is not actively involved in the diurnal changes in the carbon dioxide cycle, even though the fluctuation in the carbonate ion concentration (Fig. 14) is considerable. This indirect evidence indicates that calcium carbonate precipitation and solution do not follow inorganic solubility relationships.

4. Productivities in summer are 1.5 to 2 times that in winter.

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