

## Benthic fluxes in San Francisco Bay

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### Abstract

Measurements of benthic fluxes have been made on four occasions between February 1980 and February 1981 at a channel station and a shoal station in South San Francisco Bay, using *in situ* flux chambers. On each occasion replicate measurements of easily measured substances such as radon, oxygen, ammonia, and silica showed a variability ( $\pm 1\sigma$ ) of 30% or more over distances of a few meters to tens of meters, presumably due to spatial heterogeneity in the benthic community. Fluxes of radon were greater at the shoal station than at the channel station because of greater macrofaunal irrigation at the former, but showed little seasonal variability at either station. At both stations fluxes of oxygen, carbon dioxide, ammonia, and silica were largest following the spring bloom. Fluxes measured during different seasons ranged over factors of 2–3, 3, 4–5, and 3–10 (respectively), due to variations in phytoplankton productivity and temperature. Fluxes of oxygen and carbon dioxide were greater at the shoal station than at the channel station because the net phytoplankton productivity is greater there and the organic matter produced must be rapidly incorporated in the sediment column. Fluxes of silica were greater at the shoal station, probably because of the greater irrigation rates there. N + N (nitrate + nitrite) fluxes were variable in magnitude and in sign. Phosphate fluxes were too small to measure accurately. Alkalinity fluxes were similar at the two stations and are attributed primarily to carbonate dissolution at the shoal station and to sulfate reduction at the channel station. The estimated average fluxes into South Bay, based on results from these two stations over the course of a year, are (in  $\text{mmol m}^{-2} \text{d}^{-1}$ ):  $\text{O}_2 = -27 \pm 6$ ;  $\text{TCO}_2 = 23 \pm 6$ ; Alkalinity =  $9 \pm 2$ ; N + N =  $-0.3 \pm 0.5$ ;  $\text{NH}_3 = 1.4 \pm 0.2$ ;  $\text{PO}_4 = 0.1 \pm 0.4$ ; Si =  $5.6 \pm 1.1$ . These fluxes are comparable in magnitude to those in other temperate estuaries with similar productivity, although the seasonal variability is smaller, probably because the annual temperature range in San Francisco Bay is smaller.

Budgets constructed for South San Francisco Bay show that large fractions of the net annual productivity of carbon (about 90%) and silica (about 65%) are recycled by the benthos. Substantial rates of simultaneous nitrification and denitrification must occur in shoal areas, apparently resulting in conversion to  $\text{N}_2$  of 55% of the particulate nitrogen reaching the sediments. In shoal areas, benthic fluxes can replace the water column standing stocks of ammonia in 2–6 days and silica in 17–34 days, indicating the importance of benthic fluxes in the maintenance of productivity.

Pore water profiles of nutrients and Rn-222 show that macrofaunal irrigation is extremely important in transport of silica, ammonia, and alkalinity. Calculations of benthic fluxes from these profiles are less accurate, but yield results consistent with chamber measurements and indicate that most of the  $\text{NH}_3$ ,  $\text{SiO}_2$ , and alkalinity fluxes are sustained by reactions occurring throughout the upper 20–40 cm of the sediment column. In contrast,  $\text{O}_2$ ,  $\text{CO}_2$ , and N + N fluxes must be dominated by reactions occurring within the upper one cm of the sediment-water interface. While most data support the statements made above, a few flux measurements are contradictory and demonstrate the complexity of benthic exchange.

## Introduction

There are at least two reasons to understand the mechanisms and the rates of benthic exchange. First, exchange of dissolved substances across the sediment-water interface is of major importance in controlling the water column concentrations and speciations of several elements. Among these are oxygen and the nutrients (carbon, nitrogen, phosphorus, and silica) required for phytoplankton growth. Second, in a steady state system, the flux of dissolved species through any horizon is a measure of the depth-integrated reactions occurring below this horizon. Consequently, benthic exchange rates can be used to identify and quantify diagenetic reactions occurring in sediments. Thus, accurate estimates of benthic exchange are required for biogeochemical modeling of natural systems and also for interpretation of the sedimentary record.

Sediments are frequently considered to have biogeochemical zones (Fig. 1) that are identified by the molecules primarily used as terminal electron acceptors by microbial organisms (Claypool & Kaplan, 1974; Froehlich *et al.*, 1979). These zones have been identified from the study of pore waters, and may overlap to some degree. The sequence of these zones corresponds to and is probably controlled by the free energies generated by using different oxidants as terminal electron acceptors. In many es-

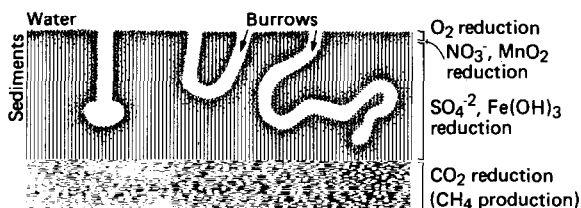


Fig. 1. Biogeochemical zonation in sediments. Because convoluted burrows may be present in estuarine sediments, it is often difficult to sample distinct biogeochemical zones. The oxygen reduction zone in San Francisco Bay (stippling) is usually only a few mm thick and parallels the sediment-water interface and the walls of some burrows. The distributions of Mn<sup>2+</sup> and NO<sub>3</sub> have not been studied in this system, but by analogy to other systems, NO<sub>3</sub><sup>-</sup> and MnO<sub>2</sub> are probably reduced within a few mm of the oxygenated zone. The SO<sub>4</sub><sup>2-</sup> and Fe(OH)<sub>3</sub> reduction zone (vertical lines) appears to extend from a few mm to at least 60 cm in this system (the bottom of the longest cores studied). If a CO<sub>2</sub> reduction zone (horizontal lines) is present in this system, it lies deeper than 60 cm. No evidence for the presence of this zone has been found in our studies.

tuarine systems the geometry of zonation may not be strictly one-dimensional because benthic macrofauna may burrow extensively and irrigate sediments. These activities may cause zonation to extend radially from burrow walls (Aller, 1980) that can follow rather convoluted patterns, making the spatial distribution of zones impossible to resolve during sampling. The thickness of each zone should depend on two kinetic factors, the rate of oxidant utilization within the sediment column and the rate of oxidant transport. Oxidant reaction rates may depend on the abundance of metabolizable carbon (or other suitable reductants), the abundance of oxidant, the presence of organisms which may catalyze reactions, temperature and, to a lesser degree, salinity and pressure. Oxidant transport rates depend both on the concentration of oxidants and the rates of processes primarily responsible for transport.

Several processes that effect transport of solutes through interstitial waters and across the sediment-water interface have been identified. These include molecular diffusion (Manheim, 1970; Li & Gregory, 1974; Lasaga, 1979; Katz & Ben-Yaakov, 1980), physical stirring of surface sediments by currents (Hammond *et al.*, 1977; Vanderborght *et al.*, 1977), macrofaunal irrigation (Grundmanis & Murray, 1977; Goldhaber *et al.*, 1977; Aller & Yingst, 1978; Hammond & Fuller, 1979; Aller, 1980), and irrigation of anoxic sediments through bubble tubes (Martens *et al.*, 1980). While rates of molecular diffusion can be estimated relatively accurately from measurements of concentration gradients and a knowledge of diffusion coefficients, the rates of stirring or irrigation *in situ* must be established by use of a tracer that has known reaction kinetics.

Benthic exchange and sediment diagenesis have been studied extensively in recent years, and excellent reviews may be found in Lerman (1977), Berner (1980), Zeitschel (1980), and Nixon (1981). The purpose of this paper is to outline processes thought to be important in estuarine benthic exchange, describe methods for estimation of benthic exchange rates, and to present data that illustrate characteristics of benthic exchange in South San Francisco Bay. Measurements of pore water chemistry are used to demonstrate those transport processes that are important in this system, and *in situ* flux measurements demonstrate temporal and spatial variability in exchange rates. The importance of benthic

exchange for nutrient cycling in the Bay is assessed and compared to other estuarine systems.

### Methods to estimate benthic fluxes

Several methods can be used to estimate benthic fluxes. Each method has limitations and may not be suitable for all environments. Confidence in estimates of benthic fluxes can be developed only if two or more methods yield similar results in a given system. Briefly, methods and their limitations are:

1) Incubation of cores and measurement of the change in concentrations in overlying water. This approach requires only the collection of a core and its incubation at *in situ* temperatures. However, it may be difficult to reproduce the *in situ* physical and biological conditions in the laboratory. Coastal and estuarine sediments with abundant macrofauna contain burrows that may be truncated or disturbed during the coring process. Such disturbances may seriously affect the observed fluxes. In deeper water, bacterial metabolism may be pressure-dependent (Jannasch *et al.*, 1976). For example, Smith (1978) found that incubation of deep sea cores at the surface indicates far greater oxygen uptake rates than *in situ* respirometer measurements indicate. However, Pamatmat (1971) has obtained reasonable agreement between the oxygen uptake in incubated cores from Puget Sound and uptake rates obtained with *in situ* chambers. Thus, the pressure effect is probably not an issue for shallow estuarine systems. In summary, the incubation of cores may be satisfactory for measuring fluxes in some cases, but data collected in this way must be interpreted with caution if large macrofauna are present.

2) Construction of a mass balance for a substance measured in the overlying water column. This approach is complicated because reactions and transport in the overlying water are often difficult to characterize accurately. An additional problem (or benefit in some cases) is that this approach integrates fluxes from a large area. In most cases, the uncertainties in deriving benthic fluxes by this method are far larger than those for other techniques.

3) Calculation of fluxes from pore water concentration profiles. This approach is less complicated logistically than other techniques and has the additional benefit of yielding information on the depth

distribution of reaction sites. One drawback is the difficulty in measuring steep concentration gradients that sometimes exist in surface sediments. Also, if reaction rates vary with depth, it may be difficult to resolve their functionality. Another drawback is the uncertainty in modeling the analytical results owing to the difficulty in quantifying transport that results from non-diffusive processes. A method of quantifying transport rates of non-diffusive processes is to use a tracer that has a known source function and reaction kinetics. Tracers that have been used include sulfate, silica, ammonia, radon, and artificial spikes such as sodium-22 and tritium. The use of sulfate (Goldhaber *et al.*, 1977) has been based on the assumption that a zone in which these compounds are conservative overlies a zone in which they are consumed, and this assumption may not be correct. The use of silica (Vanderborgh *et al.*, 1977) may not be satisfactory because reaction rate constants for this tracer appear to depend on the presence or absence of oxygen (Rea, 1981). Ammonia appears to be more reliable (Aller, 1980), but because this compound may be involved in ion exchange processes or may be metabolized if oxygen is present, some uncertainty is introduced in its application. Aller (1984) has cautioned against the use of artificially introduced tracers because the results obtained may depend strongly on the duration of the experiment.

Radon-222, however, does not have the limitations of the previously mentioned tracers. It is a naturally-occurring radioactive isotope so that its distribution will not have the scale dependence of artificial spikes, and it is a member of the noble gas family so that it is not involved in biological reactions. This isotope was first suggested as a tracer for sediment-water exchange by Broecker (1965). A description of its use in estuarine systems has been given by Hammond & Fuller (1979). Briefly, radon-222 is produced by the decay of radium-226 and decays with a 3.8-day half-life. Radium has low solubility and thus is primarily associated with solid phases, while radon has high solubility and can migrate, leading to high radon concentrations in pore waters and lower concentrations in the water column. In a system that is closed for a time greatly exceeding the radon half-life, the activity ratio of the two isotopes will be one. If the ratio is less than one, the radon deficiency is a measure of the rate of escape of radon relative to the rate of decay, and a

model to describe transport may be constructed. Models will be discussed in a later section. Among the disadvantages of using radon are: its measurement is more difficult than that of other species; present measurement strategies do not permit measurement of radon and other compounds on the same sample; and its distribution is sensitive only to irrigation processes that occur over time scales of about 1–100 days.

4) Measurement of fluxes *in situ* by placing chambers over the sediment and monitoring concentration changes in the overlying water. This method has been used frequently in estuarine systems (Pamatmat & Banse, 1969; Nixon *et al.*, 1976 and others). In shallow waters chambers can be deployed by divers, but in deeper waters this is not possible. As a result, devices of varying degrees of complexity and cost have been developed to deploy and sample remote chambers (Smith *et al.*, 1976; Weiss *et al.*, 1977; Hargrave & Connolly, 1978; Hinga *et al.*, 1979; Smith *et al.*, 1979). One complication of this technique is that turbulence within the chamber may differ from normal conditions. For example, during an experiment in San Francisco Bay, we observed large differences in fluxes of radon, oxygen, and nutrients when results from stirred and unstirred chambers were compared. This experiment was carried out during a period of below-average water column salinity, and the difference was apparently due to density stratification that developed within unstirred chambers during deployment (Hartman & Hammond, 1984). Moreover, the stirring rate may be critical. Recent work with oxygen micro-electrodes (Revsbech *et al.*, 1980) has demonstrated the presence of a boundary layer a few hundred  $\mu\text{m}$  thick in water overlying sediments (Jorgensen & Revsbech, 1985). Substances that are very reactive in sediments have fluxes limited by diffusion through this layer, and appropriate turbulence within a benthic chamber is necessary to maintain the proper boundary layer concentration. That chamber mixing rates affect the oxygen uptake rate of estuarine sediments has been clearly demonstrated by Pamatmat & Banse (1969) and Boynton *et al.* (1981).

Not all benthic fluxes depend strongly on turbulence. For example, Callender & Hammond (1982) found similar fluxes of ammonia, silica, and radon from Potomac River sediments into stirred and

unstirred benthic chambers. This result suggests that reactions involving these substances occur so slowly that boundary layer thickness does not limit transport, in the absence of stratification. Alkalinity fluxes also should show little dependence on stirring rate, although alkalinity may have a steep gradient near the sediment-water interface, because carbonate dissolution may be limited by detachment rates of molecules from surfaces. This argument is supported by the work of Keir (1980), who has shown that carbonate dissolution rates occur at a rate proportional to  $(1 - \Omega)^\eta$ , where  $\Omega$  is the degree of saturation and  $\eta$  equals 4–5. If dissolution rates were controlled by transport away from the crystal,  $\eta$  should equal one; thus his observations indicate that the dissolution rates are probably limited by processes occurring at the crystal surface. Although Santschi *et al.* (1983) showed that the dissolution rate of oolites in MANOP (Manganese Nodule Project) lander chambers depends on the rate of water circulation in the chambers, it is not clear that this result is applicable *in situ*, because they used solutions free of  $\text{Mg}^{+2}$  and  $\text{PO}_4^{-3}$ . These ions inhibit dissolution (Morse, 1978) and make it likely that dissolution should be surface-controlled.

Other drawbacks to the use of chambers are that small fluxes are difficult to measure, that they do not yield information about the depth dependence of reaction rates, that for substances involved in more than one reaction (such as nitrate) only net fluxes (not gross fluxes) are measured, and that long deployments may lead to anoxic conditions within the chambers.

In summary, in estuarine systems, benthic chambers appear to be the best technique for accurate measurement of benthic exchange, because they introduce the least disturbance and are the most sensitive technique for many substances. However, care should be taken to try to reproduce *in situ* turbulence within chambers, because oxygen fluxes, as well as fluxes of other species that may have large gradients in the top 1–2 mm of the sediment column, are likely to depend on the stirring rate. Complementary studies of pore water profiles and *in situ* benthic flux measurements may yield information about not only the magnitude of benthic fluxes, but also about the nature of transport processes and the character of diagenetic reactions.

## Interstitial water profiles in San Francisco Bay

Gravity cores and diver-collected cores (5-cm and 8-cm ID) have been obtained at a number of stations throughout San Francisco Bay, and their interstitial waters have been extracted by centrifugation and analyzed for nutrients. Details of this work and a more complete discussion of the data obtained are given by Korosec (1979) and Rea (1981). Additional cores have been collected at the same locations, sectioned and analyzed for radon and radon emanation rate. Details of these measurements can be found in Hammond & Fuller (1979) and Hartman & Hammond (1984).

Our work has focused on two areas in South San Francisco Bay, chosen for logistical reasons and because they should represent major sedimentological environments of this subestuary. One area, identified in subsequent discussions as station 27.5, lies in the channel and includes USGS stations 27 and 28 (Fig. 2). This area is about 14 m deep and has an accumulation rate calculated to range from 0.1–1 g cm<sup>-2</sup> yr<sup>-1</sup>, based on Th-234 and Pb-210 profiles (Fuller, 1982). Sediments contain large numbers of the deep burrowing polychaete *Heteromastus filiformis* as well as other organisms. The second area, identified as station 28C, lies in a shoal area about 1 m deep that may not be accumulating any sediments at present (Fuller, 1982). It is populated by large numbers of the tube-dwelling polychaete *Asychis elongata*, among other organisms. Measurements of solid phase properties at these

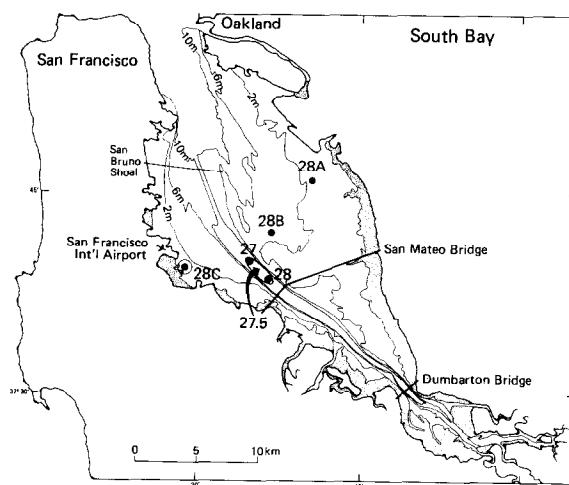


Fig. 2. South San Francisco Bay. The stippled area is intertidal. Station 27.5 refers to the channel area between USGS stations 27 and 28. Station 28C refers to the shoal area circled. Depth contours refer to depth below mean lower low water and have been taken from navigation charts.

sites are given in Table 1.

Typical profiles of nutrients and radon in pore waters from these two areas are shown in Fig. 3. At station 27.5, TCO<sub>2</sub> and NH<sub>3</sub> profiles show a zone about 10 cm thick that has small gradients. Below this zone gradients increase markedly. Profiles such as those in Fig. 3 are observed in all seasons, and TCO<sub>2</sub> profiles from station 27.5 (Fig. 4) serve as examples. These all show smaller gradients in the

Table 1. Characteristics of stations 27.5 and 28C.

A. Physical characteristics			B. Solid phase composition (dry wt %)					
Station	27.5	28C	Sta.	depth (cm)	% S <sup>b</sup>	% SiO <sub>2</sub> <sup>c</sup>	% C <sup>d</sup>	% N <sup>d</sup>
Mean depth (m)	14 m	1.5 m	27.5	6–10	0.37	13.5	1.38	0.16
Sedimentation rate <sup>a</sup> (g cm <sup>-2</sup> yr <sup>-1</sup> )	1.1–2.8 (2.1)	0–0.1 (0.1)		25–30 60–65	0.47 0.49	13.5 13.7	1.38 1.27	0.17 0.15
Net accumulation rate <sup>a</sup> (g cm <sup>-2</sup> yr <sup>-1</sup> )	0.1–1 (0.5)	0–0.03 (0.03)	28C	0–4 4–8	0.23 0.47	4.9 3.4	1.41 1.46	0.15 0.12
Average porosity	0.75	0.70		10–15	0.51	4.1	1.27	0.11

<sup>a</sup> Fuller (1982) based on profiles of Th-234 and Pb-210. Values in parentheses are best estimates.

<sup>b</sup> Analyzed by LECO combustion (B. Leslie, pers. comm.).

<sup>c</sup> Analyzed by sodium carbonate leach (M. Hamilton, pers. comm.).

<sup>d</sup> Analyzed with high temperature combustion, includes both organic carbon and carbonate. Large shell fragments were excluded from samples.

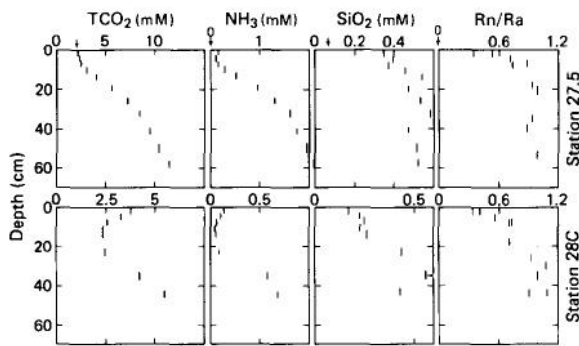


Fig. 3. Pore water chemistry at two stations in San Francisco Bay. Vertical bars show the thickness of sampling intervals. Rn/Ra measurements were made on cores collected adjacent to those used for nutrient analysis. For reference, concentrations in the overlying water are shown by arrows.

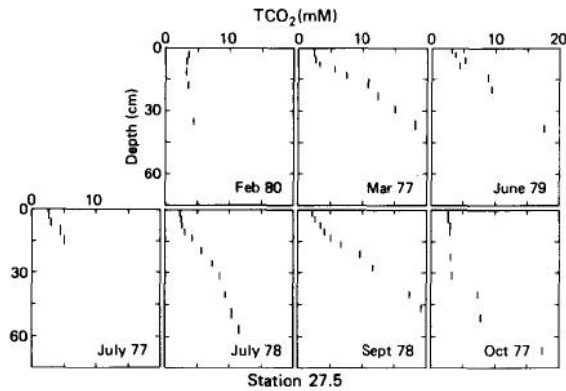


Fig. 4.  $\text{TCO}_2$  profiles in channel cores. These cores were collected at different times of the year at station 27.5. Vertical bars indicate sampling intervals.

upper portion of the core than in the lower portion. Because porosity shows little change with depth, material balance considerations require that  $\text{CO}_2$  diffusing upward from the lower portion must be transported rapidly through the upper section in order to maintain these profiles. The probable mechanism responsible for this rapid transport is irrigation, a circulation of overlying water through the abundant burrows of macrofauna. This process, identified in many other estuarine and coastal systems, is likely to occur anywhere that oxygen is sufficient and salinity is stable enough to support macrofauna. Irrigation may occur to 40–50 cm (note October 1977 in Fig. 4) but the depth of the irrigated zone does not appear to show any consistent seasonal pattern.

X-radiographs of sediment slabs prepared from cores reveal a dense population of polychaete worm burrows and illustrate their geometry. Counting of burrow lengths in radiographs like those shown indicates that the upper 25 cm of bay sediments have a burrow density of  $1\,000\text{--}7\,000\text{ m}^{-2}$  (Korosec, 1979). Burrows are not always vertical, and adjacent cores may have very different burrow densities (Fig. 5).

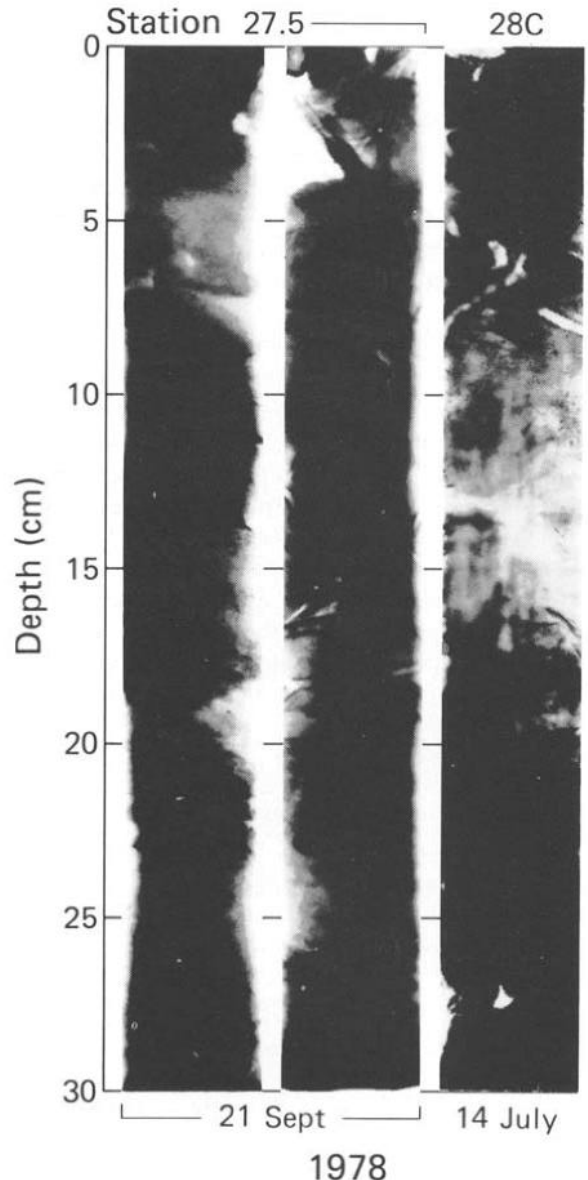


Fig. 5. X-radiographs of cores from stations 27.5 and 28C. These prints are positives of exposures made of 2-cm thick slabs prepared from gravity cores. Note that the two adjacent cores from station 27.5 have very different burrow densities.

At station 28C, both  $\text{TCO}_2$  and  $\text{NH}_3$  profiles are more complex than at station 27.5 (Fig. 3). These profiles reach local maxima in the top interval sampled, decrease to minima that are still in excess of overlying water concentrations, and increase below these minima. The increases with depth are due to biological remineralization of organic matter, and the minima in these profiles may be produced either by uniform irrigation and a production of  $\text{CO}_2$  or  $\text{NH}_3$  which decreases with depth, as Aller (1980) has shown, or by a core intersecting a horizontal burrow.

The sensitivity of a pore water profile to irrigation will depend on the relative rates of irrigation and the kinetics of nutrient release to pore waters. For example, the effects of irrigation on  $\text{TCO}_2$  and ammonia profiles are more apparent than the effect on the silica profile (Fig. 3). Radon profiles are also influenced by irrigation activities (Fig. 3). If one-dimensional molecular diffusion was the only transport process occurring, the  $\text{Rn}/\text{Ra}$  ratio would be unity at depths below 8 cm. However, measurable radon deficiencies ( $\text{Rn}/\text{Ra} < 1$ ) extend below 40 cm at station 27.5 and to about 25 cm at station 28C. That the deepest intervals sampled have  $\text{Rn}/\text{Ra} = 1$  demonstrates that these radon profiles are not artifacts of sample handling. Radon deficiencies are observed year-round at both stations and extend far deeper than a model based on one-dimensional diffusion would predict (Fig. 6). The similarity of composite radon profiles of cores collected during different seasons over a six-year period (Fig. 6) indicates that irrigation rates do not vary greatly throughout the year. These profiles can be used to quantify irrigation transport rates.

The impact of irrigation on transport has been described mathematically in a variety of ways. Radon distribution can be used to test the adequacy of these models. Goldhaber *et al.* (1977) and others have modeled irrigation by treating it as a diffusive process with a constant eddy diffusivity through the irrigated zone. In such a model, the radon/radium ratio should approach unity exponentially with increasing depth. While this may be true in some cases, radon profiles at station 27.5 (Fig. 6) are not consistent with this model because they show an extended zone with a deficiency but no gradient between about 15 and 40 cm. An alternative approach has been used by Aller (1980, 1982), who developed a model that uses molecular diffusion

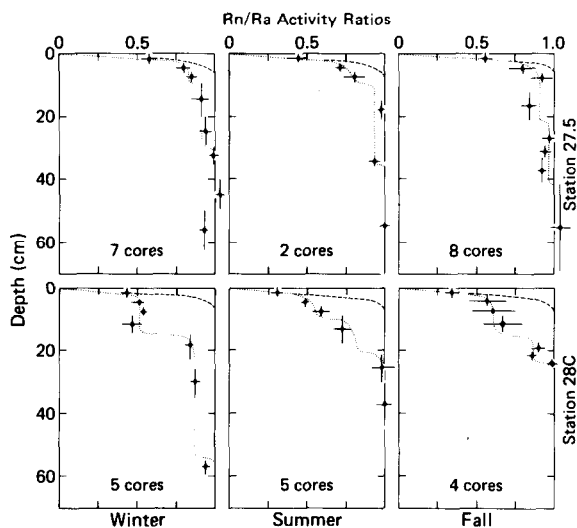


Fig. 6. Composite  $\text{Rn}/\text{Ra}$  profiles in cores. Average ratios ( $\pm 1\sigma$ ) in different intervals are indicated by crosses. The dotted line shows profiles fit to data using the three zone irrigation model. The dashed line shows the profile expected for one-dimensional molecular diffusion. A  $\text{Rn}/\text{Ra}$  ratio of 1.0 is expected for a closed system.

into worm burrows to describe irrigation. This type of model requires knowledge of the geometry of burrows that are connected to the sediment-water interface and an assumption about the residence time of water within these burrows. Such a model could reproduce the profiles observed (Fig. 6) if appropriate geometries were known. But, to independently establish the appropriate geometry and water residence time in burrows would be very difficult. Another approach is that of Hammond & Fuller (1979) and McCaffrey *et al.* (1980), who suggested that irrigation could be modeled as an advective process. However, it is not likely that water actually flows through fine-grained sediments. Instead it may flow through burrows and acquire a composition close to that of the remaining interstitial water due to molecular diffusion through burrow walls. A variation of these approaches is that of Imboden (1981), who suggested that non-Fickian models might be appropriate to describe processes like irrigation. Such a model contains a transport term that is non-local, indicating that it does not depend on the local concentration gradient. Boudreau (1984) and Emerson *et al.* (1984) have shown that equations for the radial diffusion and advective models described earlier

reduce to Imboden's (1981) formulation of transport as a non-local process. Christensen *et al.* (1984) have developed a similar equation for irrigation transport.

Following the non-local approach, a material balance for radon can be written:

$$\frac{dC}{dt} = \phi D_s \frac{\partial^2 C}{\partial x^2} - \lambda C + P - \lambda'(C - C_0) \quad (1)$$

where  $C$  = concentration in pore water (atoms  $\text{cm}^{-3}$ );  $t$  = time (s);  $x$  = depth in sediment (cm);  $\phi$  = porosity;  $D_s = D_m/\theta^2$ , the effective diffusivity ( $\text{cm}^2 \text{ s}^{-1}$ );  $D_m$  = molecular diffusivity ( $\text{cm}^2 \text{ s}^{-1}$ );  $\theta$  = tortuosity;  $\lambda$  = decay constant for radon ( $\text{s}^{-1}$ );  $P$  = radon emanation rate per unit volume of pore water (atoms  $\text{cm}^{-3} \text{ s}^{-1}$ );  $\lambda'$  = rate constant for non-local exchange of pore water with overlying water ( $\text{s}^{-1}$ ); and  $C_0$  is the radon concentration in the overlying water (atoms  $\text{cm}^{-3}$ ). The last term on the right side of Equation 1 is the non-local term that includes the combined effects of horizontal diffusion into burrows and subsequent advection to overlying waters, and thus the equation can be formulated in one dimension. If  $\phi$ ,  $D_s$ ,  $P$ , and  $\lambda'$  are constant with depth, the general solution to this equation at steady state is:

$$(\lambda + \lambda')C = P + \lambda'C_0 - A_1 e^{ax} - A_2 e^{-ax} \quad (2)$$

where  $a = [(\lambda + \lambda')/(D_s\phi)]^{1/2}$ ; and  $A_1$  and  $A_2$  = constants of integration. The constants  $A_1$ ,  $A_2$ , and  $a$  are found by applying appropriate boundary conditions and curve fitting. The radon distributions in composite profiles (Fig. 6) suggest that three zones are present in each profile: a rapidly irrigated zone, a slowly irrigated zone, and a non-irrigated zone. In each zone,  $\lambda'$  (and thus  $A_1$ ,  $A_2$ , and  $a$ ) is different.

Appropriate boundary conditions are that:  $\lambda C = P$  at infinite depth;  $C = C_0$  at the sediment-water interface; and the concentration and concentration gradients are continuous at boundaries where  $\lambda'$  changes.  $D_s$  is a function of temperature and porosity and is assumed constant for each profile. The depth to which irrigation occurs is related to the depth of burrowing, and because *Heteromastus* burrows at station 27.5 extend more deeply than *Asychis* burrows at station 28C, the thickness of the irrigated zone is not as great at the latter station. The thickness of each zone ( $h_1$  and  $h_2$  in Table 2) has been selected to match discontinuities in each profile. The constants  $A_1$ ,  $A_2$ , and  $a$  (and thus  $\lambda'$ ) for each zone have been found by least-square curve fitting of data in Fig. 6. The Rn/Ra ratio in the top 3 cm of each profile depends primarily on  $D_s$ , and this parameter was adjusted to obtain a best fit for the top interval.

Calculated values for  $D_s$  (Table 2) are very close to those expected, based on the molecular diffusivity of radon at the observed temperatures and the tortuosity predicted from the Archie relation (Berner, 1980). Results for  $\lambda'$  (Table 2) indicate that the rates of irrigation at each station do not vary greatly throughout the year. This lack of seasonality may indicate that water column currents may drive circulation through burrows (Reidl *et al.*, 1972), but this conclusion is speculative. Irrigation rates at shoal station 28C are consistently about four times greater than those at channel station 27.5. Possible causes of this difference are that burrows at the shoal station are larger, more rapidly flushed, or more abundant. These possibilities cannot be clearly distinguished. X-radiographs indicate that *Asychis* burrow diameters at the shoal station are larger (about 4 mm) than *Heteromastus* burrows at the channel station (about 3 mm) and

Table 2. Irrigation rate constants derived from radon profiles. As discussed in the text, sediments have been divided into an upper zone (1), a middle zone (2), and a lower non-irrigated zone. The residence time of pore waters is assumed to be the inverse of  $\lambda'$ .

Profile	$h_1$ (cm)	$\lambda'_1$ ( $10^{-6} \text{ s}^{-1}$ )	$h_2$ (cm)	$\lambda'_2$ ( $10^{-6} \text{ s}^{-1}$ )	$D_s$ ( $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )	
27.5 Summer	0-9	0.55	9-36	0.12	6.5	
	Fall	0-21	0.24	21-42	0.12	5.0
	Winter	0-9	0.45	9-30	0.20	3.0
28C Summer	0-9	2.0	9-21	0.52	6.0	
	Fall	0-15	1.4	15-23	0.32	5.5
	Winter	0-15	2.0	15-55	0.32	3.0



thus should be irrigated more rapidly if water flow drives the circulation. Also, *Asychis* is known to actively pump water, whereas *Heteromastus* does not (F. Nichols, pers. comm.), so both of these factors could cause more rapid irrigation at the shoal station. The burrow densities observed in X-radiographs from these stations are comparable, but the critical factor is the number of open burrows, and this cannot be determined.

Non-local irrigation transport includes two processes: horizontal diffusion into burrows and flushing of burrows. The rate of the former process depends on the density of open burrows and the rate of the latter depends on the residence time of water in open burrows. Values of  $\lambda'$  calculated reflect both. Two end-member cases may be considered. If the residence time of water in burrows is very short, the composition of water in burrows should be close to that in the overlying water, and  $\lambda'$  could be used to estimate the density of open burrows and thus the effective surface area in burrow walls that is available for exchange. This approach has been assumed but not justified by Aller (1980) and Christensen *et al.* (1984). Alternatively, if the residence time of water in burrows is long, relative to the time required for diffusional exchange between burrows and surrounding pore waters, burrow water should acquire a composition similar to that of surrounding pore waters. For simplicity, we will assume (but cannot justify) that 10% of the burrows seen in X-radiographs are open. The residence time of water in open burrows can be estimated as  $F/\lambda'$ , where  $F$  is the fraction of pore water in open burrows and  $\lambda'$  is the irrigation rate constant derived from radon profiles.  $F$  can be calculated:

$$F = \frac{\pi NR^2}{\phi} \quad (3)$$

where  $N$  = density of open burrows (#  $\text{cm}^{-2}$ );  $R$  = burrow radius (cm); and  $\phi$  = porosity. From measurements of X-radiographs, the average radius of burrows is 3–4 mm and their density is 1000–7000  $\text{m}^{-2}$  (Korosec, 1979). If 10% of these are open,  $F$  is 0.1–1.3%, and the burrow water residence time (equal to  $F/\lambda'$ ) is 0.1–8 hrs, with the range including extreme values of  $N$  and  $\lambda'$ . The use of average values for  $F$  and  $\lambda'$  yields 1.5 hrs. Exchange of burrow water with an equal volume of surrounding pore water should occur in 0.3–0.5 hrs,

based on rates of molecular diffusion (for a diffusivity of  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), although Aller (1983) has shown that mucus coatings may hinder diffusion through some burrow walls and inhibit equilibration. These calculations suggest that burrow water residence time is comparable to or greater than equilibration time, although it is difficult to establish how many burrows are open.

If the assumption of a long burrow water residence time is correct, irrigation rate constants derived from radon may be used to estimate benthic fluxes of other species by the relation:

$$J = -\phi_0 D_s C_o' + \sum_i h_i \lambda_i' (C_w - C_i) \quad (4)$$

where  $J$  = flux into sediments (moles  $\text{cm}^{-2} \text{ s}^{-1}$ );  $C_o'$  = concentration gradient through pore waters at the sediment-water interface (moles  $\text{cm}^{-4}$ );  $h_i$  = thickness of zone  $i$  (cm);  $C_w$  = concentration in the overlying water column (moles  $\text{cm}^{-3}$ );  $C_i$  = average concentration in pore waters throughout zone  $i$  (moles  $\text{cm}^{-3}$ ); and other terms are as defined in Equation 2. The first term on the right side of Equation 4 represents vertical molecular diffusion across the sediment-water interface, and the second term represents the irrigation (non-local) transport. The first term was evaluated by assuming that gradients are linear through the top interval analyzed (usually 0–2 cm) and may result in under-estimating fluxes of compounds that have large gradients through the upper few millimeters, such as  $\text{TCO}_2$ . Because oxygen and  $\text{N} + \text{N}$  (nitrate + nitrite) profiles were not measured, their diffusive fluxes could not be calculated. Average concentrations needed for the second term were evaluated by averaging all pore water measurements made through each irrigated zone during a season. Non-local fluxes of oxygen and  $\text{N} + \text{N}$  were calculated by assuming that these molecules are not present in pore water. Results of these calculations are given in Table 3.

In developing this model several assumptions have been made that may affect the accuracy of the calculated results (Table 3). First, this model assumes that the ratio of non-local transport of radon to that of nutrients is equal to the average concentration ratio in pore waters. This assumption is valid if the residence time of water in open burrows is long in comparison to the time required for burrows to equilibrate with surrounding pore waters. If

Table 3. Benthic fluxes<sup>a</sup> (mmols m<sup>-2</sup> d<sup>-1</sup>) calculated from pore water profiles of nutrients and radon. Negative values indicate fluxes into the sediments. The number of pore water profiles averaged for each calculation is given in parentheses. N.D. indicates no data is available.

Sta.	Season	O <sub>2</sub>	TCO <sub>2</sub>	N + N	NH <sub>3</sub>	PO <sub>4</sub> <sup>-3</sup>	SiO <sub>2</sub>
27.5	Summer	N.D. } -0.8 } >-1 -0.4 }	1.7 } 3.4 } 14.4 9.3 } (6)	N.D. } -0.06 } >-0.1 -0.04 }	0.38 } 0.44 } 2.4 1.60 } (4)	0.05 } 0.23 } 0.6 0.31 } (3)	0.39 } 1.03 } 2.4 1.00 } (6)
	Fall	N.D. } -0.7 } >-1 -0.4 }	3.4 } 2.3 } 7.2 1.5 } (1)	N.D. } -0.07 } >-0.1 -0.04 }	0.20 } 0.18 } 0.5 0.13 } (3)	N.D. N.D. N.D.	0.38 } 0.98 } 1.8 0.45 } (3)
	Winter	N.D. } -0.7 } >-1 -0.7 }	0.7 } 2.3 } 14.5 11.5 } (3)	N.D. } -0.08 } >-0.2 -0.09 }	0.13 } 0.20 } 1.6 1.26 } (2)	0.02 } 0.17 } 0.6 0.43 } (2)	0.36 } 0.92 } 2.8 1.50 } (3)
	Ave.	>-1	12.0	>-0.1	1.5	0.6	2.3
28C	Summer	N.D. } -1.0 } >-2 -0.8 }	3.7 } 17.5 } 27.7 6.5 } (5)	N.D. } -0.08 } >-0.1 -0.03 }	0.38 } 1.10 } 2.1 0.63 } (7)	0.00 } 0.12 } 0.3 0.13 } (3)	0.24 } 2.56 } 3.9 1.12 } (7)
	Fall	N.D. } -3.4 } >-4 -0.4 }	1.1 } 8.4 } 12.2 2.7 } (1)	N.D. } -0.14 } >-0.2 -0.02 }	0.13 } 1.18 } 1.7 0.38 } (2)	N.D. N.D. N.D.	0.19 } 4.79 } 5.9 0.95 } (1)
	Winter	N.D. } -5.4 } >-8 -2.3 }	0.7 } 11.4 } 17.0 4.9 } (2)	N.D. } -0.51 } >-0.7 -0.21 }	0.14 } 1.47 } 4.2 2.62 } (1)	0.01 } 0.25 } 0.8 0.52 } (1)	0.23 } 2.75 } 6.9 3.93 } (2)
	Ave.	>-5	19.0	>-0.3	2.7	0.6	5.6

<sup>a</sup> For each species, the format is: interface molecular diffusion flux }  
upper zone non-local flux } total flux  
lower zone non-local flux } (# cores)

equilibration does not occur, compounds with greater diffusivities or larger concentration gradients than radon will exchange more rapidly than radon, and the non-local model will under-estimate their fluxes. A second assumption of the model is that use of average irrigation rates and average pore water concentrations is appropriate, because cores with large radon deficiencies should have small nutrient concentrations in pore waters and vice versa. The averaging approach assumes that irrigation rates and nutrient enrichment are negatively and linearly correlated. A third assumption is that the sign of reaction rates does not change near burrow boundaries. For example, pore waters are enriched in Fe<sup>+2</sup> (Rea, 1981) that may be oxidized and precipitate when contact with oxygenated water occurs. Thus, this model would over-estimate the flux of Fe<sup>+2</sup> and, possibly, PO<sub>4</sub><sup>-3</sup> that might co-precipitate with ferric oxyhydroxides.

### Benthic flux measurements with chambers: Spatial and temporal variability

Benthic flux chambers (Hartman & Hammond, 1984) were deployed at the shoal and channel stations in South San Francisco Bay (Fig. 2) during 1980–1981. Replicate deployments were carried out on four occasions, with each set covering a period of about a week. Each deployment lasted about 1 day, and each chamber was sampled two or three times during this period. Samples for nutrients were filtered and analyzed by auto analyzer techniques that have been developed for estuarine conditions (Smith *et al.*, 1979; Harmon *et al.*, 1985). Oxygen was analyzed by Winkler titration (Carpenter, 1965). Alkalinity was measured using a Gran titration (Gieskes & Rogers, 1973) and pH by standard electrode techniques. TCO<sub>2</sub> was calculated from alkalinity and pH. Radon was measured by extrac-

Table 4. *In situ* benthic fluxes measured at two stations in South San Francisco Bay. Data are averages  $\pm 1\sigma_x$  where  $\sigma_x$  is the standard error. The number of measurements is in parentheses. Units are:  $\Delta t$  (average deployment time in hrs), T ( $^{\circ}\text{C}$ ), Rn (atoms  $\text{m}^{-2} \text{d}^{-1}$ ), all others ( $\text{mmol m}^{-2} \text{d}^{-1}$ ). A negative value indicates a flux into the sediment.

Date	$\Delta t$	T	Rn	O <sub>2</sub>	TCO <sub>2</sub>	Alk	N + N	NH <sub>3</sub>	PO <sub>4</sub> <sup>3</sup>	SiO <sub>2</sub>
Station 27.5										
2-80	9	12	269 $\pm$ 12 (3)	-16 $\pm$ 11 (2)	n.d.	n.d.	0.0 $\pm$ 0.3 (3)	5.0 $\pm$ 1.3 (3)	1.3 $\pm$ 0.2 (3)	7 $\pm$ 1 (3)
6-80	20	17	74 $\pm$ 8 (2)	-22 $\pm$ 8 (2)	33 $\pm$ 1 (2)	13 $\pm$ 5 (2)	0.8 $\pm$ 0.2 (2)	3.9 $\pm$ 0.8 (2)	-0.1 $\pm$ 1.3 (2)	5 $\pm$ 1 (2)
11-80	22	17	66 $\pm$ 12 (6)	-11 $\pm$ 2 (6)	16 $\pm$ 5 (6)	14 $\pm$ 4 (6)	0.3 $\pm$ 0.1 (6)	1.0 $\pm$ 0.2 (6)	0.1 $\pm$ 0.1 (6)	2.1 $\pm$ 0.3 (6)
2-81	23	12	113 $\pm$ 22 (5)	-11 $\pm$ 2 (5)	10 $\pm$ 5 (3)	6 $\pm$ 4 (3)	0.2 $\pm$ 0.2 (4)	0.4 $\pm$ 0.5 (5)	0.0 $\pm$ 0.1 (4)	2.9 $\pm$ 0.5 (5)
Ann. Ave. <sup>a</sup>			110 $\pm$ 13	-16 $\pm$ 7	20 $\pm$ 4	11 $\pm$ 4	0.4 $\pm$ 0.2	2.5 $\pm$ 0.7	0.2 $\pm$ 0.8	4.5 $\pm$ 0.8
Station 28C										
2-80	20	12	211 (1)	-13 (1)	n.d.	n.d.	-0.8 (1)	0.1 (1)	-0.1 (1)	-2 (1)
6-80	21	17	231 $\pm$ 86 (2)	-46 $\pm$ 9 (2)	43 (1)	14 $\pm$ 2 (2)	-0.1 $\pm$ 0.0 (2)	1.6 $\pm$ 0.1 (2)	0.1 $\pm$ 0.8 (2)	11 $\pm$ 1 (2)
11-80	21	16	292 $\pm$ 39 (7)	-28 $\pm$ 6 (6)	16 $\pm$ 3 (7)	6 $\pm$ 2 (7)	-0.5 $\pm$ 0.2 (7)	1.4 $\pm$ 0.2 (7)	0.1 $\pm$ 0.1 (7)	6 $\pm$ 1 (7)
2-81	23	12	209 $\pm$ 21 (4)	-17 $\pm$ 5 (3)	14 $\pm$ 5 (4)	8 $\pm$ 2 (4)	-1.1 $\pm$ 1.0 (4)	0.6 $\pm$ 0.1 (4)	0.1 $\pm$ 0.1 (4)	3.3 $\pm$ 1.7 (4)
Ann. Ave. <sup>a</sup>			249 $\pm$ 56	-30 $\pm$ 7	24 $\pm$ 8	9 $\pm$ 2	-0.5 $\pm$ 0.6	1.1 $\pm$ 0.1	0.1 $\pm$ 0.5	5.9 $\pm$ 1.3
South Bay										
Ann. Ave. <sup>b</sup>			221 $\pm$ 45	-27 $\pm$ 6	23 $\pm$ 6	9 $\pm$ 2	-0.3 $\pm$ 0.5	1.4 $\pm$ 0.2	0.1 $\pm$ 0.4	5.6 $\pm$ 1.1

<sup>a</sup> The annual average was computed as the average of February, June, and November deployments, and the uncertainty was computed from the uncertainties of each set of deployments.

<sup>b</sup> This average is computed assuming that 28C is typical of shoal areas (~80% of total) and 27.5 is typical of channel areas (~20% of total).

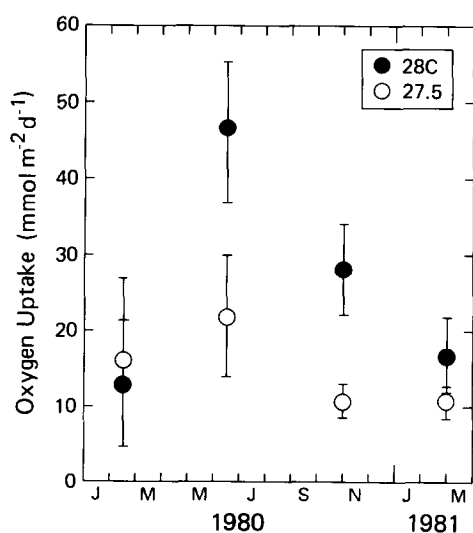


Fig. 7. Oxygen uptake versus time. Error bars indicate the standard errors of the means.

tion on charcoal and alpha scintillation (Hammond & Fuller, 1979). Chambers with a range of stirring rates were used. Only oxygen fluxes showed a significant dependence on stirring rate, with the exception of winter flux measurements discussed earlier. Oxygen fluxes into unstirred chambers were about 80% of those into stirred chambers; thus even these fluxes are not strongly dependent on the turbulence present. However, only data obtained from stirred chambers are presented here to minimize the possible role of this variable.

The data obtained (Table 4, Figs. 7-9) are presented with standard errors of the means calculated from the standard deviations of replicate deployments. The standard deviations observed reflect several sources of variability. One is analytical error. Because small changes in concentrations of TCO<sub>2</sub>, alkalinity, N + N, and phosphate were observed during chamber deployment, fluxes of these

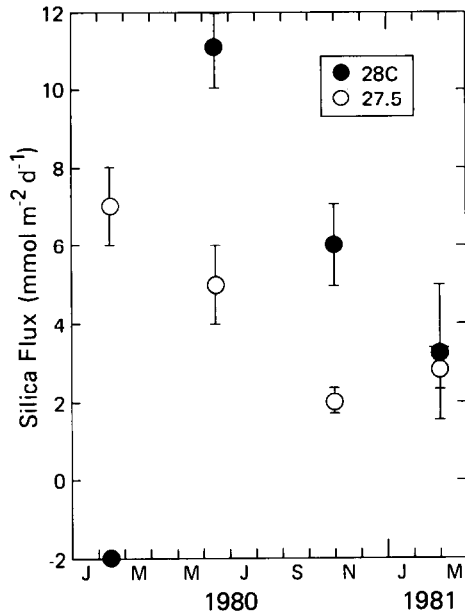


Fig. 8. Silica flux versus time. Error bars indicate the standard errors of the means. Note uptake at station 28C in February 1980.

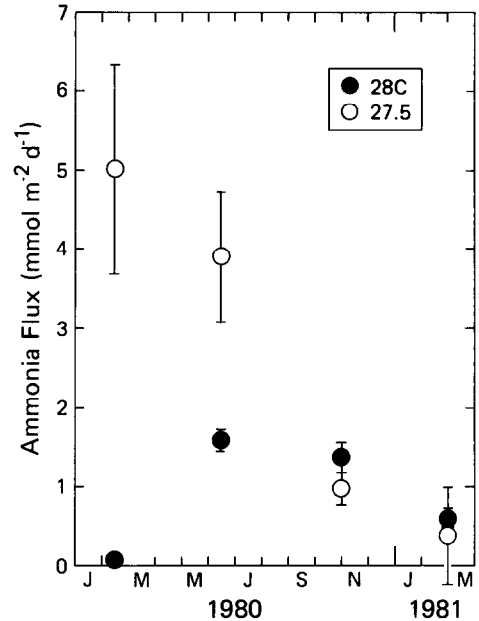


Fig. 9. Ammonia flux versus time. Error bars indicate the standard errors of the means.

molecules have large uncertainties that can be attributed to analytical errors. However, large changes in concentrations of radon, oxygen, silica, and ammonia were usually observed, and analytical uncertainty should only introduce a standard deviation of about 15% in these fluxes; yet standard deviations of 10–40% were typically observed. A second possible cause of variability in flux measurements is leakage of chambers during deployment and sampling; but because the average measured radon fluxes agree reasonably well with those predicted from the measurement of deficiencies in cores, we have concluded that errors due to leakage have not seriously biased the results (Hartman & Hammond, 1984). A third possible cause of variability is variation in stirring rate. However, because the rate of stirring had little discernable effect on any fluxes (with the exception of winter measurements discussed in the techniques section) and because the measured radon fluxes agree with deficiencies in cores, we have concluded that the rate of stirring used in our experiments has not seriously affected the results and the chambers measure accurate fluxes. A fourth possible source of variability is heterogeneity in macrofauna (Nichols & Thompson, 1985). Observations of faunal abundance by

divers and measurements of worm burrow densities in cores show substantial variability over distances of a few meters, and this factor is presumed to be the major cause of the variability in flux measurements that cannot be explained by analytical uncertainty.

Mean fluxes at a single station appear to show both substantial interannual and seasonal variability, but it is likely that some of the interannual variability is attributable to spatial variability. For example, fluxes of both radon and nutrients measured during February 1980 at station 27.5 were far larger than those measured a year later (Table 4, Figs. 8–9). The larger fluxes were measured during a shorter deployment, but similar experiments in the Potomac have shown that short deployments yield fluxes comparable to 24-h deployments (Callender & Hammond, 1982). The large radon fluxes were observed in three chambers deployed simultaneously within 5 m of each other. They are 60% greater than the average deficiency observed in cores collected from station 27.5 during winter months (Hartman & Hammond, 1984) and can be generated only by extensive irrigation. Because fluxes of silica, ammonia, and phosphate were closely correlated with the radon fluxes observed in different chambers, it is likely that the large nutrient

fluxes measured at this time were dominated by irrigation. Perhaps during February 1980, chambers were deployed in a region containing an unusually abundant and active macrofaunal community, and we conclude that these measurements may be larger than typical for this station during the winter. While this argument is not conclusive, it is likely that more representative values for benthic fluxes during the winter season can be obtained by averaging the February 1980 and February 1981 results.

When winter data are averaged, a few generalizations can be made about the results. As pore water profiles suggest, radon fluxes do not vary greatly throughout the year at either station. Radon fluxes are primarily due to irrigation, and the constancy of fluxes indicates that irrigation of burrows, whether driven by active pumping or flow of currents past orifices, must be fairly uniform throughout the year. The larger fluxes at the shallow station indicate more rapid irrigation there, as demonstrated earlier (Table 2).

Oxygen fluxes at both stations are generally larger during warmer periods, showing a temperature dependence similar to that observed in other estuaries (Officer *et al.*, 1984). However, they only vary from the annual mean by a factor of about 1.5. The shoal station has larger fluxes than the channel station, and this must indicate that it receives a larger input of organic carbon than the channel area. Net phytoplankton productivity in shoal areas is about twice that in the channel, because shoals lack a thick aphotic zone where respiration consumes the organic carbon generated (Cloern *et al.*, 1985). An isotope balance for thorium-234 has shown that in South San Francisco Bay, particles are removed from the water column to sediment in  $3 \pm 2$  days, although sediments are resuspended many times after deposition and are ultimately deposited in channel areas (Fuller, 1982). Apparently the organic carbon produced in shoal areas is deposited there and oxidized before it can be transported to channel areas. A balance for particulate organic carbon at this site requires that if the best estimate of the rate of sedimentation for station 28C (Table 1) is correct, particulates in the water column at station 28C should have an organic carbon content of about 2%, about twice that of the sediments. However, no significant difference between suspended and bottom sediments has been

observed (J. Cloern, pers. comm.), and thus the sedimentation rates (and resuspension rates) in the shoal area are probably on the upper end of the range indicated by the isotope data (Table 1).

Silica fluxes are greatest during June, the warmest month of the year. The increase in temperature should increase the concentration of silica in pore waters by 10% (Rea, 1981), although pore water data show too much variability to discern this effect. It is more likely that the supply of fresh biogenic silicious tests is largest during the spring (Cloern *et al.*, 1985) and thus dissolution rates are greatest then. To a first approximation (with the exception of the February, 1980 measurement at 28C) observed silica fluxes only vary from the annual mean by about a factor of 2 (Fig. 8). Because of the rapid removal of particles from the water column to sediments (Fuller, 1982), probably little silica is dissolved in the water column in either area; thus the inputs of particulate silica from the water column to sediments should be comparable at the two stations. The significance of the larger fluxes observed at the shallow station may be attributed primarily to the greater irrigation rates that should maintain lower pore water concentrations of silica and accelerate dissolution of silicious particles.

The nitrogen fluxes measured are dominated by ammonia. Again, the interannual variability at station 27.5 appears to be larger than the seasonal variation. However, if the two sets of February measurements are averaged, the seasonal variation is a factor of 2–4 times the annual mean flux. The largest fluxes were observed in June, following the spring bloom.  $N + N$  fluxes appear small and quite variable, but suggest that there is net nitrification at the deep station and net denitrification at the shallow station. It is important to recognize, however, that chambers measure the net reactions in the sediment column. Although only small nitrate changes are observed in chambers, evidence will be presented in a later section that both extensive nitrification and denitrification occur at station 28C. The nitrification produces lower ammonia fluxes there than at station 27.5. The reason for the contrast in nitrogen behavior at the two stations is not known but might be because the shoal station has a larger input of organic carbon, and sediments can utilize more nitrate as an oxidant.

The uncertainties in measured fluxes of alkalinity,  $TCO_2$  and phosphate make seasonal trends impossible to discern.

Table 5. Ratios of non-local model fluxes calculated from pore water profiles to measured chamber fluxes (in percent)<sup>a</sup>.

Profile	Ratio	n/n <sup>b</sup>	Rn	O <sub>2</sub>	Alk	N + N	NH <sub>3</sub>	PO <sub>4</sub> <sup>3</sup>	SiO <sub>2</sub>
Station 27.5									
Summer	I/C	5/2	–	5	94	–13	51	–	40
	Σ/C		200	–	107	–	62	–	48
Fall	I/C	2/6	–	10	23	–33	33	–	67
	Σ/C		238	–	47	–	50	–	86
Winter	I/C	2/8	–	11	222	–200	56	100	48
	Σ/C		86	–	233	–	59	103	56
Average	I/C		–	9	113	–79	46	–	52
	Σ/C		175	–	129	–	57	–	64
Station 28C									
Summer	I/C	6/2	–	6	155	100	24	–	34
	Σ/C		103	–	184	–	106	–	35
Fall	I/C	1/7	–	14	147	40	110	–	95
	Σ/C		63	–	165	–	120	–	98
Winter	I/C	1/5	138	51	318	70	(1025) <sup>c</sup>	–	–
	Σ/C				326		(1050) <sup>c</sup>	–	–
Average	I/C		–	24	207	70	67	–	65
	Σ/C		101	–	258	–	113	–	67

<sup>a</sup> I = sum of non-local irrigation transport,  
 Σ = sum of I and calculated molecular diffusion,  
 C = measured fluxes from Table 4.

<sup>b</sup> Approximate number of pore water profiles/number of chamber deployments.

<sup>c</sup> Values in parentheses are uncertain and are excluded from the average.

### Comparison of pore water models to *in situ* flux measurements

In the preceding sections we have summarized estimates of benthic fluxes based on pore water profiles and benthic flux chambers. These results are compared in Table 5. For each season, the non-local fluxes due to irrigation of zones 1 and 2 (I = last term in eq. 4) have been divided by the measured chamber fluxes (C). The total fluxes calculated from pore water profiles (Σ = J from eq. 4) are slightly larger than I, and these have also been divided by C. Based on the standard errors of the chamber flux measurements and on the variability of pore water profiles, the estimated error in these ratios is 30–40% of the ratio. The number of pore water profiles or chamber measurements used is an indicator of the reliabilities of the calculations. The ratio Σ/C for Rn should be 100%. The degree to which Σ/C for radon deviates from 100% is an indication of the effects of spatial heterogeneity inherent in comparing core data to chamber data.

The ratios in Table 5 demonstrate several things. For oxygen, I/C is only 10–20%, and thus oxygen uptake in the upper few mm must dominate oxygen consumption in sediments, rather than consumption around burrow walls. For nitrate, the irrigation model predicts uptake at station 27.5, while a small nitrate flux into chambers was observed, resulting in negative values for I/C. Pore water nitrate gradients were not measured, but nitrification in the upper few mm (where oxygen is present) must supply a flux that exceeds the non-local irrigation transport. At station 28C, the calculated irrigation fluxes can account for most of the observed nitrate uptake. However, it is likely that the situation there may be far more complex, because the nitrogen budget for this site is poorly balanced (as will be shown subsequently). Surface nitrate gradients were not measured, but it is possible that some portions of the sediment surface are sufficiently oxidized to supply nitrate, while other portions have more rapid oxygen utilization near the interface and act as nitrate sinks. At both stations,

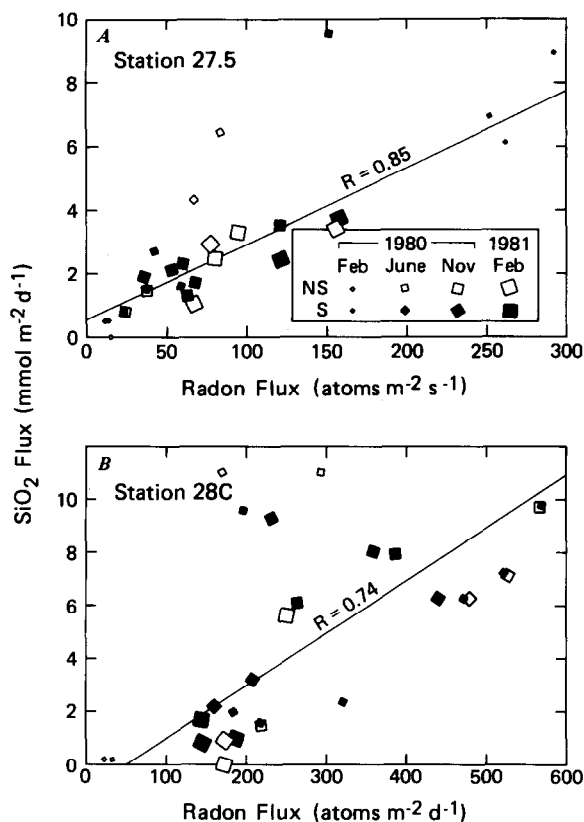


Fig. 10. Relationship between radon and silica fluxes at two stations. Data from stirred (S) and nonstirred (NS) chambers are included. NS chambers indicated erroneously low fluxes in Feb. 1980. Lines are linear regressions for all data except June 1980. This period followed the spring diatom bloom and showed unusually large fluxes at both stations, probably due to the rapid dissolution of fresh diatom tests.

N + N fluxes must be largely determined very close to the sediment-water interface.

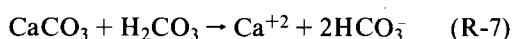
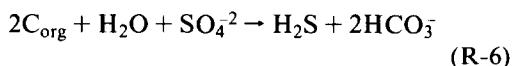
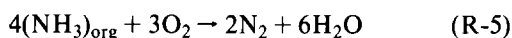
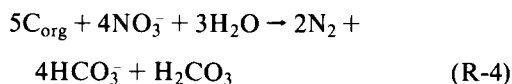
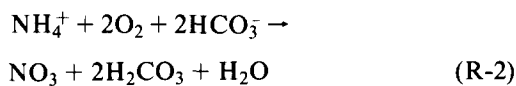
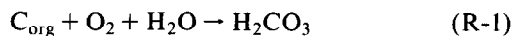
In contrast, average I/C ratios for ammonia, silica, and alkalinity are 50–200%, demonstrating that non-local transport may supply the majority of the observed fluxes and that this non-local model is suitable for estimating benthic fluxes of these substances within a factor of 2. The large range of ratios for alkalinity is attributed primarily to the large uncertainty in chamber flux measurements. These fluxes must be sustained by reactions occurring throughout the irrigation zones, and indicate that regeneration of nutrients throughout the upper 20–40 cm of sediment accounts for approximately 60% of the benthic fluxes of ammonia and silica, and accounts for 110–210% of the alkalinity flux

(averages in Table 5). That regeneration of these nutrients occurs throughout this zone, rather than being dominated by reactions occurring in only the upper few cm, is further substantiated by the relation between the radon flux and nutrient flux measured with each chamber. For example, the fall and winter deployments show a consistent relationship between silica and Rn fluxes into individual chambers (Fig. 10). The June data also indicate that these fluxes are correlated but that the silica/radon ratio is larger (Fig. 10), possibly due to a rapid dissolution of fresh diatom remains from the spring bloom. Ammonia and alkalinity show similar but more scattered correlations, while oxygen shows little correlation with radon.

When the contribution of the calculated rates of molecular diffusion is included (to obtain the  $\Sigma/C$  data in Table 5), there is still a discrepancy between fluxes of silica and ammonia calculated from pore waters and those measured with chambers. This discrepancy is probably due to an incorrect estimate of the gradient across the interface that may be steeper in the upper few mm of pore waters than our 2-cm sampling interval could accurately define. Thus, our estimates of molecular diffusion at the interface are probably somewhat too small. An alternative possibility is that one of the assumptions of the non-local model is incorrect. If burrow water does not fully equilibrate with surrounding pore water, the irrigation model will predict fluxes of oxygen and nitrate that are too small, because these compounds should equilibrate more rapidly than radon, and fluxes of alkalinity that may be too large. A lack of equilibration is more likely at station 28C than at station 27.5 because of the greater irrigation rates there and because *Asychis* tubes are mucus-lined. But more sophisticated model calculations must be done before firm conclusions can be reached about the validity of the equilibration assumption made for the non-local calculations. However, with the exception of alkalinity at station 28C, there is agreement between the calculated fluxes of ammonia, silica, and alkalinity and those measured with chambers, within the estimated accuracy of 40% (Table 5).

### Stoichiometry of diagenetic reactions

Several reactions are pertinent for this discussion:



Benthic fluxes represent the sum of depth integrated reactions. The discussion of biogeochemical zonation suggested that R-1 is the most important reaction just below the sediment-water interface (or along burrow walls). R-2 might also occur in this zone, utilizing ammonia produced by R-3 in this zone or diffusing from below. Denitrification (R-4) must be important, based on a material balance for nitrogen that will be presented subsequently, and the net effect of R-2, R-3, and R-4 may be R-5. Below the zone of denitrification, sulfate reduction (R-6) becomes important. However, the fate of the  $H_2S$  produced is uncertain. If  $H_2S$  migrates into an oxygenated zone, it will be oxidized back to sulfate and the net effect on benthic fluxes will be identical to R-1. If  $H_2S$  does not migrate, it will react with dissolved  $Fe^{+2}$  or  $Fe(OH)_3$  to form iron sulfides, most likely resulting in pyrite. Unfortunately, it is not possible to measure  $SO_4^{2-}$  changes in chambers with sufficient accuracy to identify the importance of R-6. However, the benthic flux of sulfate and the net effect of R-6 must equal the burial flux of solid phase sulfur. Even though solid phase sulfur is present, if no sediment accumulation occurs (and sediment composition does not change with time), any sulfate reduction that occurs will be balanced by sulfide oxidation. Such sulfur cycling has been observed in several marsh and estuarine systems (Jorgensen, 1977; Lord & Church, 1983; Howarth & Jorgensen, 1984). A final reaction that may be of importance is carbonate dissolution, R-7 (or the reverse, precipitation). All of these reactions (R-1

to R-7) affect  $TCO_2$  or alkalinity fluxes. Other reactions involving iron and manganese can also affect  $TCO_2$  and alkalinity, but their importance should be minor in comparison to the effects of R-1 to R-7. Using this set of reactions together with the average compositions and best estimates of sedimentation rates in Table 1 and the assumption that ammonia is released from organic matter at 1/7 the rate of carbon, we can determine the relative importance of each reaction from the average annual benthic fluxes.

At station 27.5, net accumulation rates of solid phase sulfur (assumed to be pyrite) show that sulfate reduction accounts for about half of the alkalinity flux and 10% of the  $TCO_2$  flux. The combined effects of N + N and ammonia account for about 25% of the observed alkalinity flux. The remaining 25% of the alkalinity flux is attributed to carbonate dissolution (R-7). If the contributions of sulfate reduction and carbonate dissolution are subtracted from the  $TCO_2$  flux, about  $14 \text{ mmol m}^{-2} \text{ d}^{-1}$  of  $TCO_2$  should be produced by oxygen utilization (R-1), a rate that is very close to the average annual observed oxygen flux of  $-16 \pm 7$  (Table 4). A close correlation between  $TCO_2$  fluxes and  $O_2$  fluxes may not be observed for each set of deployments if sediment composition varies seasonally. For example, if sulfate reduction is rapid following an input of organic carbon, a large  $TCO_2$  flux may be observed that is greater than that expected from oxygen uptake. The solid phase sulfide that is formed during the period of rapid sulfate reduction may be subsequently re-oxidized when less organic carbon reaches the sediments, resulting in an oxygen uptake that is not accompanied by  $TCO_2$  release. Because of the large uncertainties in our measurements, such effects are not observable in our data.

At station 28C, sediment accumulation rates are very low. Thus, unless the concentration of solids is changing, sulfate reduction should contribute little to the net alkalinity or carbon fluxes. Most alkalinity is probably derived from dissolution of relict oyster shells that are abundant in shoal sediments. If this is the case, about  $4 \text{ mmol m}^{-2} \text{ d}^{-1}$  of  $TCO_2$  flux is supplied by carbonate dissolution and the remaining  $20 \text{ mmol m}^{-2} \text{ d}^{-1}$  of  $TCO_2$  is generated by oxidation of organic matter. About  $3 \text{ mmol m}^{-2} \text{ d}^{-1}$  of oxygen consumption should be required by R-5, so the remaining measured oxygen uptake of  $-27 \text{ mmol m}^{-2} \text{ d}^{-1}$  (Table 4) is about 30% greater



than predicted from the  $\text{TCO}_2$  flux measurements and R-1. However, within the uncertainties of the estimates, the observed fluxes of  $\text{O}_2$  and  $\text{TCO}_2$  are consistent with the stoichiometries postulated above.

### Material balances for South San Francisco Bay sediments

It is important to estimate how efficiently sediments re-mineralize nutrients and carbon supplied by settling of particulate material from the overlying water in order to understand nutrient dynamics. The input of particulate organic carbon to the sediments can be estimated from measurements of productivity in the water column. Cloern *et al.* (1985) have estimated the net productivity of carbon in South San Francisco Bay to be approximately  $27 \text{ mmol m}^{-2} \text{ d}^{-1}$ . Most of this productivity must reach the sediments before it can be carried to the ocean, because the residence time of particles in the water column of South San Francisco Bay is short, relative to the residence time of water in the system (Fuller, 1982). Measurements of the  $\delta^{13}\text{C}$  of organic material in South Bay channel sediments range from  $-23$  to  $-24\text{‰}$  and indicate that the bulk of the organic matter is derived from phytoplankton (Spiker & Schemel, 1979). If the organic matter reaching sediments has a C:N ratio similar to marine plankton (about 7:1), the input of particulate nitrogen to sediments should be  $1/7$  that of carbon. The input of silica to sediments is assumed to be  $10 \text{ mmol m}^{-2} \text{ d}^{-1}$ , based on measurements of net silica uptake in the water column (Peterson, 1979).

Average benthic fluxes from South San Francisco Bay sediments can be estimated from the annual averages for stations 28C and 27.5 (Table 4) if these stations are considered to be representative of shoals (80% of bay surface area) and channels (20% of bay surface area). Measurements of benthic fluxes of radon, oxygen, ammonia and silica made in the eastern shoal (one successful deployment each at stations 28A and 28B in Fig. 2) during November 1980 were within 20% of those measured at 28C during this period. Therefore, the use of station 28C to represent shoal areas is probably valid.

Although the sediment accumulation rates at individual stations are rather uncertain, Fuller (1982)

Table 6. Budgets for particulate carbon, nitrogen and silica reaching South San Francisco Bay sediments ( $\text{mmol m}^{-2} \text{ d}^{-1}$ ).

	C	N	SiO <sub>2</sub>
Net productivity in water column <sup>a</sup>	$27 \pm 3$	$3.9 \pm 0.4$	$10 \pm 1$
Benthic fluxes	$-25 \pm 6^b$	$-1.4 \pm 0.2$	$-6 \pm 1$
Buried in sediments	$1 \pm 1$	$-0.1 \pm 0.1$	$-1 \pm 1$
Lost (to Ocean?)	$-2 \pm 1$	$-0.2 \pm 0.1$	$-2 \pm 1$
Unaccounted for	$-1 \pm 7$	$2.2 \pm 0.5$	$1 \pm 2$

<sup>a</sup> Cloern *et al.* (1985); Peterson (1979). These values are assumed to have an uncertainty of 10%. Nitrogen flux is assumed to be  $1/7$  that of carbon.

<sup>b</sup> Calculated as oxygen uptake (Table 4) less oxygen required for R-5.

has constructed a budget for Pb-210 in South San Francisco Bay as a whole that indicates an average accumulation rate of  $0.8 \text{ mg m}^{-2} \text{ d}^{-1}$ . Because most accumulation probably takes place in channel areas, the composition of sediment below the irri-

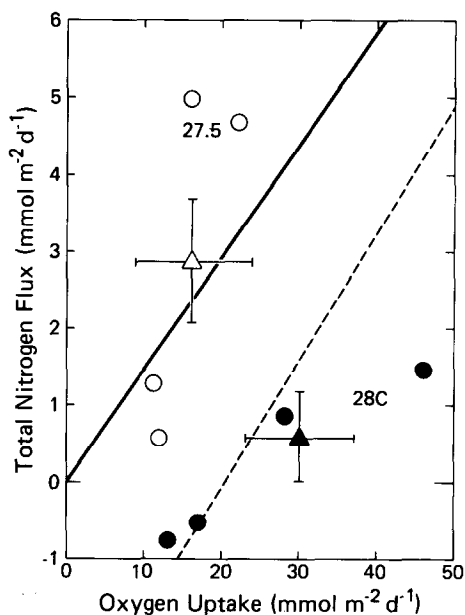


Fig. 11. Relation between oxygen uptake and total nitrogen flux observed in benthic chambers. Total nitrogen is the sum of ammonia and  $\text{N} + \text{N}$ . Ammonia fluxes are much larger than  $\text{N} + \text{N}$ . Circles are averages for each set of deployments. Triangles are annual means. The solid line indicates the expected relation if organic matter with a C:N ratio of 7 degrades stoichiometrically to yield carbon dioxide and ammonia, and the dashed line shows the trend of Nixon's (1981) compilation of the relation between ammonia and oxygen fluxes for other estuaries.

gated zone in channel sediments should be representative of material accumulating; but because measurements of solid phase composition show relatively small differences between shoal and channel areas (Table 1), this assumption is not critical. Fuller's (1982) Pb-210 budget also indicates that about 1/3 of the sediment entering South San Francisco Bay accumulates, while the remainder is carried to the ocean or other parts of the bay. If particulate nutrients produced in the water column behave like other suspended sediment, their export from South San Francisco Bay should be twice the burial flux. These calculations allow budgets to be constructed for organic carbon, nitrogen and silica produced in the water column (Table 6). Budgets for carbon and silica appear to be reasonably well constrained, as the sums of benthic fluxes, burial, and loss terms are quite close to the rates of input calculated from water column productivity. This calculation also indicates that about 90% of the carbon and 60–70% of the silica reaching the sediments is re-mineralized. About 55% of the nitrogen is unaccounted for. If both nitrification and denitrification are occurring, the missing nitrogen may be converted to  $N_2$  and lost to the atmosphere. It is likely that this occurs in shoal areas, because a plot of oxygen uptake vs. net nitrogen flux (Fig. 11) indicates a large oxygen uptake in the shoal area that is not accompanied by release of fixed nitrogen; yet cycling of these elements at the channel station occurs at ratios predicted from Redfield ratios.

The importance of benthic fluxes in replacing water column nutrients can be seen by dividing the standing nutrient stock by the average annual flux at each station (Table 7). Results of this calculation suggest that in this estuary, water column concentrations of most species are probably dominated by rates of processes other than benthic exchange. For oxygen, air-sea gas exchange is the dominant process (Hartman & Hammond, 1985). For nutrients during normal flow regimes, water transport should be dominant (Peterson *et al.*, 1985). However, replacement times in shoal areas during low flow periods are short, and benthic fluxes may play a major role in controlling ammonia and silica concentrations. In shoal areas that are far from the channel, such as those in San Pablo Bay, water exchange between shoals and channels will be slower than in South San Francisco Bay; and there,

Table 7. Replacement of water column nutrients by benthic fluxes.

	O <sub>2</sub>	ΣN	NH <sub>3</sub>	PO <sub>4</sub> <sup>3-</sup>	SiO <sub>2</sub>
Water column concentrations (μM) <sup>a</sup>					
Station 27.5					
low flow	230	20	5	20	70
high flow	270	50	20	5	140
Station 28C					
low flow	240	8	1	10	50
high flow	280	30	3	5	100
Replacement time (days) <sup>b</sup>					
Channel (27.5)					
low flow	140	70	20	1000	150
high flow	170	170	80	250	300
Shoals (28C)					
low flow	16	26	2	200	17
high flow	18	100	6	100	34

<sup>a</sup> Based on data from Conomos *et al.* (1979) and water column measurements at 28C during 1980–81. Ranges are multi-year averages observed during different seasons.

<sup>b</sup> Assuming a mean depth of 10 m for channel areas and 2 m for shoal areas. These ranges are calculated by dividing (concentration × depth) by benthic flux in various seasons.

benthic fluxes may be even more important for the water column than at station 28C, if fluxes are of comparable magnitude.

### Comparison of San Francisco Bay to other estuaries

The average budgets computed for San Francisco Bay (Tables 4 and 6) provide some interesting comparisons to those summarized by Nixon (1981) for other temperate estuaries. The gross primary productivity in South Bay is approximately 42 mmol carbon m<sup>-2</sup> d<sup>-1</sup> (Cole & Cloern, 1984), and the average benthic uptake of oxygen is about 65% of this value. Thus, the majority of the phytoplankton production must be recycled through the benthos. Nixon's (1981) compilation for other estuaries suggested that 25% is more typical. The high fraction of benthic recycling may be due to the importance of benthic grazing relative to zooplankton grazing and the absence of a thick aphotic zone over much of the estuary (Cloern, 1982). However, the relative rates of benthic oxygen consumption and ammonia release (Fig. 11) fall nicely on the trend of the regression in Nixon's (1981) compilation. Aver-

age silica fluxes are similar to the values of  $6.6 \text{ mmol m}^{-2} \text{ d}^{-1}$  estimated for Narragansett Bay (Nixon, 1981) and  $7.4 \text{ mmol m}^{-2} \text{ d}^{-1}$  estimated for Chesapeake Bay (D'Elia *et al.*, 1983).

In contrast to many other estuaries, San Francisco Bay has a small annual temperature range. For example, many estuaries in the Northeast U.S. and in Europe have a  $20\text{--}30^\circ\text{C}$  annual range. In such estuaries, benthic exchange is often nearly unmeasurable during winter months because reaction rates, diffusion rates, and macrofaunal activity all become small at low temperatures. During summer months, all of these factors increase substantially. Nixon *et al.* (1980) tried to eliminate temperature as a variable by collecting cores from Narragansett Bay before and after the annual spring bloom and incubating them at different temperatures. Their results showed that at a single temperature ammonia and phosphorus fluxes may be 3–4 times larger following the spring bloom than before. By analogy, the limited seasonal effects that are observed in South San Francisco Bay (Table 4, Figs. 7–9) are probably more related to variations in phytoplankton productivity than to temperature.

Irrigation rates in South San Francisco Bay sediments are greater than those in other coastal and estuarine systems (Emerson *et al.*, 1984), reflecting a high level of macrofaunal activity. Also, macrofaunal activity at channel stations results in bioturbation rates of solid phases that are on the upper end of those observed in other estuaries, rapidly mixing particles within 30–40 days to depths of 15–20 cm (Fuller, 1982). These activities should maintain a fresh supply of phytoplankton debris to sustain reactions at depth and may also contribute to the relatively efficient re-mineralization of solid phases.

### Remaining problems

The discussion presented here has focused primarily on results from two stations in South San Francisco Bay. Korosec (1979) has obtained a few pore water profiles and X-radiographs from other locations in San Pablo Bay and Central Bay. Fuller (1982) has measured Cs-137, Th-234 and Pb-210 profiles in other portions of the bay. Their results are similar to those from South Bay presented here and indicate the same diagenetic features and the

ubiquity of macrofaunal activity. Material balance calculations for radon (Hammond & Fuller, 1979) indicate that irrigation rates (and perhaps benthic nutrient fluxes) in San Pablo Bay are comparable to those in South Bay. However, insufficient data are available at present to make quantitative estimates of benthic fluxes for other regions. It would be interesting to extend research approaches discussed here to other regions.

Another aspect of interest is that shoal sediments appear to be capable of acting, on occasion, as a nutrient sink. The flux measurements made at station 28C in February 1980 (Table 4) showed a small net uptake of phosphate and silicate, although the oxygen and radon fluxes were comparable to those measured during the following year. Because only one chamber measurement was made, it might seem reasonable to attribute this result to some analytical error. However, when the chamber was deployed, four cores were collected by divers and incubated in the dark for measurement of oxygen uptake and nutrient fluxes. Even larger uptake rates of silica, phosphate, ammonia, and nitrate were observed during these incubations (M. Pamatmat, pers. comm.). Perhaps a benthic algal mat that had a very large nutrient uptake, even in the dark, was present. This evidence for nutrient uptake needs further attention before it can be adequately explained.

Another unresolved problem is the identification of the source of carbonate that is dissolving. Bivalves are an important part of the benthic community (Nichols & Thompson, 1985). Their presence should result in an alkalinity sink; yet alkalinity uptake was never observed. Instead, positive alkalinity fluxes were observed, and these have been partially attributed to dissolution of relict oyster shells and partially to burial of sulfides. If this is the case, the sediment composition must be changing in composition with time, resulting in a smaller fraction of carbonate or a larger fraction of sulfides.

A final major problem is the nitrogen budget. About 55% of the expected nitrogen flux is unaccounted for (Table 6). By analogy with Narragansett Bay, there is probably a net denitrification to produce  $\text{N}_2$  (Nixon, 1981). However, large  $\text{N} + \text{N}$  decreases are not observed with benthic chambers. This apparent contradiction can be explained if sediments can serve as a site for both nitrification and denitrification. Ammonia diffusing upward may be partially oxidized to nitrate in the sediment

column. The nitrate can then diffuse downward and be reduced to  $N_2$  or be transported downward by irrigation. Alternative explanations are that ammonia reaches the water column by non-local transport and is oxidized to nitrate that diffuses back into sediments; that periods of net nitrification alternate with periods of denitrification; or that assumptions of the irrigation model are incorrect and this process is more important in transport of nitrate (and oxygen) into sediments than calculations indicate. In any case, further work needs to be done to clarify the role of denitrification.

### Summary

This study of pore waters and benthic fluxes in South San Francisco Bay has shown that: (1) Rapid irrigation of the burrows of deep-dwelling macrofauna occurs to as much as 50 cm, resulting in an effective pore water residence time of 5–100 days in irrigated zones; (2) Benthic fluxes of silica, ammonia and alkalinity are primarily due to this deep irrigation, while those of oxygen and nitrate are dominated by exchange along steep gradients near the sediment-water interface that we have not measured; (3) Spatial variability of 20–40% in benthic fluxes of radon and nutrients is observed in replicate flux measurements over distances of a few meters, presumably due to variations in macrofaunal abundance; (4) Interannual variations in benthic fluxes may exist which are as large as seasonal variations, but this variability is difficult to separate from spatial variability with the limited number of measurements made to date; (5) Some seasonal variation in benthic fluxes occurs due to annual cycles in productivity and temperature, but these are far smaller than those occurring in estuaries of the NE U.S., presumably because temperature variability is smaller; (6) Extensive nitrification and denitrification undoubtedly occur in the sediment column, apparently resulting in conversion of about 55% of the fixed particulate nitrogen reaching the sediments to  $N_2$ ; (7) Reactions in sediments remineralize 70–90% of the particulate inputs of carbon, nitrogen, and silica, although much of the nitrogen is probably lost as  $N_2$ .

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