title	Distribution and Stable-Isotope Composition of Carbon in San Francisco Bay
creator	E. C. Spiker and L. E. Schemel
Subject	ecosystem, water quality, water pollution
Description	Carbon :in Estuaries, Stable Carbon Isotopes in Estuaries, METHODS. RESULTS AND DISCUSSION. Distributions of Dissolved Inorganic Carbon in North Bay Waters, Distributions of Dissolved Inorganic Carbon in South Bay Waters, Suspended Particulate Carbon and Sediment Organic Carbon, SUMMARY, ACKNOWLEDGMENTS, LITERATURE CITED
Coverage	San Francisco Bay
Temporal	1960-1980
Source	Fifty-eighth Annual Meting of the Pacific Division of the American Association for the Advancement of Science, San Francisco State University, San Francisco, California, June 12-16, 1977
Date	1977-06-12
IsPartOf	SAN FRANCISCO BAY: THE URBANIZED ESTUARY Investigations into the Natural History of San Francisco Bay and Delta With Reference to the Influence of Man (195-213)
Publisher	Pacific Division of the American Association for the Advancement of Science c/o California Academy of Sciences Golden Gate Park San Francisco, California 94118
Issued	1979
Type	text
Format	8-1/2" x 11" bound document
Identifier	ISBN 0-934394-01-6
Language	English
Rghts	Copyrighted, Pacific Division of the American Association for the Advancement of Science

Abstract

Observed distributions of alkalinity, pCO_2 and $\delta^{13}C(\Sigma CO_2)$ indicate that dissolved inorganic carbon (DIC) was primarily supplied to San Francisco Bay by ocean, Delta, and municipal waste waters during the low Delta-outflow period from March 1976 to March 1977. Delta-derived alkalinity was typically about half that of ocean water and increased slightly with time. The pCO_2 values were highest (2 to 3 times the atmospheric value of approximately 325 ppm) in the Sacramento River and southern boundary of South Bay and decreased to nearatmospheric values seaward of the Golden Gate. The $\delta^{13}C(\Sigma CO_2)$ was lowest in the Sacramento River (approx.-10 %), increasing to marine values in the Gulf of the Farallones (approx.+2 %). Golden Gate values were approximately 2% less than those seaward, indicating that at least 10% of the $\Sigma CO2$ was biogenic and is apparently the product of respiration and the mineralization of organic matter in the Bay. South Bay alkalinity and pCO_2 levels increased southward, whereas $\delta^{13}C(\Sigma CO_2)$ and salinity decreased. Municipal waste discharged into South Bay is the most probable source of the excess biogenic CO2.

Distributions of particulate organic carbon (POC) in North Bay were influenced by *in situ* phytoplankton production and seaward dilution of riverine and estuarine Poe. Apparent depletions of pCO2 in North Bay coincide with chlorophyll α, POC, and $\delta^{13}C(\Sigma CO_2)$ increases. The $\delta^{13}C(POC)$ values during March 1977 approached those predicted for *in situ* algal production, suggesting that about 80 to 90% of the POC was produced in the seaward part of the estuary. *In situ* algal production was an important source of POC in the river. However, in the null-zone associated turbidity max/mum, less than two-thirds of the POC appears to be riverborne, the remaining one-third being produced in the estuary or associated with resuspended bottom sediment. South Bay suspended POC appears to be a mixture of resuspended bottom sediments, *in situ* produced POC and land-derived organic carbon. Based on $\delta^{13}C$ data, *Spartina* salt-marsh grass does not appear to be a significant source of detritus in the Bay.

The $\delta^{13}C$ of sediment total organic carbon (TOC) indicates that riverine carbon from the Delta is diluted in the Bay by estuarine and marine carbon. The suspended POC and sediment TOC $\delta^{13}C$-measurements approached marine values seaward of the Golden Gate.

DISTRIBUTION AND STABLE-ISOTOPE COMPOSITION OF CARBON IN SAN FRANCISCO BAY

ELLIOTT C. SPIKER AND LAURENCE E. SCHEMEL
U. S. Geological Survey National Center, Reston, VA 22092
U. S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025

Observed distributions of alkalinity, pCO_2 and $\delta^{13}C(\Sigma CO_2)$ indicate that dissolved inorganic carbon (DIC) was primarily supplied to San Francisco Bay by ocean, Delta, and municipal waste waters during the low Delta-outflow period from March 1976 to March 1977. Delta-derived alkalinity was typically about half that of ocean water and increased slightly with time. The pCO_2 values were highest (2 to 3 times the atmospheric value of approximately 325 ppm) in the Sacramento River and southern boundary of South Bay and decreased to near-atmospheric values seaward of the Golden Gate. The $\delta^{13}C(\Sigma CO_2)$ was lowest in the Sacramento River (approx. -10 $^{\circ}/oo$), increasing to marine values in the Gulf of the Farallones (approx. +2 $^{\circ}/oo$). Golden Gate values were approximately 2 $^{\circ}/oo$ less than those seaward, indicating that at least 10% of the ΣCO_2 was biogenic and is apparently the product of respiration and the mineralization of organic matter in the Bay. South Bay alkalinity and pCO_2 levels increased southward, whereas $\delta^{13}C(\Sigma CO_2)$ and salinity decreased. Municipal waste discharged into South Bay is the most probable source of the excess biogenic CO_2.

Distributions of particulate organic carbon (POC) in North Bay were influenced by *in situ* phytoplankton production and seaward dilution of riverine and estuarine POC. Apparent depletions of pCO_2 in North Bay coincide with chlorophyll *a*, POC, and $\delta^{13}C(\Sigma CO_2)$ increases. The $\delta^{13}C(POC)$ values during March 1977 approached those predicted for *in situ* algal production, suggesting that about 80 to 90% of the POC was produced in the seaward part of the estuary. *In situ* algal production was an important source of POC in the river. However, in the null-zone associated turbidity maximum, less than two-thirds of the POC appears to be riverborne, the remaining one-third being produced in the estuary or associated with resuspended bottom sediment. South Bay suspended POC appears to be a mixture of resuspended bottom sediments, *in situ* produced POC and land-derived organic carbon. Based on $\delta^{13}C$ data, *Spartina* salt-marsh grass does not appear to be a significant source of detritus in the Bay.

The $\delta^{13}C$ of sediment total organic carbon (TOC) indicates that riverine carbon from the Delta is diluted in the Bay by estuarine and marine carbon. The suspended POC and sediment TOC $\delta^{13}C$-measurements approached marine values seaward of the Golden Gate.

The importance of carbon in estuaries is fundamental because estuaries are valuable environments for carbon fixation by aquatic plants and this estuarine production is essential in maintaining some fisheries (Woodwell et al. 1973). The San Francisco Bay estuarine system (Fig. 1) receives carbon from natural sources as well as large amounts from the surrounding urban area, primarily in the form of municipal wastes. In this chapter, we discuss the sources and dynamics of carbon in San Francisco Bay waters by presenting distributions of some important organic and inorganic forms and their stable carbon isotope compositions.

Carbon in Estuaries

Dissolved inorganic carbon (DIC) in estuarine waters comprises dissolved carbon dioxide (CO_2) and the ionic species of dissociated carbonic acid:

$$H_2O + CO_2 \overset{K_1}{\rightleftharpoons} H^+ + HCO_3^- \overset{K_2}{\rightleftharpoons} 2H^+ + CO_3^{2-} \quad \text{(eq. 1)}.$$
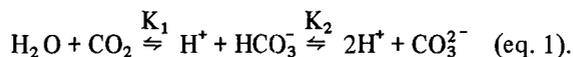
Concentrations of these species depend on constants, K_1 and K_2, which are temperature and salinity dependent. A detailed discussion of DIC in estuaries is presented by Mook and Koene (1975).

DIC is most commonly described in terms of four measurable quantities: alkalinity (A), total CO_2 (ΣCO_2), negative logarithm of the hydrogen-ion activity (pH), and partial pressure of the CO_2 dissolved in the water (pCO_2). Alkalinity is the amount of hydrogen ion, in milliequivalents per liter (meq·liter^{-1}), required to convert carbonic and weaker acids to their undissociated forms:

$$A = C_{HCO_3^-} + 2C_{CO_3^{2-}} + C_{B(OH)_4^-} + C_{(OH^--H^+)} + C_{ma} \quad \text{(eq. 2)}.$$

The boric acid concentration ($C_{B(OH)_4^-}$) is low in river water and it increases to account for about 4 to 5% of the alkalinity in sea water (Skirrow 1975). The excess hydroxide concentration, $C_{(OH^--H^+)}$, is very low in the pH range naturally occurring in estuaries and can be ignored. The alkalinity due to other miscellaneous weak acids and bases, C_{ma}, can be important but, in general, over 95% of the alkalinity is attributable to carbonate and bicarbonate ions, which comprise all but a few percent of the total DIC in estuarine waters (eq. 1).

Although ΣCO_2, the total amount of CO_2 which can be removed from a solution after acidification, can be measured, in practice A is more easily determined to a higher degree of accuracy (Skirrow 1975). Furthermore, A is perhaps a more useful measurement because it is not affected by the addition or removal of molecular CO_2, as occurs during photosynthesis. In an estuary with a single large freshwater inflow, mixing with ocean water can result in a conservative (linear) alkalinity-salinity distribution, if the river and ocean compositions remain constant over the time necessary for water to mix through the estuary (water-replacement time). When internal sources or sinks are significant, a nonlinear distribution occurs and the degree of nonlinearity is related to their relative importance (Liss 1976). Nonconservative alkalinity distributions can result from precipitation or dissolution of carbonate minerals and from processes which release acids or bases. For example, utilization of ammonium or nitrate ions by phytoplankton during photosynthesis and other biochemical processes can produce measurable effects (Brewer and Goldman 1976).

The pH and pCO_2 of estuarine water will change if molecular CO_2 is added or removed. For example, CO_2 respired by organisms dissociates (eq. 1), increasing the hydrogen-ion activity and thus lowering the pH. Similarly, pCO_2 will increase because it is directly related to the concentration of dissolved CO_2. From freshwater to seawater, the magnitude of such a pH or pCO_2 change will vary primarily because of the salinity and temperature dependence of the dissociation constants and variations in the chemical composition of the water. The measurable quantities of the CO_2 system can be estimated if salinity, temperature, and any two of these four variables are known (Skirrow 1975). Using two salinity-alkalinity couples typical of the Bay, calculated changes in pH and ΣCO_2 are presented in Table 1 for increases in pCO_2 of 100 ppm (parts per million of 1 atmosphere). The decreases in pH correspond to relatively small increases in ΣCO_2. At lower salinity and alkalinity the changes in pH or pCO_2 represent smaller changes in CO_2.

The high sensitivities of pH and pCO_2 to changes in CO_2 make them excellent choices for studying photosynthetic processes in estuaries (Park 1969). Considering the precisions achievable for these measurements, very small changes are detectable. For the examples in Table 1, ±0.003
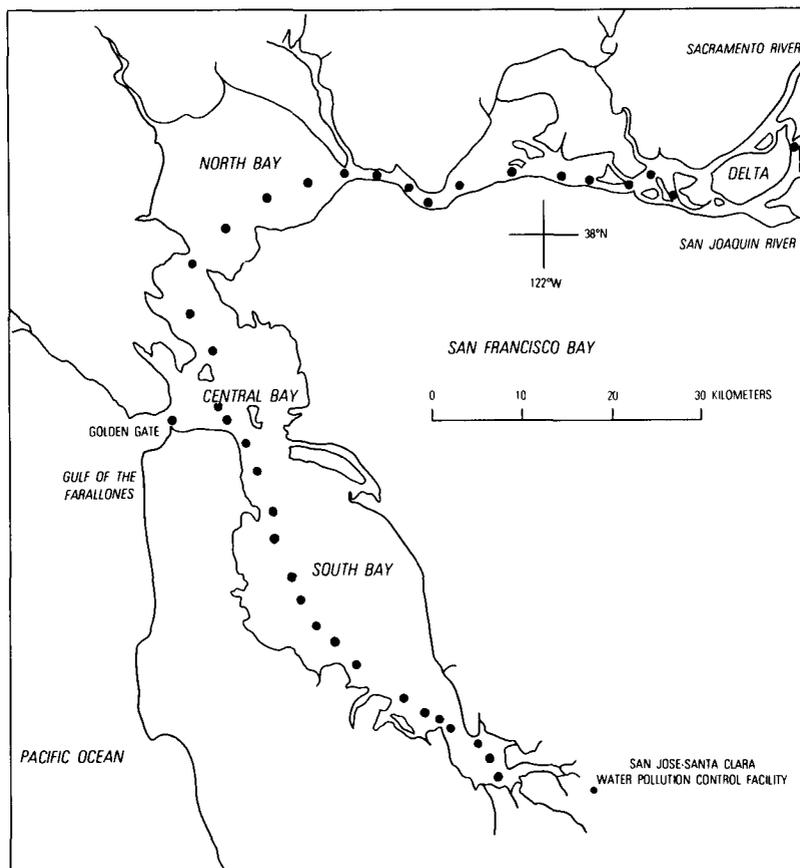
Fig. 1. The San Francisco Bay system and adjacent Pacific Ocean.

pH is equivalent to ±0.02 to 0.6 μM·liter^{-1} CO_2 and ±3.0 ppm pCO_2 corresponds to ±0.2 to ±1.0 μM·liter^{-1} CO_2. Analytically, pCO_2 offers some advantages in estuaries. Uncertainties in electrometric pH measurements can arise from variation of ionic strength, which is salinity and temperature dependent. Measurements of pCO_2 are not directly affected by this and analytical methods are adaptable to automated and continuous measurement (Schemel and Dedini 1979a).

Observed pCO_2 levels in rivers and coastal waters indicate that estuaries are typically oversaturated with CO_2. For example, pCO_2 was reported in excess of 1000 ppm in the Columbia River (Park et al. 1969) and 2000 ppm in the Hudson River (Hammond 1975). Values exceeding the atmospheric level (approx. 325 ppm) in coastal waters are often the result of mixing with river water (Kelley and Hood 1971; Gordon et al. 1973). The high pCO_2 in river and estuarine waters can be attributed to the mineralization of organic carbon, which is more abundant in these environments than in the ocean (Head 1976).

Following the approach taken by Mook and Koene (1975) in discussing pH distributions in estuaries, conservative pCO_2 distributions can be calculated, assuming that A and ΣCO_2 are conserved. Although the biological reactivity and other properties of CO_2 are such that conservative distributions might rarely be observed, these estimates can be useful in evaluating the relative importance of processes involving CO_2 in estuaries. The family of curves in Figure 2 illustrates the results of conservatively mixing ocean and river waters at constant temperature. Longitudinal

TABLE 1. CALCULATED CHANGES IN pH AND ΣCO_2
CORRESPONDING TO pCO_2 INCREASES FROM 300 TO 400 PPM
AND 900 to 1000 PPM AT TWO SALINITIES AND TEMPERATURES.[a]

Salinity (°/oo)	Temperature °C	Alkalinity (meq·liter⁻¹)	pCO₂ 300 to 400 ppm		pCO₂ 900 to 1000 ppm	
			pH change	ΣCO_2 change (mM·liter⁻¹)	pH change	ΣCO_2 change (mM·liter⁻¹)
6	10	1.48	-0.118	+0.018	-0.044	+0.008
6	20	1.48	-0.114	+0.020	-0.045	+0.008
24	10	1.96	-0.112	+0.036	-0.044	+0.012
24	20	1.96	-0.107	+0.042	-0.042	+0.011

[a] Calculations were made using expressions for the dissociation constants of carbonic and boric acids and the solubility of CO_2 based on the data of Buch (1951), Lyman (1956), and Weiss (1974).

temperature variations will, of course, influence the shapes of the curves. Net removal of CO_2 by processes operating in the estuary would cause the observed levels to be lower relative to the mixing curve, while CO_2 sources, such as respiration and mineralization of organic matter, would increase the pCO_2 levels.

Organic carbon is an important but difficult component to fully evaluate in estuarine waters. Measurements of organic carbon are normally made on two fractions, dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC and POC are separated by filtration; POC is the fraction greater than about 0.5 to 1.0 μm in diameter (Parsons 1975). The concentrations of DOC and POC are similar in estuaries (Head 1976). POC is composed of both living organisms, such as plankton, and detrital (nonliving) material. The phytoplankton POC fraction is often estimated as the chlorophyll a concentration multiplied by an empirical factor, the carbon to chlorophyll a ratio. Because this ratio often varies (Banse 1974), for practical purposes, the chlorophyll a concentration alone is used as an indicator of relative phytoplankton POC abundance.

Riverine POC concentrations are typically higher than those in the marine environment (Head 1976). Although POC abundance generally decreases between the river and ocean because of dilution and deposition, resuspension of bottom sediments, primarily by wind-induced turbulence, may also influence local POC abundance in the Bay. Phytoplankton production can also be a major factor contributing to the seasonal abundance of POC in estuaries (Biggs and Flemer 1972). Seasonal POC data (Schemel and Dedini 1979b) indicate that this is important in the Bay.

Stable Carbon Isotopes in Estuaries

Differences in the thermodynamic and kinetic properties of the stable carbon isotopes, ^{12}C and ^{13}C, result in measurable isotope-composition variations in natural substances. For example, carbonate minerals contain more ^{13}C than organic matter produced by photosynthesis. The stable carbon isotope composition is expressed as the difference in parts per thousand (°/oo) between the substance and the PDB reference standard (Craig 1957):

$$\delta^{13}C(°/oo) = \frac{(R_s - R_{st}) \times 10^3}{R_{st}} \quad (eq.\ 3)$$

R_s and R_{st} are the $^{13}C/^{12}C$ ratio of the substance and standard, respectively. A δ-value of -10 °/oo means that the $^{13}C/^{12}C$ ratio of the substance is 10 °/oo lower than that of the standard.
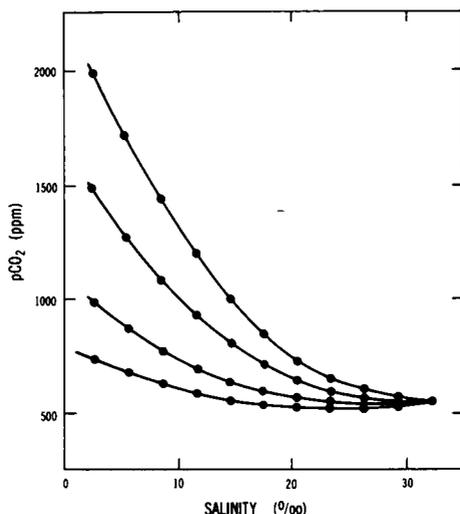
Fig. 2. Calculated conservative pCO_2 distributions for conditions typical of San Francisco Bay. Values of pCO_2 are estimated assuming conservation of ΣCO_2 and alkalinity ($A = 1.174 + 0.034$ [S $°/oo$]) at $10°C$, using expressions for the dissociation constants of carbonic and boric acids and the solubility of CO_2 based on the data of Buch (1951), Lyman (1956), and Weiss (1974).

Many processes operating in aqueous systems produce changes in the stable carbon isotope composition of DIC and POC. An observed $\delta^{13}C$ of the total dissolved inorganic carbon, $\delta^{13}C(\Sigma CO_2)$, is the product of the sources and sinks of carbon and the result of isotope fractionation occurring between solid, dissolved, and gaseous phases (Mook et al. 1974; Wigley et al. 1978). Major sources are biogenic carbon from the mineralization and respiration of organic matter (approx. -20 to -30 $°/oo$), atmospheric carbon dioxide (approx. -7 $°/oo$), and carbon derived from the dissolution of carbonate minerals (approx. 0 $°/oo$). The effect of adding carbon from an identifiable source can be estimated by a mass balance calculation,

$$\delta_p = \delta_i f + \delta_x(1\text{-}f), \quad (eq.\ 4)$$

where δ_i, δ_p and δ_x are the $\delta^{13}C$ of the initial solution, the product, and the input carbon, respectively, and f and (1-f) are the fractions of the initial and input carbon sources.

The isotopic effects of processes involving fractionating outputs, such as photosynthetic utilization of CO_2 or outgassing, can be described by Rayleigh distillation equations for equilibrium (see Hendy 1971; Claypool and Kaplan 1974; Katz et al. 1977). For example, preferential utilization of ^{12}C during photosynthesis results in a ^{13}C enrichment of the residual solution, thus increasing the $\delta^{13}C(\Sigma CO_2)$. The isotopic composition resulting from a single output is estimated by:

$$\delta_r = [\delta_i + 1000\ (1\text{-}f)\ ^{(1/a_{so}\text{-}1)}] - 1000 \quad (eq.\ 5)$$

where δ_r and δ_i are the $\delta^{13}C$ of the residual and initial solution; f is the fraction of carbon removed from the solution, a_{so} is the fractionation factor between solution(s) and the output species(o): $a_{so} = R_s/R_o$, where $R = {}^{13}C/{}^{12}C$ of each. The composite effect of multiple sources and sinks in aqueous systems is discussed by Wigley et al. (1978).

The $\delta^{13}C(\Sigma CO_2)$ of fresh water ranges from zero to as low as -25 $°/oo$. Dissolution of carbonate minerals produces a solution with an intermediate $\delta^{13}C$ value of about -11 $°/oo$ (Fig. 3).
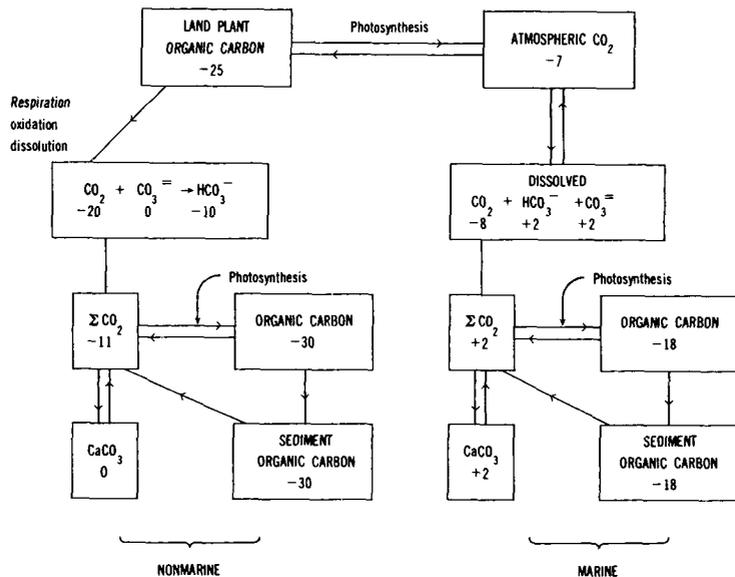
Fig. 3. Major carbon cycle oxidation and reduction processes and their attendant isotope fractionation effects.

More negative values are due mostly to the addition of biogenic CO_2, and more positive values may be a result of photosynthetic activity and atmospheric exchange (Broecker and Walton 1959; Oana and Deevey 1960; Parker and Calder 1970; Mook 1970; Rau 1978). In lakes with sufficient water-residence time, atmospheric exchange may result in a ^{13}C enrichment towards equilibrium $\delta^{13}C$ values (approx. +2 $°/oo$), as in the surface ocean (Kroopnick 1974). Thus, seasonal trends are controlled by variations in biologic processes, atmospheric exchange, and the surface and ground-water base runoffs.

The $\delta^{13}C(\Sigma CO_2)$-salinity distribution has been observed to be near-conservative in the Hudson and Mississippi estuaries (Sackett and Moore 1966), and in the Western Scheldt estuary (Mook 1970). The forms of $\delta^{13}C$ conservative mixing curves in estuaries depend on the concentrations of carbon, C, and the $\delta^{13}C$, δ, in the river and ocean waters, $C_r\delta_r$ and $C_o\delta_o$, respectively. The $\delta^{13}C$ of the conservative mixture is:

$$\delta \text{mix} = \frac{C_r\delta_r f + C_o\delta_o(1\text{-}f)}{C_{\text{mix}}} \quad \text{(eq. 6)}$$

The fraction of river (fresh), f, water is calculated from the salinity.

The $\delta^{13}C$ of estuarine and near-shore surface-sediment total organic carbon, $\delta^{13}C$ (TOC), and suspended particulate organic carbon, $\delta^{13}C$ (POC), increases from the river (approx. -27 $°/oo$) to ocean (approx. -19 $°/oo$). This is generally attributed to the mixing of carbon from land plants and freshwater algae (approx. -25 to -30 $°/oo$) with estuarine and marine algae (approx. -12 to -25 $°/oo$; Sackett and Thompson 1963; Hunt 1970; Shultz and Calder 1976; Gearing et al. 1977). The $\delta^{13}C$ of algae produced in the estuary is primarily related to the isotopic composition of the CO_2 source and the isotopic fractionation resulting from photosynthesis. The observed fractionation between ΣCO_2 and cell carbon may have a wide range (approx. -13 to -33 $°/oo$), because of growth-rate differences, temperature, and species (see Wong and Sackett 1978). In order to approximate the importance of estuarine primary production, we assume an apparent photosynthetic

200

fractionation effect of -19 °/oo. Thus, if the $\delta^{13}C(\Sigma CO_2)$ varies (river to ocean) from -10 to +2 °/oo, then, the $\delta^{13}C$ of algae produced *in situ* would vary from -29 to -17 °/oo. Alternatively, the $\delta^{13}C(POC)$ distribution may be related to conservative dilution (eq. 6). Predicted $\delta^{13}C(POC)$ distributions based on conservative dilution and algal production are a reference for estimating the importance of these processes as well as identifying inputs from point sources and resuspended bottom sediments. Terrestrial organic carbon (approx. -25 °/oo), and *Spartina* salt-marsh grasses (approx. -13 °/oo) are two point sources of detritus that can be identified (Haines 1977; Fry et al. 1977).

METHODS

Measurements were made in San Francisco Bay during March and September 1976 and March 1977 at locations established in the channels (Fig. 1). Additional measurements were made in the Gulf of the Farallones during September 1976 and in North Bay during January 1976. Near-surface sediments were collected with a van Veen sampler in August 1973. Specific sampling locations, numerical values for the measurements, and a more detailed discussion of the analytical methods are found in Schemel et al. (1978).

Water samples were taken with a submersible pump or pumped through a hull fitting near the bow of the vessel at a 2-m depth. Salinity, temperature, and pCO_2 of the pumped water were continuously measured (Schemel and Dedini 1979a; Table 2). Salinity was measured with an induction salinometer on the vessel. *In situ* temperatures were measured at the submersible pump and at the hull-fitting intake.

The pCO_2 was estimated by continuously equilibrating a circulating volume of air with the sample-water flow and measuring the pCO_2 of the dried air with an infrared analyzer (Broecker and Takahashi 1966; Gordon and Park 1972). The accuracy of the method was tested by comparing measured values with values calculated from discrete pH and alkalinity measurements. Results compare within 6% (Table 3).

Discrete samples were collected for chlorophyll *a, A*, POC, and $\delta^{13}C$ analyses. Chlorophyll *a* was determined by the spectrophotometric method described by Strickland and Parsons (1972). *A* was determined by measuring the pH of a 50-ml filtered sample after addition of 0.010N HCL (Strickland and Parson 1972). POC samples were collected on precombusted glass-fiber filters and

TABLE 2. PRECISION AND ESTIMATED ACCURACY OF MEASUREMENTS.

Parameter	Precision	Estimated Accuracy
Salinity	±0.01 °/oo	±0.05 °/oo
Temperature	±0.1°C	±0.2°C
pCO_2	±0.3% of full scale	±5% of value
Chlorophyll *a*	±8% of value	not estimated
Particulate organic carbon	±5 μM (approx. ±20 μM C·liter^{-1})	not estimated
Alkalinity	±0.02 meq·liter^{-1}	not estimated
$\delta^{13}C$	±0.2 °/oo	not estimated

TABLE 3. COMPARISON OF MEASURED AND CALCULATED pCO_2.[a]

Date	Salinity ($^\circ/oo$)	Calculated pCO_2 (ppm)	Measured pCO_2 (ppm)	(% of calculated)
04Mar76	26.3	502	532	106
09Mar76	29.8	432	434	100
10Mar76	29.0	445	442	99
30Mar76	28.5	514	536	104
18Mar76	13.2	596	617	104
23Mar76	4.5	703	672	96
25Mar76	4.4	651	645	99
24Aug76	30.0	730	689	94
26Aug76	30.1	639	655	103
31Aug76	4.4	948	910	96
02Sep76	5.1	818	831	102
21Sep76	30.5	1218	1212	100
23Sep76	32.5	757	753	99

[a] The pCO_2 was calculated from discrete pH and alkalinity measurements using expressions for the dissociation constants of carbonic and boric acids and the solubility of CO_2 based on the data of Buch (1951), Lyman (1956), and Weiss (1974).

analyzed by a modification of the DOC method of Menzel and Vaccaro (1964; Schemel and Dedini 1979b).

Water samples for $\delta^{13}C(\Sigma CO_2)$ measurements were pressure-filtered (5 psi nitrogen) through Whatman GF/C glass-fiber filters directly into 500-ml bottles, poisoned with 2 ml saturated $HgCl_2$ solution, sealed, and refrigerated. CO_2 was extracted from acidified samples on a vacuum line. POC for $\delta^{13}C$ analyses was collected on precombusted GF/C glass-fiber filters and frozen. Near-surface sediment samples for $\delta^{13}C(TOC)$ analyses were stored in plastic cups, refrigerated, then dried at 50°C. Carbonate was removed from POC and sediment samples by acidification with HCl. Samples were combusted in a vacuum line, and the CO_2 was purified before isotopic analysis (method after Craig 1953; Degens 1969). The $^{13}C/^{12}C$ ratio of the CO_2 was measured with a 15-cm, 60°-sector ratio mass spectrometer.

RESULTS AND DISCUSSION

Delta outflow was abnormally low during most of the study period (Fig. 4; Conomos 1979). As a result, salinity was higher in the Bay, large segments of the Delta contained brackish water, and the null zone (Peterson et al. 1975a; Arthur and Ball 1979; Conomos 1979) moved landward. Water replacement time in North Bay was probably about 6 to 12 weeks, except in January 1976, a period of higher river flow, when water replacement time was about 3 weeks or less (Peterson et al. 1978). Because removal (flushing) of accumulated dissolved constituents from South Bay depends, in part, on the winter increase in Delta outflow (Conomos 1979), this flushing was probably minimal between September 1976 and March 1977.

Our observations from North Bay are related to salinity; the inner estuary extends from the confluence of the Sacramento and San Joaquin rivers to the region of mid-salinity (approx. 15
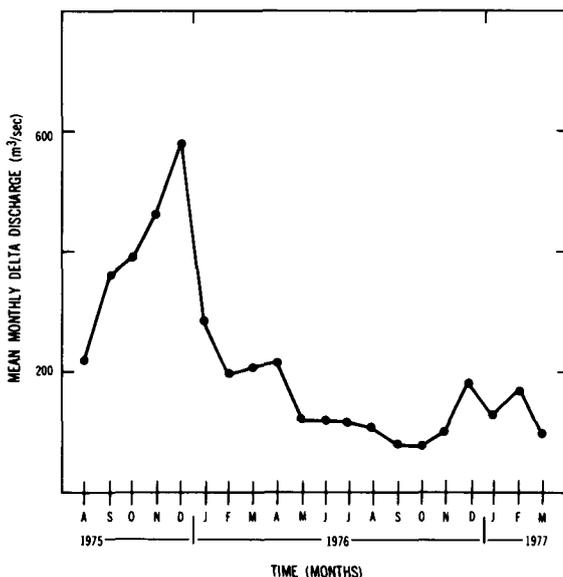
Fig. 4. Mean monthly Delta outflow ($m^3 \cdot s^{-1}$) from August 1975 through March 1977. Data from U. S. Bureau of Reclamation.

$^\circ/oo$), and the outer estuary extends from the mid-salinity region to the Golden Gate. Upstream measurements (termed river) refer to Sacramento River unless otherwise noted. Observations in South Bay are related to distance from the Golden Gate.

Distributions of Dissolved Inorganic Carbon in North Bay Waters

Although variable, the alkalinity of Delta outflow was about half that of sea water (Fig. 5). Delta-outflow alkalinity was higher in March 1977 than March 1976, indicating a subtle but general increase in river-water alkalinity over the extended period of low outflow. The alkalinity distribution in North Bay was near-conservative in March 1976 and 1977 and September 1977, which suggests that the alkalinities of Delta outflow and ocean water were relatively invariant for at least 6 to 12 weeks, the time necessary for river water to mix through the estuary. Thus, for the purposes of this discussion, we make the general assumption that Delta outflow and ocean water are the major contributors to the DIC distribution in North Bay and that the distribution would be conservative if influenced by mixing alone. The net effects of other supply and removal processes operating in North Bay might then be indicated by pCO_2 or $\delta^{13}C(\Sigma CO_2)$ anomalies relative to conservative mixing of river and ocean waters.

While samples for $\delta^{13}C(\Sigma CO_2)$ analysis were taken in San Francisco Bay during March 1976 and 1977 and September 1976 (Figs. 6, 7, 8), the only Gulf of the Farallones sampling occurred during September 1976 (Fig. 7). Marine values were observed in the Gulf of the Farallones, but values were significantly lower at the Golden Gate even though salinity was only 1.4 $^\circ/oo$ lower in the near-surface water. In addition, pCO_2 was over 200 ppm higher at the Golden Gate than seaward. Golden Gate $\delta^{13}C(\Sigma CO_2)$ values (2- and 30-m depth) are about 2 $^\circ/oo$ less than predicted by conservative mixing of river and ocean waters, and suggest that about 10% of the ΣCO_2 is biogenic (eq. 4). Thus, processes which supply biogenic CO_2, such as respiration and the mineralization of organic matter, are effective in influencing the DIC in even high-salinity water at the Golden Gate.

The $\delta^{13}C(\Sigma CO_2)$ values at the Golden Gate were also lower than marine values in March 1976 and 1977; this may be typical of low Delta-outflow conditions. In normal years, when river flow is higher and water replacement time is shorter, the isotopic distribution may indicate a smaller biogenic fraction or may even appear conservative. Although the dynamic nature of the sources and sinks are not illustrated by the near-conservative ΣCO_2 distribution (Peterson 1979), isotopic data suggest that biogenic CO_2 produced within the estuary is exchanging with the DIC before it escapes to the atmosphere. If isotopic equilibrium exists between the DIC species, then there are two opposing effects to consider. Outgassing CO_2 is isotopically lighter (more negative $\delta^{13}C$) than the parent solution by about 9 °/oo (Mook et al. 1974), thus the $\delta^{13}C$ of the residual solution is increased (eq. 5). However, the input of biogenic CO_2, which is much lighter (approx. -20 to 25 °/oo) will more effectively decrease the $\delta^{13}C(\Sigma CO_2)$. Values at the Golden Gate indicate that the supply of biogenic CO_2 is significant relative to the effect of outgassing. In addition, if isotopic
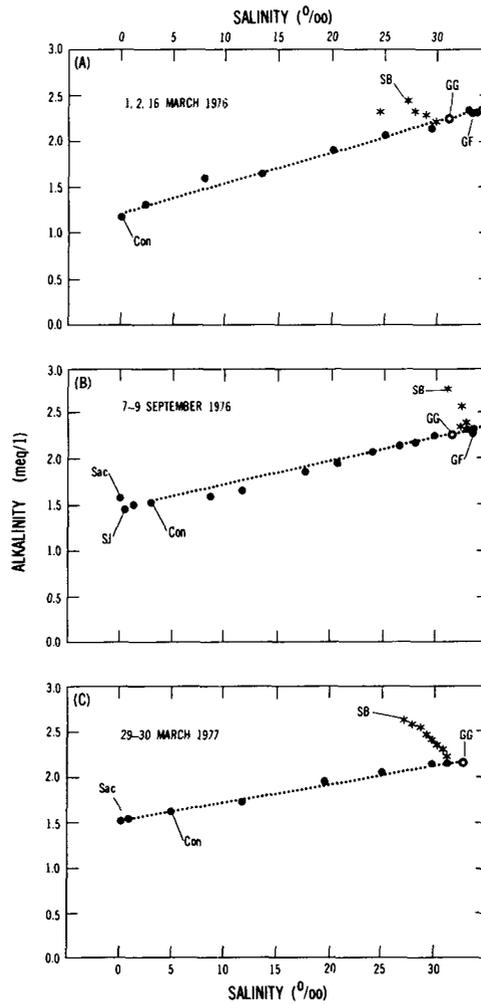

Fig. 5. Alkalinity distributions in San Francisco Bay and the Gulf of the Farallones; March 1976 (A), September 1976 (B), and March 1977 (C). Symbols: Sac, Sacramento River; Con, confluence of Sacramento and San Joaquin rivers; GG, Golden Gate; SB, South Bay; GF, Gulf of the Farallones; SJ, San Joaquin River.

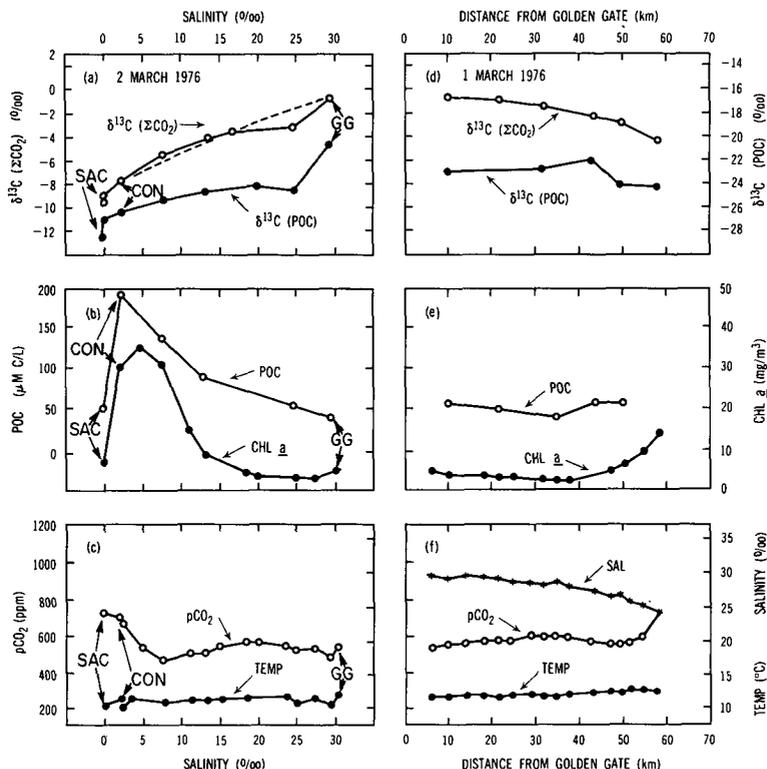Fig. 6. Temperature (TEMP), salinity (SAL), chlorophyll a (CHL a), pCO_2, particulate organic carbon (POC), $\delta^{13}C(\Sigma CO_2)$, and $\delta^{13}C(POC)$ in North Bay, 2 March 1976 (a, b, c) and South Bay, 1 March 1976 (d, e, f). Estimated conservative mix distribution is indicated by dashed line. Symbols: Sac R, Sacramento River; Con, confluence of Sacramento and San Joaquin rivers; GG, Golden Gate.

exchange with the atmosphere is significant, an estimate of the biogenic carbon input would be larger (see Wigley et al. 1978).

Estuarine CO_2 sources may also affect North-Bay DIC during times of higher Delta outflow. January is typically a period of low mean wind speed, low water temperature and high river flow (Conomos 1979). During January 1976, pCO_2 levels slightly exceeded that predicted by conservative mixing (Fig. 9), suggesting that CO_2 sources exceeded CO_2 sinks in North Bay.

Biological processes, particularly photosynthesis, can produce large pCO_2 variations in only a few days, which is considerably less than the water replacement time in North Bay during our observations. Phytoplankton biomass, as indicated by chlorophyll a concentration, was relatively high in the estuary in March 1976 (Fig. 6). Within the 2-wk period between the January and March samplings, pCO_2 levels became depleted by 200 to 400 ppm near the chlorophyll a maximum. This depression corresponds to an uptake of about 15 to 30 μM·liter^{-1} CO_2. Similarly, CO_2 uptake estimated from the $\delta^{13}C(\Sigma CO_2)$ anomaly is about 45 ± 20 μM·liter^{-1} CO_2 (eq. 5), assuming that the $\delta^{13}C$ of the biogenic (utilized) CO_2 is -26 °/oo.

During March 1977, chlorophyll a was abundant in the outer estuary (Fig. 8). In this region, pCO_2 was depleted about 250 ppm below that estimated by conservative mixing, corresponding to about 75 μM·liter^{-1} CO_2. Similarly, the high $\delta^{13}C(\Sigma CO_2)$ values indicate a net utilization of about

205

70 ± 20 μM·liter^{-1} CO_2, if the $\delta^{13}C$ of the biogenic carbon is -20 °/oo (eq. 5).

Chlorophyll a was less abundant and the effects of net photosynthesis were less apparent in North Bay during September 1976 (Fig. 7).

Distributions of Dissolved Inorganic Carbon in South Bay

Salinity in South Bay normally decreases southward because of dilution by municipal waste and local streams (Conomos 1979; Conomos et al. 1979). The effectiveness of these sources in influencing South-Bay water increases southward because the sectional volume of the basin decreases southward and the degree of mixing with North Bay water probably decreases southward.

In contrast to North Bay, alkalinity typically increased with decreasing salinity in South Bay (Fig. 5). South-Bay pCO_2 was about two times the atmospheric level during March 1976 and 1977 and over three times the atmospheric level in the southernmost reach during September 1976 (Figs. 6, 7, 8). The $\delta^{13}C(\Sigma CO_2)$ typically decreased southward, indicating that the carbon source is biogenic. Analysis of waste water from the San Jose-Santa Clara water pollution control facility (Fig. 1), the major single source of municipal waste in South Bay, was 4.0 mM·liter^{-1} ΣCO_2 with a $\delta^{13}C$ value of -13 °/oo (sampled November 1977). Thus, it appears that the abundance of DIC in South Bay primarily relates to the increasing waste-enrichment of waters to the south.
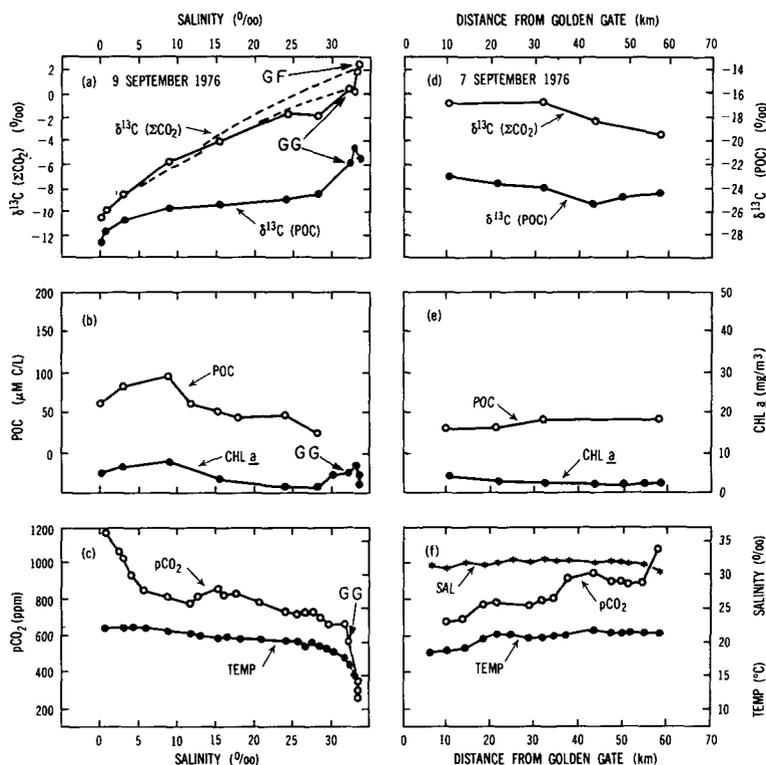

Fig. 7. Temperature (TEMP), salinity (SAL), chlorophyll a (CHL a), pCO_2, particulate organic carbon (POC), $\delta^{13}C(\Sigma CO_2)$, and $\delta^{13}C(POC)$ in North Bay, and the Gulf of the Farallones, 8, 9 September 1976 (a, b, c) and South Bay, 7 September 1976 (d, e, f). Symbols: GG, Golden Gate; GF, Gulf of the Farallones. Estimated conservative mix distributions are indicated by dashed lines.
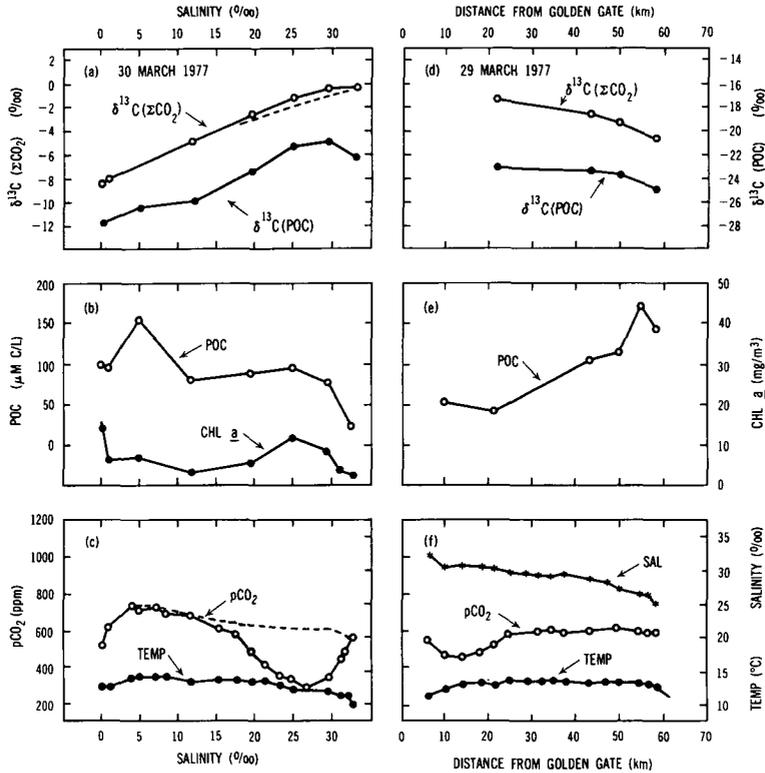
Fig. 8. Temperature (TEMP), salinity (SAL), chlorophyll a (CHL a), pCO_2, particulate organic carbon (POC), $\delta^{13}C(\Sigma CO_2)$, and $\delta^{13}C(POC)$ in North Bay, 30 March 1977 (a, b, c), and in South Bay, 19 March 1977 (d, e, f). Estimated conservative mix distributions are indicated by dashed lines.
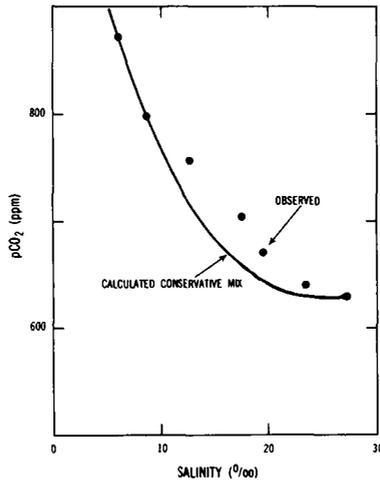

Fig. 9. Near-surface (2m) pCO_2 in North Bay, 27 January 1976. Conservative mix distribution was estimated using the alkalinity and pCO_2 values near the confluence of the Sacramento and San Joaquin rivers and at a salinity of 27.3 °/oo.
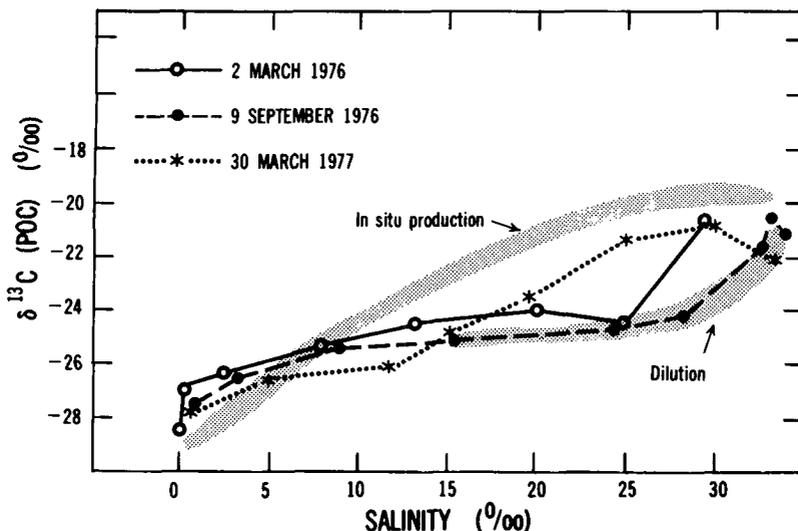
Fig. 10. δ^{13}C(POC) with respect to salinity in North Bay, 2 March 1976 (−o−), 9 September 1976 (--●--), and 30 March 1977 (·····*·····). Estimated distributions are based on *in situ* production and dilution models.

Suspended Particulate Carbon and Sediment Organic Carbon

In North Bay, an estuarine circulation cell maintains a turbidity (suspended particle) maximum in the null zone (Arthur and Ball 1979; Conomos 1979). The phytoplankton maximum associated with the null zone is maintained by advective transport and *in situ* phytoplankton production in this region of longer advective water-replacement time (Peterson et al. 1975a, b).

In general, POC abundance in North and South bays correlates well with chlorophyll *a* abundance (Figs. 6, 7, 8) indicating that phytoplankton production is an important source. Seaward of the river or apparent phytoplankton-POC sources in North Bay, concentrations decrease, indicating dilution and possibly deposition of POC. The δ^{13}C(POC) is particularly useful in evaluating the relative importance of processes and identifying major POC sources. Observed δ^{13}C(POC) distributions in North Bay are related to theoretical distributions based on conservative dilution seaward of the turbidity maximum and production by phytoplankton (Fig. 10). The distribution resulting from dilution is a concave-upward curve (eq. 6) because of the high POC concentration at low salinity. The distribution which would result from *in situ* algal production alone is estimated from the δ^{13}C(ΣCO_2) distribution and an average photosynthetic fractionation of -19 ‰. The δ^{13}C(ΣCO_2) varies from -10 to +2 ‰ over the salinity range 0 to 35 ‰, thus the estimated δ^{13}C(POC) will vary from -29 to -17 ‰.

In the outer estuary during March 1977, the δ^{13}C(POC) maximum, coincident with pCO_2 depletion and increased chlorophyll *a* and POC abundance, approached values predicted for *in situ* production (Fig. 10). An estimated 80 to 90% of the POC was produced locally (eq. 4). This was not observed when phytoplankton were less abundant in September and March 1976. Then, the distributions appeared to be primarily the result of dilution, with possible contributions from locally-resuspended bottom sediment.

The δ^{13}C(POC) values in the river were 2 to 4 ‰ less than those of land plants (approx. -25 ‰), indicating algal production (approx. -29 ‰) was an important source during all our samplings. The values in the turbidity maximum were several ‰ higher than the values upstream, but were similar to the δ^{13}C(TOC) in the bottom sediment (Fig. 11). The observed values indicate

less than two-thirds of the POC in the turbidity maximum was riverborne (eq. 4) and, therefore, that the remainder was produced in the estuary or derived from resuspended sediments.

The spatial distribution of sediment δ^{13}C(TOC) is consistent with known sources of carbon in the Bay. Riverine carbon dominates the region landward of the null zone, and seaward there is a near-linear δ^{13} increase with distance to marine carbon values in the Gulf of the Farallones (Fig. 11). The δ^{13}C(TOC) in bottom sediments is more negative than the δ^{13}C(POC) observed in the water column in both North and South bays. This can be interpreted as a larger fraction of land-plant carbon in the sediments, reflecting deposition predominantly during periods of high Delta outflow. Alternatively, selective preservation and isotopic fractionation effects related to decomposition could account for the low sediment values (Degens et al. 1968; Eadie and Jeffrey 1973).

The value in sediment 16 km seaward of Golden Gate (-21.2 °/oo) is within the range of mid-latitude marine POC, indicating that less than 10% of the carbon in these sediments is land derived. If this offshore carbon is considered as a mixture of three sources (marine, land-derived, and estuarine phytoplankton), then the fraction of land-derived carbon is probably even smaller.

In South Bay, local sources of riverborne sediments are small and suspended particle concentrations are probably controlled by wind-driven resuspension of bottom sediment and phytoplankton during most of the year (Conomos and Peterson 1977; Schemel and Dedini 1979b). During winter, Delta-derived low-salinity water, a source of suspended particulate matter, often penetrates South Bay (Conomos 1979). The apparent sources of suspended particulate matter predict that South Bay POC is a time-variable mixture of these carbon sources. In general, its carbon-isotope composition (-22 to -25 °/oo) is close to that predicted for in situ phytoplankton production (-18 to -24 °/oo) and resuspended bottom sediment (about -24 °/oo; Fig. 11). In March 1976 mid-Bay values were highest, possibly because of phytoplankton production. In September 1976 levels were lowest, perhaps indicating a component of land-derived POC. The March 1977 values were similar to those for bottom sediment and were between those of the two previous surveys, and suggest that the increased POC abundance observed southward during March 1977 (Fig. 8) was the result of bottom-sediment resuspension rather than in situ production.

Bottom-sediment values are apparently time and source integrated. In spite of abundant South Bay tidal and marsh areas, detritus originating from Spartina marsh grass (δ^{13}C, approx. -13 °/oo) was not identifiable as an important carbon source.
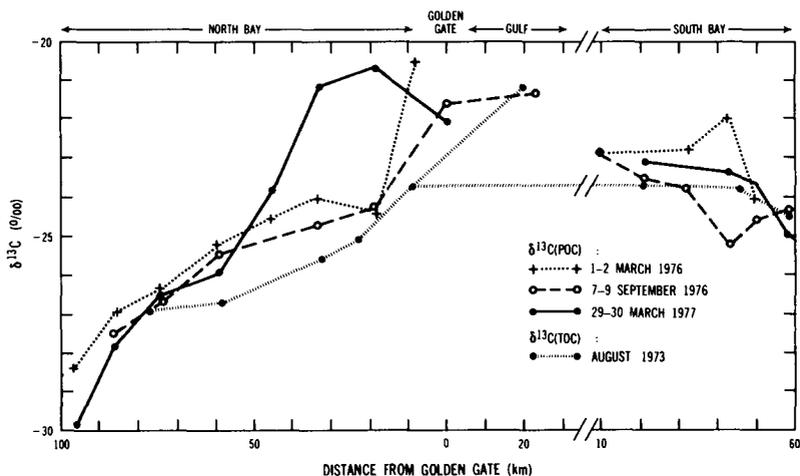

Fig. 11. δ^{13}C(POC) and δ^{13}C(TOC) in San Francisco Bay and the Gulf of the Farallones as a function of distance from the Golden Gate.

209

SAN FRANCISCO BAY

SUMMARY

Although our results are insufficient to define seasonal variations or describe details of the carbon cycle and fluxes through the estuary, they do substantiate the importance of some processes, sources, and sinks in the Bay. Respiration and mineralization in the water and sediments are important sources of inorganic carbon, and plant production and atmospheric outgassing remove significant amounts of inorganic carbon. Municipal waste effluent is an apparent source of biogenic carbon in South Bay. The Bay is a trap for riverine POC, whereas marine algae constitute most of the sediment-associated TOC seaward of the Golden Gate.

ACKNOWLEDGMENTS

LITERATURE CITED

Arthur, J. F., and M. D. Ball. 1979. Factors influencing the entrapment of suspended material in the San Francisco Bay-Delta estuary. Pages 143-174 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.

Banse, K. 1977. Determining the carbon-to-chlorophyll ratio of natural phytoplankton. Mar. Biol. 41:199-212.

Brewer, P. G., and J. C. Goldman. 1976. Alkalinity changes generated by phytoplankton growth. Limnol. Oceanogr. 21:108-117.

Briggs, R. B., and D. A. Flemer. 1972. The flux of particulate carbon in an estuary. Mar. Biol. 12:11-17.

Broecker, W. S., and T. Takahashi. 1966. Calcium carbonate precipitation on the Bahama Banks. J. Geophys. Res. 71(6):1575-1602.

Broecker, W. S., and A. Walton. 1959. The geochemistry of C^{14} in fresh-water systems. Geochim. Cosmochim. Acta 16:15-38.

Buch, K. 1951. Das Kohlensaure Gleichgewichts System in Meerwasser. Hausforskingsinstitutets Skrift Helsingfors, No. 151, Helsingfors. 18 pp.

Claypool, G. E., and I. R. Kaplan. 1974. The origin and distribution of methane in marine sediments. Pages 99-139 *in* I. R. Kaplan, ed. Natural Gases in Marine Sediments. Plenum Publishing Corp., New York.

Conomos, T. J. 1979. Properties and circulation of San Francisco Bay waters. Pages 47-84 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.

Conomos, T. J., and D. H. Peterson. 1977. Suspended-particle transport and circulation in San Francisco Bay: An overview. Pages 82-97 *in* M. Wiley, ed. Estuarine Processes. Vol. 1. Academic Press, New York.

Conomos, T. J., R. E. Smith, D. H. Peterson, S. W. Hager, and L. E. Schemel. 1979. Processes affecting seasonal distributions of water properties in the San Francisco Bay estuarine system. Pages 115-142 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.

Craig, H. 1953. The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acta 3:53-92.

Craig, H. 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta 12:133-149.

Degens, E. T. 1969. Biogeochemistry of stable carbon isotopes. Pages 304-329 in E. Eglington and M. T. J. Murphy, eds. Organic Geochemistry. Springer-Verlag, Berlin.

Degens, E. T., M. Behrendt, B. Gotthardt, and E. Reppmann. 1968. Metabolic fractionation of carbon isotopes in marine plankton-II. Data on samples collected off the coasts of Peru and Ecuador. Deep-Sea Res. 15:11-20.

Eadie, B. J., and L. M. Jeffrey. 1973. $\delta^{13}C$ analysis of oceanic particulate organic matter. Mar. Chem. 1:199-209.

Fry, B., R. S. Scalon, and P. L. Parker. 1977. Stable carbon isotope evidence for two sources of organic matter in coastal sediments: seagrasses and plankton. Geochim. Cosmochim. Acta 14:1875-1877.

Gearing, P., F. E. Plunker, and P. L. Parker. 1977. Organic carbon stable isotope ratios of continental margin sediments. Mar. Chem. 4:251-266.

Gordon, L. I., and P. K. Park. 1972. A continuous pCO_2 measurement system. Tech. Rept. 240, Oregon State Univ., Corvallis, Ore. 77 pp.

Gordon, L. I., P. K. Park, J. J. Kelley, and D. W. Hood. 1973. Carbon dioxide partial pressures in North Pacific surface waters, pt. 2. General late summer distribution. Mar. Chem. 1:191-198.

Haines, E. B. 1977. The origins of detritus in Georgia salt marsh estuaries. Oikos 29:254-260.

Hammond, D. E. 1975. Dissolved gases and kinetic processes in the Hudson River estuary. Ph.D. Thesis. Columbia University, New York. 161 pp.

Head, P. C. 1976. Organic processes in estuaries. Pages 53-91 in J. D. Burton and P. S. Liss, eds. Estuarine Chemistry. Academic Press, New York.

Hendy, C. H. 1971. The isotopic geochemistry of speleotherms, pt. 1. The calculation of the effects of different modes of formation on the isotopic composition of speleotherms. Geochim. Cosmochim. Acta 35:801-824.

Hunt, J. M. 1970. The significance of carbon isotope variations in marine sediments. Pages 27-35 in G. D. Hobson and G. C. Spears, eds. Advances in Organic Geochemistry. Pergamon, Oxford.

Katz, A., Y. Kolodny, and A. Nissenbaum. 1977. The geochemical evolution of the Pleistocene Lake Lisan—Dead Sea system. Geochim. Cosmochim. Acta 41:1609-1626.

Kelley, J. J., and D. W. Hood. 1971. Carbon dioxide in the Pacific Ocean and Bering Sea: upwelling and mixing. J. Geophys. Res. 76(3):745-752.

Kroopnick, P. 1974. Correlations between ^{13}C and ΣCO_2 in surface waters and atmospheric CO_2. Earth and Planetary Sci. Letters 22:397-403.

Liss, P. S. 1976. Conservative and non-conservative behavior of dissolved constituents during estuarine mixing. Pages 93-130 in J. D. Burton and P. S. Liss, eds. Estuarine Chemistry. Academic Press, New York.

Lyman, J. 1956. Buffer mechanism of sea water. Ph. D. Thesis. University of California, Los Angeles, Calif. 196 pp.

Menzel, D. W., and R. F. Vaccaro. 1964. The measurement of dissolved organic and particulate carbon in seawater. Limnol. Oceanogr. 9:138-142.

Mook, W. G. 1970. Stable carbon and oxygen isotopes of natural waters in the Netherlands. Pages 163-190 in Isotope Hydrology 1970. Int. Atomic Energy Agency, Vienna.

Mook, W. G., J. C. Bommerson, and W. H. Staverman. 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth and Planetary Sci. Letters 22:169-176.

Mook, W. G., and B. K. S. Koene. 1975. Chemistry of dissolved inorganic carbon in estuarine and coastal brackish waters. Estuarine Coastal Mar. Sci. 3:325-336.

Oana, S., and E. S. Deevey. 1960. Carbon-13 in lake waters and its possible bearing on paleolimnology. Amer. J. Sci. 258-A:253-272.

Park, P. K. 1969. Oceanic CO_2 system: an evaluation of ten methods of investigation. Limnol. Oceanogr. 14(2):179-186.

Park, P. K., L. I. Gordon, S. W. Hager, and M. C. Cissel. 1969. Carbon dioxide partial pressure in the Columbia River. Science 166:867-868.

Parker, P. L., and J. A. Calder. 1970. Stable carbon isotope ratio variations in biological systems. Pages 107-127 *in* D. W. Hood, ed. Organic Matter in Natural Waters. Institute of Marine Science, Occasional Publication No. 1. University of Alaska, College, Alaska.

Parsons, T. R. 1975. Particulate organic carbon in the sea. Pages 365-383 *in* J. P. Riley and G. Skirrow, eds. Chemical Oceanography. Vol. 2. Academic Press, New York.

Peterson, D. H. 1979. Sources and sinks of biologically reactive oxygen, carbon, nitrogen, and silica in northern San Francisco Bay. Pages 175-193 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.

Peterson, D. H., T. J. Conomos, W. W. Broenkow, and P. C. Doherty. 1975a. Location of the non-tidal current null zone in northern San Francisco Bay. Estuarine Coastal Mar. Sci. 3:1-11.

Peterson, D. H., T. J. Conomos, W. W. Broenkow, and E. P. Scrivani. 1975b. Processes controlling the dissolved silica distribution in San Francisco Bay. Pages 153-187 *in* L. E. Cronin, ed. Estuarine Research. Vol. 1. Academic Press, New York.

Peterson, D. H., J. F. Festa, and T. J. Conomos. 1978. Numerical simulation of dissolved silica in the San Francisco Bay. Estuarine Coastal Mar. Sci. 7:99-116.

Rau, G. 1978. Carbon-13 depletion in a subalpine lake: Carbon flow implications. Science 201:901-902.

Sackett, W. M., and W. S. Moore. 1966. Isotopic variations of dissolved inorganic carbon. Chem. Geol. 1:323-328.

Sackett, W. M., and R. R. Thompson. 1963. Isotopic organic composition of recent continental derived clastic sediments of eastern Gulf Coast, Gulf of Mexico. Bull. Amer. Assoc. Petrol. Geol. 47:525-531.

Schemel, L. E., A. E. Alpine, B. E. Cole, L. A. Dedini, and E. C. Spiker. 1978. Water and sediment measurements in San Francisco Bay. U. S. Geol. Surv. Open-File Rept. 78-973. 28 pp.

Schemel, L. E., and L. A. Dedini. 1979a. A continuous water-sampling and multiparameter-measurement system for estuaries. U. S. Geol. Surv. Open-File Rept. 79-273. 92 pp.

Schemel, L. E., and L. A. Dedini. 1979b. Particulate organic carbon in San Francisco Bay, California, 1971-1977. U. S. Geol. Surv. Open-File Rept. 79-512. 30 pp.

Shultz, D. J., and J. A. Calder. 1976. Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments. Geochim. Cosmochim. Acta 40:481-485.

Skirrow, G. 1975. The dissolved gases-carbon dioxide. Pages 1-192 *in* J. P. Riley and G. Skirrow, eds. Chemical Oceanography. Vol. 2. Academic Press, New York.

Strickland, J. D. H., and T. R. Parsons. 1972. A practical handbook of seawater analysis. Fish. Res. Bd. Can. Bull. 167. 311 pp.

Weiss, R. F. 1974. Carbon dioxide in water and seawater: The solubility of non-ideal gas. Mar. Chem. 2:203-215.

Wigley, T. M. L., L. N. Plummer, F. J. Pearson, Jr. 1978. Mass transfer and carbon isotope evolution in natural water systems. Geochim. Cosmochim. Acta 42:1117-1139.

Wong, W. W., and W. M. Sackett. 1978. Fractionation of stable carbon isotopes by marine phytoplankton. Geochim. Cosmochim. Acta 42:1809-1815.

Woodwell, G. M., P. H. Rich, and C. A. Hall. 1973. Carbon in estuaries. Pages 221-240 *in* G. M. Woodwell and E. V. Pecner, eds. Carbon in the Biosphere. NTIS:CONF-720510.