SAN FRANCISCO BAY: THE URBANIZED ESTUARY

The Pacific Division of the American Association for the Advancement of Science % California Academy of Sciences, San Francisco, California 94118

SOURCES **AND SINKS** OF BIOLOGICALLY REACTIVE OXYGEN, CARBON, NITROGEN, **AND** SILICA IN NORTHERN **SAN** FRANCISCO BAY

DAVID H. PETERSON

U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025

The distributions of biologically reactive dissolved oxygen, carbon, nitrogen, and silicon (OCNSi) in the main channels of northern San Francisco Bay appear to be related to winter and summer variations in the dynamics of the estuary. At moderate or higher (>500 m³·s⁻¹) river flow, OCSi distributions in the estuary frequently are nearly conservative. Thus, during high river discharge periods, the relative effects of additional estuarine sources and sinks (waste inputs, phytoplankton production and remineralization, or atmospheric- and benthic-exchange processes) appear to be minimal. At such river flows replacement time for estuarine water is on the order of weeks, whereas the OCNSi replacement (turnover) times due to additional sources and sinks are longer. The turnover time of NH3-N, however, is shorter. The river and ocean are probably not major sources of NH3 to the estuary.

Marked departures from near-conservative OCNSi distributions occur during low river flow (<200 m³·s⁻¹) when the magnitudes of the local sources and sinks may exceed river and ocean inputs. As an overview, however, several processes seem to control these distributions at comparable rates and no one factor dominates: dissolved oxygen is typically 5 to 10% below saturation concentrations; dissolved carbon dioxide is 150-200% above saturation concentrations and in approximate balance with oxygen consumption; phytoplankton production keeps pace with waste inputs of nitrogen; and dissolved silica is maintained above concentrations that would be limiting for phytoplankton growth.

Knowledge of estuarine hydrodynamics and of the appropriate sources and **sinks** is needed to predict micronutrient and dissolved-gas distributions in an estuary. **This** chapter presents a series of inferences about the processes which control oxygen, carbon, nitrogen, and silica (OCNSi), based on their observed distributions. These elements were studied because an understanding of their behavior is basic to our knowledge of natural water chemistry in an estuary. The discussion is limited to the northern part of the San Francisco Bay estuary between the Golden Gate and Rio Vista herein termed North Bay (Fig. 1). The southern reach (South Bay), from the Golden Gate to **San** Jose, has only a small freshwater **inflow** and is not discussed here (see Conomos 1979; Conomos et al. 1979).

Under certain assumptions and with appropriate rate measurements we can estimate sources and sinks of these elements throughout North Bay. To some extent the magnitudes and positions of these sources and sinks are, of course, always shifting and changing. Thus, to put the sources and sinks into perspective and to illustrate how they might interrelate with one another, a simple conceptual model of North Bay is used. The model, which has fixed dimensions and receives seasonally varying runoff and insolation, is used for discussion purposes with the understanding it can provide only gross budgets.

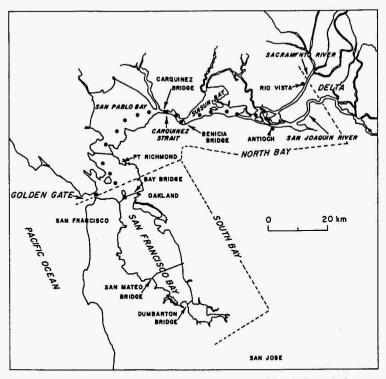


Fig. 1. San Francisco Bay and environs. The study area, North Bay, is between the Golden Gate, the entrance to the ocean, and Rio Vista. All field data presented herein were collected at indicated main-channel stations.

PREVIOUS WORK

Most of the interest in processes controlling water chemistry in the Bay concerns understanding the effects of increasing municipal and agricultural waste loads coupled with a decreasing freshwater inflow. These problems, related to urbanization, seem to have been largely ignored until the first surveys of the dissolved oxygen in the seaward regime of the Bay (Miller et al. 1928). It was not until the early 1960's that such studies were extended from river to ocean (McCarty et al. 1962; Storrs et al. 1963, 1964). Subsequent studies treated near-surface oxygen distributions (Bain and McCarty 1965) and processes controlling oxygen in the landward estuary and lower river (Bailey 1967; California Departments of Water Resources and Fish and Game 1972). The distribution of dissolved CO₂ in the Bay has only recently been investigated (Spiker and Schemel 1979).

During spring and summer, 1964, the abundance and distribution of inorganic nitrogen and phosphorus in North Bay indicated light as the prime factor limiting phytoplankton productivity (Bain and McCarty 1965). It appeared, however, that inorganic nitrogen may be depleted to growth-rate limiting concentrations in the fall. As an extension of these results the potential impact of massive nitrogen inputs from agricultural waste was assessed by Brown (1975). Although the significance of nitrogen to phytoplankton production is not fully understood, it is considered more important than phosphorus in setting an upper limit on phytoplankton biomass. Dissolved silica is different because its principal source is natural runoff and its seasonal patterns are related to river supply and to phytoplankton removal (Peterson et al. 1975). Although a quantitative synthesis of OCNSi distributions has not been attempted for the entire Bay system, distributions of these constituents have been simulated with a numerical model of phytoplankton dynamics in

the landward portion of the estuary and in the lower river (DiToro et al. 1977). From this work it is apparent that phytoplankton plays a major role in determining water chemistry.

REVIEW OF WINTER AND SUMMER FEATURES

The data base is from our near-monthly surveys of hydrographic properties (Smith et al. 1979) at 20 stations spaced nearly equally between Rio Vista and Golden Gate (Fig. 1). Sampling and analytical procedures for micro nutrients and dissolved gases have been described elsewhere (Peterson et al. 1975; Peterson et al. unpublished). Analytical methods are summarized in Table 1 of this chapter. The methodology for and typical observations of particulate nitrogen and dissolved organic nitrogen are given in Peterson et al. (unpublished) and of particulate carbon in Spiker and Schemel (1979).

Distributions of biologically reactive substances are determined by circulation patterns and rates of both the water and biochemical constituents. Sacramento-San Joaquin river (Delta) inflow supplies more than 90% of the freshwater to the estuary. It averages 600 m³·s⁻¹ but ranges from 2,000 m³·s⁻¹ in winter to less than 200 m³·s⁻¹ in summer. River inflow is the prime seasonal regulator of water residence time in the northern part of the estuary (Conomos 1979).

Strong winds in the Bay can move water at speeds exceeding other nontidal components (>10 cm·s·¹, cf. Hansen 1967, Elliot 1976 and Weisberg 1976); such effects, however, have not yet been studied quantitatively for this estuary (Conomos 1979). Mean monthly wind speeds range seasonally between 2 m·s·¹ in December and 6 m·s·¹ in June, and generally persist in a landward direction opposing the natural nontidal surface flow (Conomos 1979). Wind stress on water is also important for increasing gas-exchange rates between atmosphere and water, for resuspending bottom material (which decreases light), and, perhaps, for increasing mixing rates between shoal and channel waters.

The salt field is a driving component of gravitational circulation in the estuary and influences the solubility of dissolved O_2 and CO_2 . Sea salt may penetrate to Rio Vista (Fig. 1) in summer, depending on the river inflow (Conomos 1979, Fig. 18). Surface-to-bottom differences, about $3^{\circ}/\circ \circ$, typify a partially to well-mixed estuary, except during winter floods. A salt-driven estuarine circulation pattern has been identified for the main channels, but seasonal and spatial details of this circulation are unknown.

Phytoplankton abundance is correlated with variations in water circulation in a general way except during extended periods of extremely low river inflow. Phytoplankton biomass, estimated with fluorometric chlorophylla observations, decreases in winter (Fig. 2) and increases in summer, particularly in the landward portions of the estuary (Fig. 3). These observations are plotted against salinity, rather than against location, to minimize variability due to tides (10 to 15 km·cycle). Although short-term events such as spring tides, wind storms, and cloudy days may alter the OCNSi distributions, data suggest that effects of common short-term (tidal and diurnal) events do not exceed seasonal effects.

Mean-monthly sunlight ranges from 37 Einsteins·m⁻²·d⁻¹ (about 200 langleys·d⁻¹) in December to 110 in June (Conomos et al. 1979, Fig. 3). Light-saturation levels (10 to 30 Einsteins·m⁻²·d⁻¹, Peterson et al. unpublished) probably continue year-round at the water surface with some local interruptions caused by dense fog. Photic depth, which ranges from about 6 m near the ocean to 0.5 m inland, is determined by the concentrations of suspended particles. The near-surface concentrations average about 10 mg·liter⁻¹ near the ocean to 50 mg·liter⁻¹ inland in winter and 5 mg·liter⁻¹ near the ocean, and about 100 mg/liter⁻¹ inland in summer (Conomos and Peterson 1977; Conomos et al. 1979).

The relative importance of conservative and nonconservative processes can be inferred from

TABLE 1. ANALYTICAL METHODS

Property	Method	Principal Analysts
S (°/00), T(°C)	Salinity-temperature meter (Schemel and Dedini 1979).	L. E. Schemel and L. A. Dedini
O ₂ (pg-atoms-liter-')	Modified Winkler titration (Carpenter 1965 a, b); for calculation of % saturation see Weiss (1970).	A. Hutchinson and R. E. Smith
CO ₂ (µg-atoms·liter ⁻¹)	Calculated from equations of Smith and Broenkow (1978) using electrometric observations of pH (Schemel and Dedini 1979) and alkalinity (Strickland and Parsons 1968); also, see Spiker and Schemel (1979) for comparison of observed and calculated pCO ₂ .	L. E. Schemel and L. A. Dedini
NH ₃ (μg-atoms·liter ⁻¹)	AutoAnalyzer: adaptation of Solorzano (1969) similar to Head (1971); more details are in Table III of Peterson et al. (1978).	S. W. Hager and D. D. Harmon
NO ₂ , NO ₃ (μg-atoms·liter ⁻¹)	Technicon method number AAIII 100-70W (Technicon Corp., Terrytown, N. Y.).	S. W. Hager and D. D. Harmon
SiO ₂ (pg-atoms-liter-')	Technicon method number AA 105-71W.	S. W. Hager and D. D. Harmon
Chlorophyll <i>a</i> (fluorescence units)	Spectrophotometric (Strickland and Parsons 1972).	B. E. Cole and A. E. Alpine

micronutrient distributions in the estuary. In summer, when phytoplankton biomass increases, micronutrient concentrations are lower than those resulting from a mixture of river and ocean waters. Nevertheless their concentrations are generally well above rate-limiting levels. Consequently, a summer minimum in phytoplankton abundance typical of ocean waters at temperate latitudes is not found in the Bay.

A linear relation between a biologically reactive substance and salinity suggests the relative importance of conservative and nonconservative processes to its distribution. For extreme examples, dissolved silica always exhibits near-linear salinity correlations in winter, whereas during a low river-flow period in summer 1961 (see McCarty et al. 1962) silica was observed below rate-limiting concentrations (10 μ g-atoms·liter⁻¹, cf.: Paasche 1973 a, b; Goering et al. 1973; Davis et al. 1973). Other micronutrients with more complex histories exhibit less consistent winter-linearity and summer non-linearity with salinity. At times during winter even fluorometric chlorophyll-a distributions seem to be near-linear with respect to salinity (Fig. 2).

The complexity of nitrogen sources and sinks may best be understood when their seasonal three-dimensional distributions are known. Present two-dimensional data demonstrate that NO_3

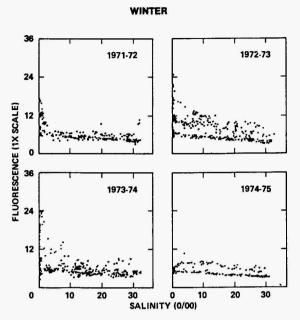


Fig. 2. Winter (October through April) fluorescence (mostly chlorophyll a) distributions with salinity during the years indicated in each panel. Data from near-monthly surveys (Smith et al. 1979).

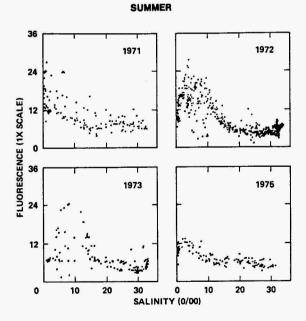


Fig. 3. Summer (May through September) fluorescence (mostly chlorophyll a) distributions with salinity during the years indicated in each panel. Data from near-monthly surveys (Smith et al. 1979).

concentrations are exceedingly variable in the river, whereas NH_3 concentrations are lower in the river than in the estuary (Figs. 4, 5). Phytoplankton productivity experiments show that NH3 utilization is preferred before NO_3 , if ambient NH_3 concentrations remain above 2 μ g-atoms·liter⁻¹ (Peterson et al. unpublished). By late summer (August and September) both these inorganic nitrogen species may be depressed below rate-limiting concentrations (Fig. 5). And, because total N:P is generally less than 16:1 by atoms, nitrogen is considered to be the growth-limiting micronutrient.

The seasonal distributions of dissolved O_2 and CO_2 are less well defined than the micronutrient distributions. Oxygen is generally slightly below saturation concentrations and CO_2 is generally well above saturation concentrations throughout the year (an exception is discussed in the last section).

SOURCES AND SINKS

To compute annual OCNSi sources and sinks (Table 2) I first approximate the atmospheric exchange rates of O_2 and CO_2 from their average or typical concentrations in the Bay, and then superimpose the photosynthetic activities of the phytoplankton on effects of atmospheric exchange processes to establish their influence on micronutrient circulation and dissolved O_2 and CO_2 distributions. Next, exchange rates between the substrate and overlying water are included and compared with the contributions from river inflow and waste. Finally, I discuss the problem of defining exchange at the ocean boundary.

Atmosphere

Oxygen is a useful parameter for initial calculations because its seasonal and spatial variations are small. Average near-surface oxygen concentrations along the main channel are 94% of saturation with respect to the atmosphere (Fig. 6). Thus the Bay waters act as an oxygen sink, and the oxygen-invasion rate from the atmosphere can be estimated using the stagnant boundary layer model (cf. Broecker and Peng 1974):

Oxygen flux =
$$D \frac{C_S - \alpha P}{\mu}$$

where D is the molecular diffusivity of gas, μ is the film thickness, C_s is the gas concentration at the bottom of the film, α is the gas solubility, and P is the partial pressure of gas in the air.

Typical summer and winter dissolved oxygen concentrations range from 500 to 700 μ g-atoms·liter⁻¹ depending on seasonally varying water temperature and salinity (Fig. 7). Using this range of values and assuming that near-surface O_2 is at 94% of saturation concentrations, $C_3 \cdot \alpha P$ ranges from -32 to -45 pg-atoms O_2 :liter⁻¹ (a value of -40 μ g-atoms·liter⁻¹ is used in the calculation, Table 3). Other assumptions include: average temperature is 10°C in winter and 20°C in summer (this requires an accompanying change in D); μ is estimated from wind speeds (Emerson 1975) of 6 m·s⁻¹ in summer and 2 m·s⁻¹ in winter. An annual mean oxygen surface-exchange rate is made from the average winter and summer exchange rates using the North Bay volume (4.12 x 10^9 m³) and area (6 x 10^8 m²; Selleck et al. 1966).

Dissolved CO_2 in the estuary is generally 125 to 250% above saturation concentrations (Spiker and Schemel 1979). Saturation concentration is about 12 pg-atoms-liter-' depending primarily on alkalinity, temperature, and salinity (see Skirrow 1975). Thus, the CO_2 evasion rate from the estuary is estimated following a similar calculation as above for O_2 , $C_3 - \alpha P$ is assumed to be 12 μ g-atoms-liter-1 in both winter and summer (Table 3), or about 200% saturation.

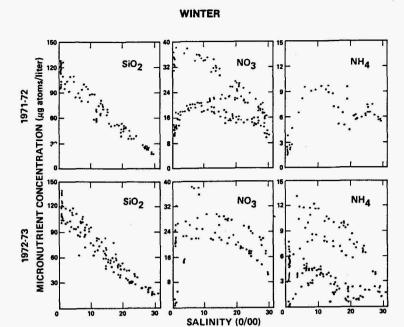


Fig. 4. Winter (October through April) micronutrient distributions with salinity during years indicated in each panel. Data from near-monthly surveys (Smith et al. 1979).

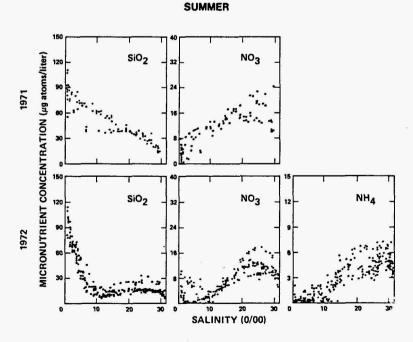


Fig. 5. Summer (May through September) micronutrient distributions with salinity during years indicated in each panel. Data from near-monthly surveys (Smith et al. 1979).

TABLE **2.** ORDER-OF-MAGNITUDE ESTIMATES OF OCNSi SOURCES AND SINKS (REAL AND POTENTIAL) FOR NORTHERN SAN FRANCISCO BAY ESTUARY?

OXYGEN			CARBON			NI	TROGE	N	SILICON			
SOURCES/SINKS ^b	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
BOUNDARIES Atmosphere	+540	+56	+ 8.2	94	- 13	- 1.9					0	
Substrate	-640	-67	- 9.8	+170	+ 24	+ 3.5	+34	+4	+0.60	+ 85	+ 5 ^d	+0.8
Ocean ^c	- 580	- 60	- 8.7		?			?			?	
River dissolved inorganic particulate	+580	+60	+ 8.7	+780 +270	+110 + 38	+16 + 5.5	+26 +27	+3.2	+0.45 +0.47	+290	+17	+2.5
WATER COLUMN photic depth	+430	+45	+13	-180	-25	- 7.2	-34	-4	- 1.2	-170	-10	-1.5
aphotic depth	-330	-34	- 10	+100	+ 14	+ 4	+ 9	+1	+0.28			
Total Depth	+100	+11	+ 1.6	- 80	- 11	- 1.6	-25	- 3	- 0.4	-170	-10	-1.5
ANTHROPOGENIC Waste	- 86	- 8.9	- 1.3	+ 29	+ 4	+ 0.6	+21	+2.5	+0.36			

Note that these rates illustrate mean-annual approximations and that seasonal variations may be large (see text). Values are reported as (1) metric tonnes per day; (2) milligram-atoms per meter² per day; and (3) microgram-atoms per liter per day. **Two figures** are generally given for ease in following the calculations and do not indicate precision.

b Sources (+) mean the element is introduced to the water column as a dissolved species (with the exception of river-borne particles); sinks (-) mean the dissolved species is converted to a particulate phase or leaves the system. See the text for a discussion of assumptions. Volume = 4.12 x 10⁹ m³, area = 6 x 10⁸ m², depth = 7 m.

See text for discussion of uncertainties.

From Hammond and Fuller (1979).

One-half total volume.

DISSOLVED OXYGEN (median value of percent saturation)

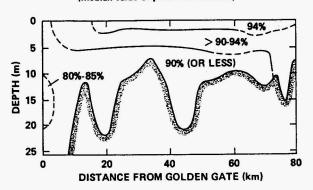


Fig. 6. Longitudinal and depth distribution of dissolved oxygen % saturation (median value) from near-monthly surveys over the period from Fall 1971 to 1974.

Phytoplankton

The photosynthetic rates utilized in the calculations are from observations made in 1976 and 1977, when phytoplankton biomass and associated activity in the inner estuary were probably below typical levels (Peterson et al. unpublished). Net 24-hour oxygen production and carbon assimilation, averaged over the photic depth, ranged from 43 to 100 and 35 to 87 mg-atoms·m⁻²·d⁻¹ respectively, in the outer estuary, and from 16 to 72 and from 13 to 27 mg-atoms·m⁻²·d⁻¹, respectively, in the turbid landward regime for "sunny" spring and fall days (75 Einsteins·m⁻²·d⁻¹). Photic depth ranged from 3.4 to 7.3 m in the seaward portion of the estuary and from 0.5 to 2.3 m landward.

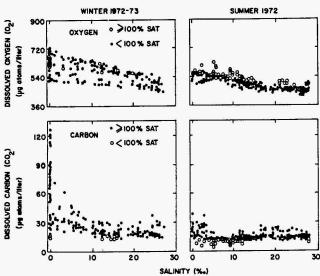


Fig. 7. Winter and summer (1972) dissolved oxygen and carbon dioxide distribution with salinity. Note the different symbol for above and below 100% saturation with respect to atmosphere and compare with summer (1972) fluorescence (Fig. 3) and micronutrient (Fig. 5) distributions.

TABLE 3. ASSUMED PARAMETERS AND ESTIMATES OF AVERAGE NET GAS-EXCHANGE RATES BETWEEN THE ATMOSPHERE AND SAN FRANCISCO BAY^a

Parameter ^b	Winter C	Summer	Winter C	Summer
$C_{\rm S}$ - αP (µg-atoms·liter ⁻¹)	- 40	- 40	+12	+12
D (10 ⁻⁵ cm ² ·s ⁻¹)	1.57	2.06	1.25	1.64
$\mu(10^{-6}\mathrm{m})$	240	80	240	80
flux (mg-atoms·m ⁻² ·d ⁻¹)	- 23	- 89	+ 5.4	+21

a (-indicates a sink, + a source).

Rates of dark-bottle biochemical mineralization, O_2 consumption, and CO_2 production were of the same order as the analytical precision and probably estimated an upper limit to the real rates in the aphotic water column. Seventy percent of the values were between 4.8 and 17 pg-atoms-liter- \cdot 'd-1 for O_2 consumption and between -1.2 and 4.8 pg-atoms-liter- \cdot 'd-1 for CO_2 production. Ten and 4 μ g-atoms-liter- \cdot 1:d-1 respectively are the values used in Table 2.

In the oxygen-production and carbon-assimilation model, I assume that photic processes occur in half the North Bay volume and aphotic processes in the other half. The average North Bay depth, 7 m, is used. I also assume that photic depth-integrated rates represent the upper half-volume, and that dark-bottle experimental rates represent the lower half-volume. Photic depth productivity selected for oxygen and carbon are well within the observed ranges (Table 2) but may seem low compared to values inferred in the literature. An upper limiting value for the Bay might be the annual average of 80 mg-atoms C·m-2·d-1 as observed in the New York Bight (Malone 1976). Ambient chlorophyll-a levels are similar in the two regions but average specific productivity is higher in New York Bight and the photic depth there is deeper (see also Cloern 1979).

Photosynthetic nitrogen assimilation is six times carbon assimilation (by atoms), and average dark bottle (aphotic) nitrogen mineralization is estimated to be 0.28 μ g-atoms·liter·1·d-1 (ranging from 0.02 to 0.4). These values were also applied to "photic and aphotic" North Bay volumes (Table 2). The estimate of silica utilization by phytoplankton was made using a numerical model (Peterson et al. 1978) and it appears consistent with the other values if a major fraction of the phytoplankton consists of diatoms.

Substrate

The processes of atmospheric-oxygen invasion and carbon evasion at the surface and of net oxygen production and carbon assimilation within the water do not balance. For the present it seems attractive to assume that these processes are balanced by exchange with the substrate (Table 2). Experimental observations of benthic oxygen consumption and NH_3 release made during winter indicate similar rates for O_2 and NH_3 as we have estimated (Hammond and Fuller 1979).

Sacramento-San Joaquin River (Delta Outflow)

Transport of river-borne nitrogen is estimated by multiplying the river concentration of dissolved inorganic nitrogen species (NH₃, NO₃, NO₂) by mean-monthly discharge and, for about

b cf. Broecker and Peng 1974.

half the months when no observations were available, by using a linear interpolation of concentration. Because concentrations are highest during high river discharge, monthly nitrogen income varies by several orders of magnitude from winter to summer (220 metric tonnes per day [t·d⁻¹] in February, 1.5 in July, 1973, 80 t·d⁻¹ in January and 1.6 in July, 1974). The annual average dissolved inorganic nitrogen transport was 31 t·d⁻¹ in 1973 and 21 t·d⁻¹ in 1974. Mean flows for these years were 720 and 1,100 m³·s⁻¹, respectively, whereas the mean annual discharge is 600 m³·s⁻¹. From the few observations available it appears that dissolved organic nitrogen is about equal in abundance to inorganic forms (Peterson et al. unpublished). Thus, measuring inorganic nitrogen underestimates the total dissolved nitrogen supply by a factor of two.

River-borne particulate nitrogen and carbon is estimated assuming: (1) a mean annual sediment load (Conomos and Peterson 1977); (2) that the sediment is 3% organic carbon (unpublished data); and (3), that sediment contains 0.3% organic nitrogen by weight (see Storrs et al. 1966).

Dissolved inorganic carbon is estimated from alkalinity. The month-to-month variations in alkalinity in the river, typically 0.8 to 1.5 meq·liter⁻¹, are not well understood. We assume that a value of 1.25 meq·liter⁻¹ is representative of average flow (600 m³·s⁻¹) and that both dissolved inorganic carbon and alkalinity are mostly the bicarbonate species (1.2 mg-atoms C·liter⁻¹). In the river, pCO₂ frequently exceeds thrke times the saturation level and is probably an important source of dissolved CO₂ in the estuary (Fig. 7). However, because the bicarbonate species represents most of the inorganic carbon supplied to the estuary, dissolved CO₂ levels in the river can be ignored here.

Waste

Municipal and industrial waste sources (Table 4) are averaged over the region from below Rio Vista to the San Mateo Bridge (Fig. 1), which includes the upper reaches of South Bay, because a substantial portion of the waste is released in this segment. To some unknown extent this waste is mixed with waters of the central region and may be available for transport into North Bay. Estimated loads have been averaged by volume over the input region (6.23 x 10⁹ m³) but estimates are given only for the volume of the North Bay, 4.12 x 10⁹ m³ (Table 3). This may overestimate the waste contributions from point sources to North Bay. Waste from non-point sources, such as urban runoff into local streams, although believed to be significant, is unknown and is not estimated.

The Sacramento and San Joaquin rivers are not solely a natural source of substances to the estuary; much of their water is used and reused before arriving at the Bay. The relative magnitude of anthropogenic contributions to the enormous winter runoff of nitrogen is unknown. Streams draining agricultural land have high nitrogen concentrations (Omernick 1976), however, and it is likely that fertilizer is an important source of nitrogen brought to the Bay. Livestock waste is another likely source. Nitrogen reported as fertilizer for the 1975 agricultural consumption total for the State of California is 1,300 t·d⁻¹ (California Department of Food and Agriculture 1976). While this total should be corrected to reflect only that portion used within the Sacramento-San Joaquin drainage basin, this high value illustrates that only a small leakage could supply substantial amounts of nitrogen to-the Bay.

An examplary reference model documenting waste sources has been made for the New York Bight (Gross 1976; Mueller 1976). This region is of interest here even though its features are not the same (e.g. dredging, barging of waste, and atmospheric washout of nitrogen are important there) because the bulk of the wastes (from New York) are discharged near the mouth of the estuary as in San Francisco Bay (from San Francisco to Oakland).

TABLE 4. POINT SOURCE WASTE LOADS (METRIC TONNES PER DAY) FOR CENTRAL AND NORTH SAN FRANCISCO BAY^a

	Property								
Location ^b	BOD	Organic Nitrogen	NH ₃	NO ₃					
South Central (San Mateo to Bay Bridge)	79	6.9	10	1.0					
Central-North (Bay Bridge to Pt. Richmond)	25	2.5	2.2	0.3					
San Pablo Bay (Pt. Richmond to Carquinez)	13	0.8	3.4	0.5					
Carquinez Straits (Carquinez to Benicia Bridge)	0.6	0.09	0.09	0.02					
Suisun Bay (Benicia Bridge to Antioch)	15	0.7	3.3	0.2					
TOTAL	130	11	19	2					

Unpublished data for **1975**, supplied by California State Water Quality Control Board, San Francisco Bay Region.

Ocean

The direction of net exchange at the river, atmosphere and bottom boundaries is usually apparent (e.g. from river to estuary). At the ocean boundary, however, it is difficult to determine the direction of net exchange without knowledge of circulation. In the Hudson River estuary, for example, the net transfer of nutrients is clearly from estuary to ocean (Garside et al. 1976; Simpson et al. 1977). Because average water replacement time there is short (a few days), in situ production is not the only major supply of phytoplankton found in the estuary. Rather, incoming near-bottom water has been identified as a dominant source of phytoplankton (Malone 1977). Establishing the net exchange of phytoplankton between the San Francisco Bay estuary and the coastal ocean is not so simple. Several difficulties in qualitatively describing the exchange process for the Bay are apparent.

If, rather than attempting an independent evaluation of exchange processes at the ocean boundary, we assume a steady-state budget, then dissolved-oxygen exchange between the ocean and Bay equals the supply of O_2 from river, atmosphere, and net photosynthesis in the water column **minus** O_2 consumption by the bottom. **This** predicts a net O_2 loss from the Bay to the ocean (580 t·d⁻¹; see Table 2).

The average distribution of dissolved O_2 suggests that the above calculation is qualitatively correct (as % saturation, Fig. 6). Incoming waters at the bottom tend to be low in dissolved O_2 because they often originate from wind- or estuarine-water-induced upwelling of low-oxygen deep water offshore (Conornos 1979). The central part of the Bay also receives a large quantity of sewage. Effects of the latter process are not clearly separated from those of the former but the relation of decreasing O_2 with decreasing NH_3 , when the NH_3 concentrations are below maximum natural levels (about $3 \mu g$ -atoms·liter⁻¹, suggest upwelling as the primary low-oxygen source near the mouth of the Bay.

Incoming low-oxygen near-bottom waters may cause part of the decrease in oxygen concentration with increasing depth in the interior of the estuary (lowering our estimates of benthic O_2

b Location areas indicated in Fig. 1.

consumption). Of course, a more obvious cause is simply that the contributing atmospheric, phytoplankton, and riverine sources are near-surface phenomena, while benthic consumption is a near-bottom phenomenon. In either case the landward-flowing near-bottom waters tend to be lower in O_2 than the seaward-flowing surface waters, thus maintaining an advective loss of O_2 from the Bay.

The key to understanding estuarine-transport processes is, however, in the nonadvective flux terms (Kinsman et al. 1977). The few observations made in San Francisco Bay (restricted to the main channel) suggest that horizontal eddy diffusion contributes about 70% of the sea-salt to the estuary (Conomos 1979, Fig. 25). The eddy exchange coefficients for sea salt may also apply to dissolved O_2 . However, the net exchange of oxygen by eddy diffusivity remains qualitatively unknown because the horizontal oxygen gradients are small and not well-described, especially seaward of the Golden Gate. If we assume the converse, or a gain of O_2 from the ocean to Bay, then, O_2 consumption by the substrate becomes even more important (unless we also reverse the net O_2 flows as described).

Carbon exchange is more complicated than oxygen exchange because both particulate and dissolved phases are involved. Also, the inorganic reactions of dissolved inorganic carbon must be considered (cf. Skirrow 1975). Ignoring such complexities for dissolved ${\rm CO_2}$, making the same calculation as for dissolved ${\rm O_2}$ shows a loss of ${\rm CO_2}$ from Bay to ocean (equal to river input).

We do not know if this calculated **loss** is reasonable because the average depth distributions of dissolved CO_2 near the ocean boundary have not been estimated. In the Bay pCO_2 generally exceeds atmospheric equilibrium values, whereas pCO_2 in surface ocean waters near the Bay is probably lower. **This** suggests some loss of CO_2 from the Bay to ocean, although this process represents a very small portion of the total exchange. The bulk of the inorganic carbon is in the form of dissolved bicarbonate. Its concentration in river water is about half that of seawater, whereas the concentration of particulate organic carbon is usually several times greater in the river than in the adjacent ocean (see also Spiker and Schemel 1979). Preliminary observations indicate that the concentration of dissolved organic carbon is about 80 μ g-atoms·liter⁻¹ for oceanic waters and about two times greater for the Sacramento River. Thus, dissolved organic carbon is quantitatively important, but its participation in the carbon circulation of the estuary is unknown.

The supply of river-borne particulate organic carbon is very large because the supply of sediment to the Bay is also very large. The supply of river-borne particulate organic carbon may rival in situ net phytoplankton production averaged over the photic depth (Table 2). It follows that, because the sediment supply is large, subtracting the accumulation rate of carbon or nitrogen in bottom sediments from their supply rates would not provide a reliable estimate of their loss to the ocean. Expected uncertainties in either the river supply or bottom accumulation rates of carbon or nitrogen, for example, are of the same magnitude as their waste-input rates (note that this large sediment dilution effect is also manifest in the general absence of high concentrations of anthropogenic trace elements in the bottom sediments [McCulloch et al. 1971; Peterson et al. 19721.)

The near-surface plume of NH₃ enriched water which commonly extends outside the Golden Gate reveals that NH₃ is almost continuously released from the Bay. Nitrate, however, appears to be transferred from the ocean to Bay or vice versa (Fig. 4).

The net exchange of dissolved silica is almost invariably from the Bay to ocean, as illustrated by higher silica concentrations in outflowing (surface) than inflowing (near-bottom) waters (Fig. 8, Panels A, B and C). In instances when silica concentrations in the Bay are depressed below ocean concentrations, the concentrations at the Golden Gate are lower at the surface than in near-bottom water, and net exchange is probably reversed from the ocean to the Bay (Fig. 8, Panel D).

Biogenic silica, primarily diatom remains, accumulates in bottom sediment. Dissolution supplies silica to the interstitial water and, ultimately, to the overlying water column. Hammond and

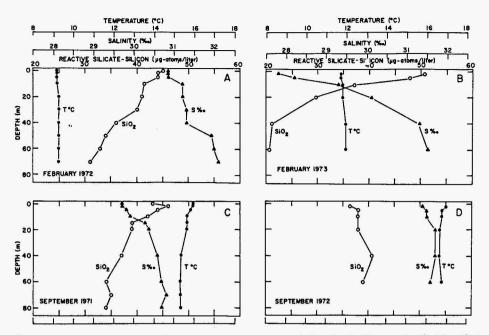


Fig. 8. Depth distribution of salinity, temperature and dissolved silica at the Golden Gate. A, B, winter; C, summer of high river discharge; D, summer of low river discharge.

Fuller (1979) have measured this rate in situ to be about 5 mg atoms·m-2·d-1. This measurement provides a lower limit to an estimate of incoming sedimentation of biogenic silica, assuming abiogenic silica dissolution to be negligible, because complete dissolution is not expected. In this sense both the estimated silica utilization in the water and Hammond and Fuller's observed supply from the bottom seem reasonable.

There is, then, a large export of dissolved silica from the Bay to the ocean, but this export is probably less than the river supply because there must be some loss associated with accumulation of bottom sediment. The average oxygen distribution at the Golden Gate also indicates a net loss of O_2 from the Bay to ocean, opposite to what one might intuitively expect. For example, average landward nontidal flow is 5 km·d·l and seaward flow is 6 km·d·l (Conomos 1975). Assuming that these velocities characterize half the cross-sectional area at the Golden Gate (44 x 10^3 m²), that incoming waters are at 85% saturation concentrations (510 μ g-atoms·liter·l), and that outflowing waters are at 95% of saturation (570 μ g-atoms·liter·l), advective net transfer is 190 t·d·l (about one-third the river supply). Perhaps there is also a net loss of nitrogen from the Bay; furthermore, atmospheric evasion along with net exchange to the ocean seems to be a mechanism for loss of dissolved CO_2 from the Bay. Also, there is probably a net transport of dissolved organic carbon from the Bay, especially if the river supply does not participate in biochemical processes in the estuary. Describing the direction of net exchange for carbon, however, will require a better knowledge of its distribution at the ocean boundary and in sediments.

SEASONAL VARIATIONS

Winter and summer distributions of gases and nutrients (Figs. 2, 3, 4, 5, 7) illustrate the effects of water circulation and of nonconservative sources and sinks. When water circulation is strong (when river inflow is high), the effects of sources and sinks not directly associated with the

river or ocean are minimized and the overall distributions tend to be linearly related to salinity. When circulation weakens (when river flow is low), effects of these sources and sinks become increasingly apparent. Winter (November through April) is typically characterized by river flows greater than 500 m³·s⁻¹, and summer by flows of 200 to 300 m³·s⁻¹ or less. The lower flows are probably the main reason why the distributions tend to be nonlinear in summer. To contrast seasonal effects we will approximate the water-replacement time in the estuary at 500 m³·s⁻¹ as 20 days and at $100\,\text{m}^3\cdot\text{s}^{-1}$ as 70 days (Peterson et al. 1978).

Winter

River inflow is clearly a major source of substances to the estuary and, generally, must increase in importance with increasing winter discharge. During winter, photosynthetic processes are minimized because the standing crop of phytoplankton is less than in summer (Cloern 1979) and sunlight is about one-third that of summer values; atmospheric exchange may weaken because wind speeds average one-third those of summer values (Conomos 1979); and benthic activity is assumed to be subdued because of lower water temperatures. Thus, source or sink values are possibly lower than average while the river supply is about the same or greater. In a simplified model a reduction by a factor of two seems justified in the winter rates of net water column photosynthesis and atmospheric and benthic exchanges.

With regard to the level of dissolved O_2 in winter, net photosynthetic processes produce less O_2 in winter than in summer, atmospheric oxygen invasion is less in winter, and benthic oxygen consumption is also less. Therefore, the dissolved oxygen concentration in the estuary is controlled more by its concentration at the river and ocean boundaries than internal sources or sinks. If, for example, dissolved O_2 is near 100% saturation concentration in the river in winter, then the estuary would also tend to approach 100% saturation concentrations (depending on the O_2 concentrations at the ocean boundary). Similar reasoning applies to the other elements.

The relative importance of water circulation and of nonconservative sources and sinks is demonstrated by comparing replacement times of various elements in the water column, for each rate of supply or removal, with the water-replacement time, assuming the winter rates discussed above (Table 5). The dissolved-OCNSi concentrations used are based on the distributions presented herein; representative winter particulate carbon and nitrogen concentrations were chosen to be 60 and 6 µg-atoms·liter⁻¹ respectively. If the water replacement time is clearly less than the substance-turnover time, then that source or sink is relatively ineffective.

The winter ratios of water-replacement time to OCSi (sources/sinks) turnover time are all less than one. Thus, near-conservative OCSi distributions are predicted to be a common occurrence in winter. This is indeed observed.

Near conservative winter distributions, then, are a consistent pattern for dissolved silica and to a lesser extent for chlorophyll-a fluorescence (or phytoplankton) and for dissolved O_2 . Most of the NO_3 and, as might be expected from its low concentration in river and sea water, all of the NH_3 distributions appear nonconservative. It follows that the NH_3 sources may be relatively strong, even in winter, as is suggested by the distributions and calculations.

Summer

Nonconservative effects during summer are illustrated by increasing the rates of atmospheric and benthic exchange and net photosynthesis in Table 2 by 50% and decreasing river inflow from 600 m³·s⁻¹ to 100 m³·s⁻¹, a relatively low but not unusual river flow. Total inorganic carbon, primarily in the form of bicarbonate, is predicted to maintain conservative or near-conservative distributions in summer (Table 5).

TABLE 5. RATIO OF WATER REPLACEMENT TIME TO SUBSTANCE REPLACEMENT TIME DURING WINTER (W) AND SUMMER (S) $^{\rm b}$

	Substance													
Sources and	Oxygen		Σα	ΣCO_2^c Carbon POC^d			NO ₃		Nitrogen NH3		PON ^e		Silicon	
Sinks	W	S	W	S	W	S	W	S	W	S	w	S	\mathbf{W}	S
Atmosphere	0.13	1.4	0.01	0.11										
Substrate	0.16	1.7	0.02	0.21					1	16				
River														
Dissolved- inorganic	0.29	0.17	0.18	0.39	1		0.45	80.0					0.7	0.5
Particulate					1.8	0.71								
Water Column														
Net photo- synthesis	0.03	0.28			0.26	1.8					0.66	4.7	0.2	2.6
Waste	0.04	0.15	0.007					0.66	3.5					
(See note ^a)	600	600	1,700	1,700	60	90	20	10	6	4	6	9	20	60

Concentrations (μ g-atoms·liter⁻¹ at/ ℓ) in estuary.

b High value means water replacement is less important than source or sink in influencing substance distribution; water replacement is assumed to be 20 days in winter, 70 days in summer.

c Total dissolved inorganic carbon primarily as bicarbonate.

d Particulate organic carbon.

Particulate organic nitrogen.

In summer 1972 the distributions were complex, but they largely reflected the effects of photosynthetic processes in the inner estuary, where the salinity was less than 15°/00. In this instance the usual distributions of dissolved O₂ and CO₂ were reversed: oxygen was above saturation concentrations with respect to the atmosphere and carbon dioxide was depressed below saturation concentrations. In that case photosynthetic rates must balance or must exceed the carbon supply associated with both benthic oxygen consumption and atmospheric invasion. The approximation of net photosynthetic effects is now probably low, especially for this section of the estuary. The selected value can be easily revised upwards, however, in part because we do not know very well what the real net photosynthetic rate is over the entire water column.

As noted, the similar magnitudes of many of the estimated sources and sinks emphasize this dynamic nature of the system. In summer 1972 (Fig. 7) photosynthetic O₂ production needed only about 50 pg-atoms-liter' to achieve equilibrium concentrations, making net atmospheric exchange zero. Assuming a daily increase in net photosynthetic dissolved oxygen equal to the precision of the method, or, about 10 µg-atoms·liter⁻¹·d⁻¹, we conclude that it would take only 5 days to make up this deficit! It should also be noted that photosynthetic production:mineralization processes disturb the dissolved CO₂ equilibration with the atmosphere disproportionately, as compared with O₂ equilibration, primarily because the ratio of O₂ to CO₂ in the atmosphere is very small (O:C = 630:1 by atoms).

The last example illustrating the dynamic nature of the system is suggested by comparing the summer of 1971 with 1972. In 1971 river inflow was stronger, averaging 400 m³·s⁻¹, as compared with 200 in 1972, and photosynthetic effects in 1971 appear relatively weaker (Figs. 3, 5). Thus, it is apparent from the observations that the calculations as made have considerable freedom for adjustment up or down and will still appear realistic.

During periods of high river flow, then, many nonconservative substances appear to be passing through the estuary. During low river flow, however, the magnitudes of local sources and sinks may exceed river and ocean inputs. Also, their estimated magnitudes indicate that several processes control the oxygen, carbon, nitrogen and silicon distributions at comparable rates. With more observations, future refinement in the above estimates of sources and sinks and water replacement times is expected. It is important that such refinement be accompanied by observations from the main channels into the "unknown" waters overlying the shoals of the Bay and into the shelf waters entering the Bay.

ACKNOWLEDGMENTS

I thank W. W. Broenkow and D. E. Hammond for their critical reviews, and my colleagues at the U. S. Geological Survey for their comments and for the pleasure of working with them in the field.

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