

**THE BEHAVIOR OF ^{14}C AND ^{13}C IN ESTUARINE WATER:
EFFECTS OF *IN SITU* CO_2 PRODUCTION
AND ATMOSPHERIC EXCHANGE**

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ABSTRACT. The effects of nonconservative sources (inputs) and sinks (outputs) of carbon are indicated by the behavior of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of the total dissolved inorganic carbon (ΣCO_2) in San Francisco Bay and Chesapeake Bay. Isotopic distributions and model calculations indicate that in North San Francisco Bay the net CO_2 flux to the atmosphere and carbon utilization in the water column are balanced by benthic production. Municipal waste appears to be a dominant source in South San Francisco Bay. In Chesapeake Bay, atmospheric exchange has increased the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in the surface water. Decomposition of organic matter in the water column is indicated to be the dominant source of excess ΣCO_2 in the deep water.

INTRODUCTION

Understanding biochemical cycles in estuaries has become critical as a result of man's activities and urban sprawl. However, the interpretation of biological and chemical variations is generally difficult because they are due to complex processes that are variable in both time and space. Estuaries are open systems in which the overall chemistry is determined by the coupling of hydrodynamic transport and biochemical processes. The influence of internal sources and sinks on the distribution of reactive substances is modulated by the river flow and flushing time of the estuary. When *in situ* processes are significant in comparison to flushing rates, non-conservative distributions may result.

Double isotopic labeling of carbon is particularly useful for analysis of sources and sinks of carbon in estuaries, and can provide additional factors for testing reaction models. This paper discusses the distributions of $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ of the total dissolved inorganic carbon (ΣCO_2) in San Francisco Bay and Chesapeake Bay.

$\delta^{13}\text{C}$ (ΣCO_2) distributions have been investigated in several estuaries (Sackett and Moore, 1966; Mook, 1970; Strain and Tan, 1979; Spiker and Schemel, 1979). $\delta^{13}\text{C}$ (ΣCO_2) in fresh water ranges from zero to as low as -25‰ . Dissolution of carbonate minerals ($\delta^{13}\text{C} \cong 0\text{‰}$) with biogenic carbon ($\delta^{13}\text{C} \cong -25\text{‰}$) in the soil zone usually produces a solution with an intermediate value of about -12‰ . 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. $\Delta^{14}\text{C}$ (ΣCO_2) in many lakes and rivers is less than the $\Delta^{14}\text{C}$ of atmospheric CO_2 (see, for example, Thurber and Broecker, 1970). The magnitude of the deficiency is primarily a function of the amount of carbonate mineral dissolution, and the degree of equilibration with atmospheric CO_2 .

The form of a $\delta^{13}\text{C}$ or $\Delta^{14}\text{C}$ conservative mixing curve depends on the ΣCO_2 (C) and the isotopic composition (R) of the river and ocean waters, $R_r C_r$ and $R_o C_o$, respectively. The isotopic composition of the two-component mixture is given by

$$R_{\text{mix}} = \frac{fR_r C_r + (1 - f) R_o C_o}{C_{\text{mix}}}$$

The freshwater fraction, f , is calculated from the salinity. A linear distribution is predicted when $R_r = R_o$, or $C_r = C_o$. Care must be taken when estimating the river and ocean compositions, as these estimates may strongly affect the calculated distribution.

Methods

Water samples were collected at selected midchannel stations in San Francisco Bay and the adjacent Gulf of the Farallones (fig 1) (Spiker and Schemel, 1979), and Chesapeake Bay (fig 2).

Samples for $\delta^{13}\text{C}$ analysis were pressure-filtered through a glass-fiber filter (effective retention $\cong 1.2\mu$), poisoned with HgCl_2 , sealed, and refrigerated on shipboard. ΣCO_2 was extracted from acidified samples on a vacuum line, and its volume was measured manometrically. Analytical precision is $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$ and ± 4 percent for ΣCO_2 . The $^{13}\text{C}/^{12}\text{C}$ ratios are reported in the usual δ notation referenced to the PDB standard (Craig, 1957).

$\Delta^{14}\text{C}$ measurements were made on the CO_2 extracted from a 200L water sample on shipboard by passing tank nitrogen through the acidified water and then through a CO_2 -free NaOH solution. The CO_2 was

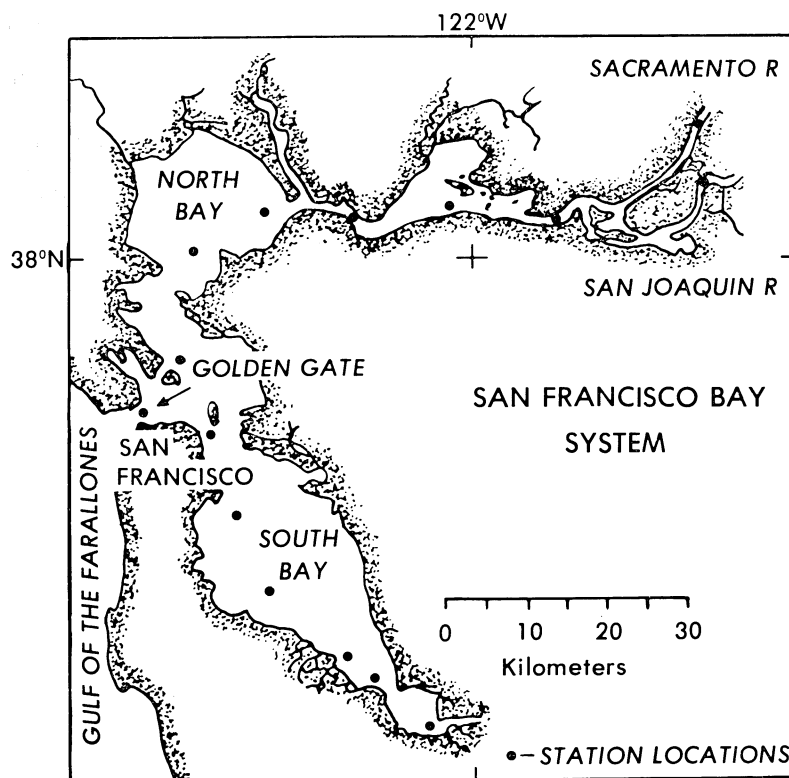


Fig. 1. San Francisco Bay system, California, and adjacent Pacific Ocean.

later released from this solution and analyzed for ^{14}C activity by using low-background gas proportional counters. Sample activities are normalized to a $\delta^{13}\text{C}$ value of -25‰ , and compared to age-corrected 95 percent activity of oxalic acid, normalized to a $\delta^{13}\text{C}$ value of -19‰ (equations given by Stuiver and Polach, 1977). Analytical precision is $\cong \pm 6\text{‰}$.

RESULTS AND DISCUSSION

San Francisco Bay is a complex estuarine system; fresh water enters the system principally in the northern arm (North Bay), a partially- to well-mixed estuary of the Sacramento and San Joaquin rivers (fig 1). The southern arm (South Bay) of the system receives little fresh-water input and depends on modest exchanges with the North Bay for removal (flushing) of accumulated dissolved constituents. Seasonal variations in water chemistry are related to water circulation patterns and



Fig 2. Chesapeake Bay system.

water residence time, a function of the highly variable river inflow (Peterson, 1979). River inflow was abnormally low during the study period (1976-1978) and water replacement time in North Bay was approximately 6 to 12 weeks. Flushing of South Bay was minimal as a result (Conomos, 1979).

Spiker and Schemel (1979) have discussed the distributions of carbon and $\delta^{13}\text{C}$ in San Francisco Bay water and sediments. Some of their results are given here as figure 3A, B. $\Delta^{14}\text{C}$ data from several cruises during the period 1976 to 1978 are also shown in figure 3C. Although ΣCO_2 was nearly conservative in North Bay, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ were depressed. $\delta^{13}\text{C}$ values in the outer reach of North Bay were as much as 2‰ less than that predicted by simple mixing. $\Delta^{14}\text{C}$ values were as much as 60‰ below the conservative mixing curve in midestuary (this may be in

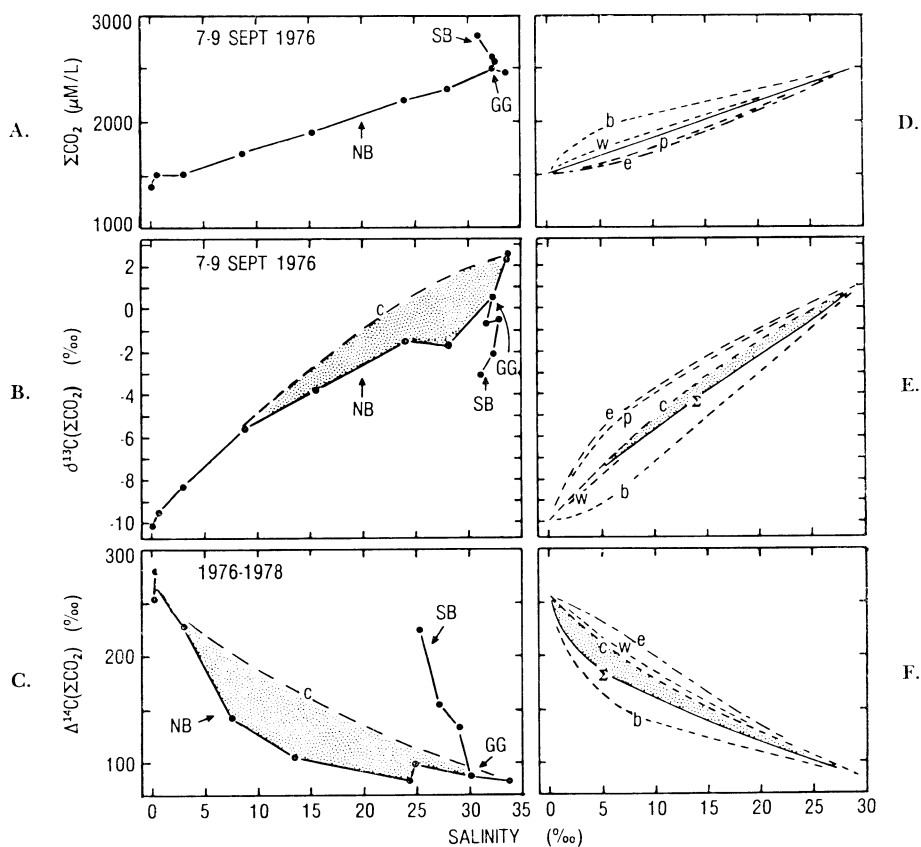


Fig 3. ΣCO_2 , $\delta^{13}\text{C}$ (ΣCO_2) and $\Delta^{14}\text{C}$ (ΣCO_2) at 2m depth in San Francisco Bay (A, B, C). Simulated distributions in North Bay (D, E, F) resulting from benthic production (b), net photosynthetic utilization (p), waste input (w), atmospheric exchange (e), and distribution of the resulting solution (Σ). The anomaly over the conservative distribution (C) is represented by the shaded area. Designations: NB, North Bay; SB, South Bay; GG, Golden Gate.

part due to temporal effects not obvious from these limited data). Assuming this data approximates a steady-state distribution, these distributions indicate a source of isotopically depleted (light and old) inorganic carbon, such as biogenic CO_2 produced by benthic respiration ($\delta^{13}\text{C} \cong -24\text{‰}$; $\Delta^{14}\text{C} \cong -200\text{‰}$, $\cong 1800$ yr BP). Midchannel surface sediments in the inner and outer reaches of North Bay gave ^{14}C ages of 2200 and 2400 years BP, respectively.

In contrast to ΣCO_2 in North Bay, ΣCO_2 in South Bay typically increased as salinity decreased southward. In South Bay, the $\delta^{13}\text{C}$ decreased southward and the $\Delta^{14}\text{C}$ increased southward. These variations indicate a source of ^{13}C depleted biogenic carbon having relatively high ^{14}C content, such as municipal waste ($\delta^{13}\text{C} \cong -25\text{‰}$; $\Delta^{14}\text{C} \cong 400\text{‰}$, \cong atmospheric CO_2). Apparently, the abundance of ΣCO_2 in South Bay is primarily related to the increasing municipal-waste enrichment of waters to the south. Dissolved nutrient, alkalinity, and pCO_2 levels are also typically elevated (Spiker and Schemel, 1979).

The interpretation of nonconservative distributions may be aided by the use of models that simulate the effects of mixing and *in situ* processes. Rattray and Officer (1979) have recently derived a simplified analytic expression for a steady-state one-dimensional model of dissolved silica in North Bay. This solution is a convenient method for analyzing dissolved inorganic carbon distributions in North Bay, and it also provides a basis for simulating nonconservative isotopic variations. The technique used here is first to estimate the net carbon anomaly over a conservative distribution, and then to determine the carbon isotope composition of the resultant solution following the theory and methods of Wigley, Plummer, and Pearson (1978). The various assumptions and details of this model are not discussed in this paper.

The sources and sinks of inorganic carbon considered are listed in table 1 with their approximate rates and isotopic compositions. These rates are taken from Peterson (1979). Gas exchange with the atmosphere (invasion and evasion) is based on a stagnant-boundary layer model; the mass-transfer coefficient was estimated to be about 13×10^{-4} cm/s, and the pCO_2 of the bay water was estimated to be about 650ppm.

TABLE 1
Rates and isotopic compositions used in model for sources
and sinks of ΣCO_2 , North San Francisco Bay

	Rate* $\mu\text{M/L/d}$	$\delta^{13}\text{C}$	$\Delta^{14}\text{C}$ ‰	$\epsilon^{13}\text{C}$	$\epsilon^{14}\text{C}$
<i>Sources (inputs)</i>					
Benthic respiration	3.5	-24	-200	na	na
Invasion from the atmosphere	1.9	-7	400	na	na
Municipal waste	0.6	-25	400	na	na
<i>Sinks (outputs)</i>					
Evasion to the atmosphere	3.9	na	na	-9	-18
Net photosynthetic utilization	1.6	na	na	-20	-40

* Rates from Peterson (1979).

River flow was assumed to be $100\text{m}^3/\text{s}$, and estuary length was assumed to be 160km . The salinity distributions are from Peterson, Festa, and Conomos (1978). The amount of fractionation between the output carbon and the solution ($\epsilon = \text{output} - \text{solution}$) depends slightly on temperature and solution composition, primarily a function of pH (Mook, Bommerson, and Staverman, 1974; Mook and Koene, 1975; Wigley, Plummer, and Pearson, 1978).

The predicted distributions resulting from these calculations are shown in figure 3D, E, F. When all the processes listed in table 1 are considered (curve Σ) ΣCO_2 is nearly conservative, and $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ are depressed in the high-salinity and mid-salinity regions, respectively. Benthic exchange, which supplies isotopically depleted (light and old) inorganic carbon to solution appears to be particularly effective in controlling the isotopic composition of the solution.

The agreement with both the observed chemical and isotopic distributions is good considering the inherent simplifications of the calculations. For example, the effect of exchange with South Bay water, and the waste input — predominantly in the outer reach of North Bay — have

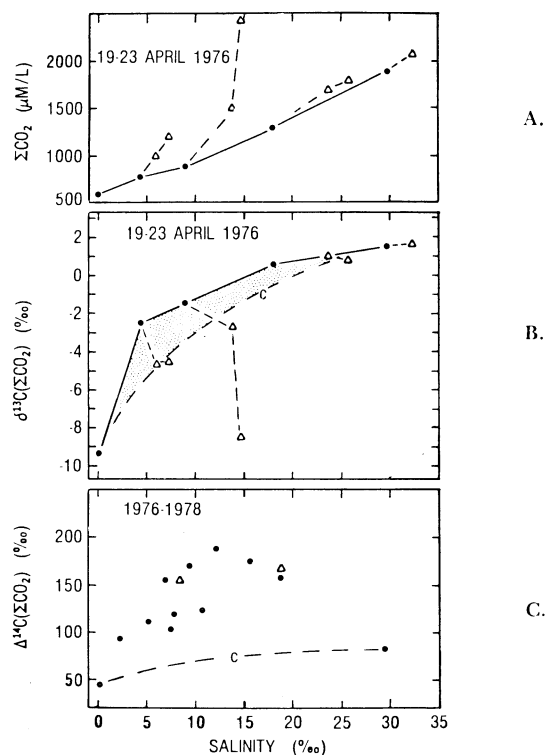


Fig 4. ΣCO_2 , $\delta^{13}\text{C}$ (ΣCO_2), and $\Delta^{14}\text{C}$ (ΣCO_2) in Chesapeake Bay. Designations: C, conservative distribution; —●—, surface-water (2m) distribution; —△—, subsurface distribution. $\delta^{13}\text{C}$ (ΣCO_2) anomaly over the conservative distribution is represented by the shaded area.

been averaged over the whole salinity range. Because the estimated input and output rates given by Peterson (1979) did produce isotopic distributions similar to that observed, our results tend to support his conclusion that the net flux to the atmosphere and net photosynthetic utilization are balanced by exchange with the bottom.

Chesapeake Bay

Chesapeake Bay is one of the major estuarine systems of the world (fig 2). Although primarily an estuary of the Susquehanna River, it is a complex system composed of the bay proper and several tributary estuaries. It is a well-stratified or salt-wedge estuary, is approximately 300 km long, and has a water residence time of about one year.

$\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ in the surface water were significantly enriched over conservative values in the mid-salinity region (fig 4). Net photosynthetic utilization of carbon may be partially responsible for this enrichment. However, CO_2 exchange with the atmosphere is probably the only process that could enrich both ^{13}C and ^{14}C so effectively. Atmospheric-equilibrium $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values are approximately 2‰ and 400‰, respectively.

Measurements made at several depths in vertical profiles show $\delta^{13}\text{C}$ decreasing and ΣCO_2 increasing as depth increases, indicating a flux to the bottom water of excess ΣCO_2 having a $\delta^{13}\text{C}$ composition of about -14‰. These changes suggest that about 70 percent of the inorganic carbon production is contributed by the oxidation of organic matter and about 30 percent is contributed by an isotopically heavy inorganic carbon source as ΣCO_2 derived from dissolution of carbonate shells or fermentation reactions (Oana and Deevey, 1960). The near-bottom water typically becomes anoxic in some areas during the summer.

$\Delta^{14}\text{C}$ compositions of two near-bottom samples were similar to that of the surface water. This similarity indicates that the deep-water excess ΣCO_2 is derived from sources having a $\Delta^{14}\text{C}$ composition similar to that of the surface water; these sources may be organic matter and shell material that formed in the surface water. Thus, in contrast to North San Francisco Bay, decomposition of organic matter recently produced in the water column (or recently deposited on the bottom) appears to dominate decomposition of older benthic organic matter. Apparently, dissolved nutrients are remineralized primarily in the water column by herbivore grazing (McCarthy, Taylor, and Taft, 1977).

CONCLUSION

A comparison of San Francisco Bay and Chesapeake Bay demonstrates that *in situ* processes have different effects in these systems, which differ considerably with respect to their hydrodynamics. Isotope distributions can indicate the coupled effects of processes that may result in a nearly conservative ΣCO_2 distribution. Because ^{13}C and ^{14}C label sources and sinks differently, the study of both isotopes in estuaries is especially useful.

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REFERENCES

- Conomos, T J, 1979, Properties and circulation of San Francisco Bay waters, *in* Conomos, T J, ed, San Francisco Bay: The urbanized estuary: San Francisco, Am Assoc Advancement Sci, p 47-84.
- Craig, Harmon, 1957, Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide: *Geochim et Cosmochim Acta*, v 12, p 133-149.
- McCarthy, J J, Taylor, W R, and Taft, J L, 1977, Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences: *Limnol Oceanog*, v 22, p 996-1011.
- Mook, W G, 1970, Stable carbon and oxygen isotopes of natural waters in the Netherlands, *in* Isotope hydrology 1970: Vienna, IAEA, p 163-190.
- Mook, W G, Bommerson, J C, and Staverman, W H, 1974, Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide: *Earth and Planetary Sci Letters*, v 22, p 169-176.
- Mook, W G, and Koene, B K S, 1975, Chemistry of dissolved inorganic carbon in estuarine and coastal brackish waters: *Estuarine Coastal Mar Sci*, v 3, p 325-336.
- Oana, S and Deevey, E S, 1960, Carbon 13 in lake waters and its possible bearing on paleolimnology: *Am Jour Sci*, v 258-A, p 253-272.
- Peterson, D H, 1979, Sources and sinks of biologically reactive oxygen, carbon, nitrogen, and silica in Northern San Francisco Bay, *in* Conomos, T J, ed, San Francisco Bay: The urbanized estuary: San Francisco, Am Assoc Advancement Sci, p 175-193.
- Peterson, D H, Festa, J F, and Conomos, T J, 1978, Numerical simulation of dissolved silica in the San Francisco Bay: *Estuarine Coastal Mar Sci*, v 7, p 99-116.
- Rattray, Maurice, and Officer, C B, 1979, Distribution of a non-conservative constituent in an estuary with application to the numerical simulation of dissolved silica in the San Francisco Bay: *Estuarine Coastal Mar Sci*, v 8, p 489-494.
- Sackett, W M and Moore, W S, 1966, Isotopic variations of dissolved inorganic carbon: *Chem Geol*, v 1, p 323-328.
- Spiker, E C and Schemel, L E, 1979, Distribution and stable-isotope composition of carbon in San Francisco Bay, *in* Conomos, T J, ed, San Francisco Bay: The urbanized estuary: San Francisco, Am Assoc Advancement Sci, p 195-212.
- Strain, P M and Tan, F C, 1979, Carbon and oxygen isotope ratios in the Saguenay Fjord and the St Lawrence estuary and their implications for paleoenvironmental studies: *Estuarine Coastal Mar Sci*, v 8, p 119-126.
- Stuiver, Minze and Polach, H A, 1977, Reporting of ¹⁴C data: *Radiocarbon*, v 19, p 355-363.
- Thurber, D L and Broecker, W S, 1970, The behavior of radiocarbon in the surface waters of the Great Basin, *in* Olsson, I U, ed, Radiocarbon variations and absolute chronology, Nobel symposium, 12th, Proc: New York, John Wiley & Sons, p 379-400.
- Wigley, T M L, Plummer, L N, and Pearson, F J, 1978, Mass transfer and carbon isotope evolution in natural water systems: *Geochim et Cosmochim Acta*, v 42, p 1117-1139.