title	The Use of Radon-222 to Estimate Benthic Exchange and Atmospheric Exchange Rates in San Francisco Bay
creator	D. E. Hammond and C. Fuller
Subject	benthic, ecology, aquatic invertebrates
Description	ANALYTICAL TECHNIQUES, RESULTS AND DISCUSSION, Radon in Sediments, Nutrients in Interstitial Waters, Flux Chambers, Water Column Analyses, Vertical Mixing in the Water Column, CONCLUSIONS, ACKNOWLEDGMENTS, LITERATURE CITED
Coverage	San Francisco Bay
Temporal	1970-1980
Source	Fifty-eighth Annual Meting of the Pacific Division of the American Association for the Advancement of Science, San Francisco State University, San Francisco, California, June 12-16, 1977
Date	1977-06-12
IsPartOf	SAN FRANCISCO BAY: THE URBANIZED ESTUARY Investigations into the Natural History of San Francisco Bay and Delta With Reference to the Influence of Man (213-230)
Publisher	Pacific Division of the American Association for the Advancement of Science c/o California Academy of Sciences Golden Gate Park San Francisco, California 94118
Issued	1979
Type	text
Format	8-1/2" x 11" bound document
Identifier	ISBN 0-934394-01-6
Language	English
Rghts	Copyrighted, Pacific Division of the American Association for the Advancement of Science

Abstract

Using a slurry technique, measurements of radon-222/radium-226 in San Francisco Bay sediments range from 0.3 to equilibrium. Radon deficiency generally decreases with increasing depth. A small deficiency may exist as deep as 40 cm in some cases. This deficiency is attributed primarily to irrigation of sediments by polychaete worms. If irrigation is modeled as an advective process, an irrigation rate of 3 $cm \cdot d^{-1}$ is calculated as a lower limit at a station in South Bay in August 1976. Using this model and nutrient measurements in interstitial waters, fluxes across the sediment-water interface for ΣCO_2, NH_4^+, PO_4^{3-}, and SiO_2 are calculated to be 40, 4, 0.03, and 6 $mmol \cdot m^{-2} \cdot d^{-1}$ at this station. The flux of radon across the sediment-water interface is estimated to be 200±70 $atoms \cdot m^{-2} \cdot s^{-1}$ on the basis of integrated radon deficiencies and benthic flux chamber measurements.

Simultaneous measurements of radon and wind speed in July 1977 suggest that flow-induced turbulence, rather than wind speed, is the primary factor controlling gas exchange across the air-water interface. From a radon mass balance, the mass transfer coefficient for radon across this interface is calculated to be 1.0±0.5 $m \cdot d^{-1}$. Using this information, a vertical mixing coefficient in the water column of South Bay is calculated to be greater than 1×10^{-2} $cm \cdot s^{-1}$, indicating the water column mixes more rapidly than once in 12 h. The volume transport of sand bedforms in Central Bay is estimated to be 8×10^{6} $m^3 \cdot d^{-1}$.

THE USE OF RADON-222 TO ESTIMATE BENTHIC EXCHANGE AND ATMOSPHERIC EXCHANGE RATES IN SAN FRANCISCO BAY

DOUGLAS E. HAMMOND AND CHRISTOPHER FULLER
Department of Geological Sciences, University of Southern California
Los Angeles, California 90007

Using a slurry technique, measurements of radon-222/radium-226 in San Francisco Bay sediments range from 0.3 to equilibrium. Radon deficiency generally decreases with increasing depth. A small deficiency may exist as deep as 40 cm in some cases. This deficiency is attributed primarily to irrigation of sediments by polychaete worms. If irrigation is modeled as an advective process, an irrigation rate of 3 $cm \cdot d^{-1}$ is calculated as a lower limit at a station in South Bay in August 1976. Using this model and nutrient measurements in interstitial waters, fluxes across the sediment-water interface for ΣCO_2, NH_4^+, PO_4^{-3}, and SiO_2 are calculated to be 40, 4, 0.03, and 6 $mmol \cdot m^{-2} \cdot d^{-1}$ at this station. The flux of radon across the sediment-water interface is estimated to be 200±70 $atoms \cdot m^{-2} \cdot s^{-1}$ on the basis of integrated radon deficiencies and benthic flux chamber measurements.

Simultaneous measurements of radon and wind speed in July 1977 suggest that flow-induced turbulence, rather than wind speed, is the primary factor controlling gas exchange across the air-water interface. From a radon mass balance, the mass transfer coefficient for radon across this interface is calculated to be 1.0±0.5 $m \cdot d^{-1}$. Using this information, a vertical mixing coefficient in the water column of South Bay is calculated to be greater than 1×10^{-2} $cm \cdot s^{-1}$, indicating the water column mixes more rapidly than once in 12 h. The volume transport of sand bedforms in Central Bay is estimated to be 8×10^6 $m^3 \cdot d^{-1}$.

The distribution of chemical and biological properties in estuarine waters and sediments is strongly influenced by physical processes, including turbulent mixing and exchanges across the sediment-water and air-water interfaces. Unfortunately, the rates of these processes are often difficult to estimate. Extrapolation of laboratory experiments to field conditions may introduce major scaling errors, and field measurements using introduced tracers are difficult to do in large systems. One solution to these problems is to model the distribution of naturally-occurring tracers in terms of these physical processes. This paper discusses preliminary results of the use of naturally-occurring radon-222 to estimate the rate of vertical mixing in the water column and the rate of exchange across the sediment-water and air-water interfaces in San Francisco Bay.

The use of this isotope in marine systems was first proposed by Broecker (1965), and it has recently been used in estuarine systems to study exchange across the sediment-water interface (Hammond et al. 1977).

Radon is a noble gas with a 4-day half-life. It is produced primarily in sediments by the decay of radium-226 (Fig. 1). A fraction of the radon which is produced in sediments will escape to the overlying water column, leaving a deficiency in sediments, so that the activity ratio of radon to radium is less than one. This deficiency is a measure of the rate of exchange across the sediment-water interface. Once radon is in the water column, it is mixed vertically and will either decay there or escape to the atmosphere. In a steady state system, the depth-integrated radon deficiency in sediments (in activity units) must equal the radon flux (in atoms per area time) across the

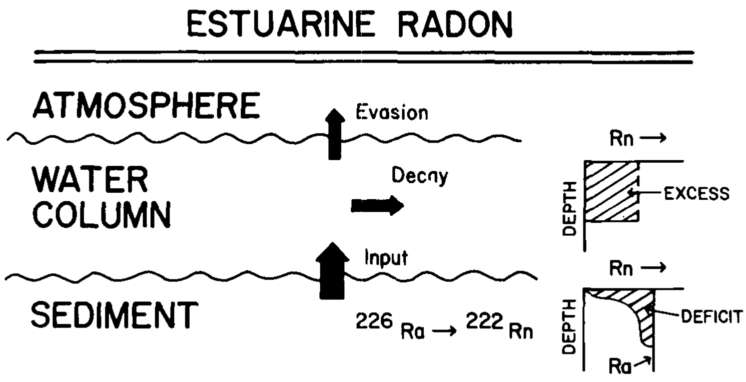

Fig. 1. Radon transport in estuaries. Vertical profiles of radon in the water column and in sediments are shown schematically. The shaded areas are integrated excess in the water column and integrated deficiency in sediments.

sediment-water interface. It must also equal the depth-integrated decay rate of excess (unsupported by decay of dissolved or suspended radium) radon in the water column plus the flux across the air-water interface.

ANALYTICAL TECHNIQUES

Measurements of radon in the water column were made using techniques described by Broecker (1965) and Mathieu (1977). Briefly, this involves collection of a 20-liter water sample in an evacuated bottle, extraction of radon onto activated charcoal at dry-ice temperatures with a helium carrier, and (alpha) counting radon and its two polonium daughters in a phosphored chamber. Measurements on samples from flux chambers were done on 2-liter samples. Analytical precision is about 5%.

Measurements in sediments were made by collecting gravity cores (5-cm ID), extruding mud sections, adding these to 100 ml of estuary water to create a slurry, and purging to measure radon as described by Hammond et al. (1977). These analyses were nearly always completed within 24 hours of sample collection. The supported radon in sediments (referred to as radium) was measured by storing the slurry for 1-4 weeks and extracting the new crop of radon which had been produced. Radium analyses were repeated until the standard deviation in this parameter was less than 5%. Key et al. (1977) have noted that there may be a problem with using the slurry technique to measure supported radon in deep sea sediments. They find that measurements of supported radon at depth are consistently 10-20% greater than the initial measurements. They attribute this to the physical process of creating a slurry but do not elucidate the mechanism. Our laboratory has observed a similar effect for marine sediments from basins in the southern California borderlands, but with muds from San Francisco Bay (Table 1) and from the Hudson River Estuary (Hammond et al. 1977), equilibrium ratios of radon and supported radon have been observed at depth.

It is possible that a problem may arise due to the 0.086 MeV recoil energy received by a radon atom as radium-226 decays. Extrapolating range-energy relations for fission fragments in aluminum (Friedlander et al. 1964:100) to low energy suggests the range should be about 0.02 $mg \cdot cm^{-2}$, equivalent to 800Å in a silicate phase or 2000Å in water. Assuming sediment grains are cubic with an edge of length r, the distance between grains arranged in a primitive cubic lattice is

TABLE 1. RADON/RADIUM IN SAN FRANCISCO BAY SEDIMENT CORES

Station Number	Date	Interval (cm)	Radium-226 dpm·g^{-1}	Radium-226 dpm·cm^{-3}	Rn/Ra	Integrated Deficiency[a]
28C	8-09-76	0- 2	0.23	0.17	0.33	
		2- 4	0.17	0.22	0.25	
		4- 6	0.24	0.18	0.71	
		6- 8	0.30	0.19	0.66	
		12-14	0.18	0.19	0.83	†163
	3-07-77	0- 2	0.24	0.22	0.31	
		2- 3	(0.51)	0.33	0.30	
		3- 4	0.31	0.32	0.43	
		4- 6	0.28	0.22	0.66	
		6- 8	0.26	0.24	0.61	†175
	7-12-77	0- 3	0.20	0.15	0.25	
		3- 6	0.25	0.18	0.49	
		6- 9	0.28	0.23	0.42	
		9-12	0.14	0.20	0.79	†188
	10-19-78	0- 3	0.23	0.20	0.46	
		3- 6	0.24	0.20	0.85	
		6- 9	0.25	0.20	0.89	
		12-15	0.23	0.20	0.82	
		21-24	0.24	0.21	0.86	†138
27		0- 1.5	0.31	0.22	0.37	
		1.5- 3	0.30	0.23	0.78	
		3- 4.5	0.27	0.23	0.75	
		4.5- 6	0.30	0.26	0.81	
		6- 8	0.24	0.26	0.84	† 92
28	10-22-77	0- 3	0.29	0.22	0.58	
		3- 6	0.30	0.21	0.33	
		6- 9	0.30	0.20	0.59	
		12-15	0.25	0.19	0.83	
		17-20	0.30	0.18	0.92	†209
	12-12-77	0- 3		0.19	0.52	
		3- 6		0.22	0.88	
		6- 9		0.22	1.12	
		18-21		0.24	0.97	
		51-54		0.27	1.15	
	12-12-77	0- 3		0.20	0.59	
		6- 9		0.20	0.96	
		18-21		0.26	0.87	
		27-30		0.25	0.98	
		42-45		0.23	1.38	
		51-54		0.28	1.00	
	12-14-77	0- 3		0.23	0.60	
		3- 6		0.23	0.92	
		6- 9		0.22	0.98	
		24-27		0.22	0.93	
		39-42		0.23	0.93	
	12-14-77	15-18		0.20	0.82	
		24-27		0.23	1.00	
		33-36		0.24	0.90	
		42-45		0.25	1.10	
		60-63		0.24	1.03	
		78-81		0.25	1.00	177

[a] Integrated deficiency of radon (atoms·m^{-2}·s^{-1}).

$R = 2r[(1-\phi)^{-1/3}-1]$ where ϕ is sediment porosity. Typical values for r and ϕ in San Francisco Bay are 6 μm and 0.7, so that R = 6 μm or 30 times the recoil range. In deep sea sediments we might choose 3 μm and 0.5 so that R = 1.5 μm or 8 times the recoil range. To rigorously calculate the change in the probability of recoil from one grain to another would require data on the position of radium in sediment grains and the statistical variation in grain spacing before and after the slurry is created. The calculation above shows that radon recoil may cause problems in measuring emanation from fine-grained, low porosity sediments, but should not be a problem for estuarine sediments. Thus the slurry technique should be satisfactory for measuring supported radon in these sediments.

On 9 August 1976, duplicate gravity cores were collected at station 28C. One core was sectioned for radon, the second was sectioned and squeezed to obtain interstitial water. Sections were squeezed at room temperature (about 5°C above *in situ*) in Reeburgh (1967) squeezers with water passing through a fiber filter (Whatman #42) and an 0.45 μm Nucleopore filter. Since only two squeezers were available and sediment permeability was low, squeezing was not completed until 2 days after the core was collected. The core was stored in its liner during this operation and a fresh horizon was exposed prior to loading each sample. The initial 4-5 cm^3 of water was discarded, then 3 cm^3 was taken for nutrient analysis, 1 cm^3 for ΣCO_2, and a second 5-cm^3 aliquot for nutrient analysis. ΣCO_2 analyses were performed on 12 August 1976 using a Swinnerton stripper and gas chromatograph. The precision of these analyses is 3%. Nutrient samples were refrigerated for one week and diluted aliquots were analyzed with a Technicon AutoAnalyzer. Despite this storage time, analyses of the two aliquots for nutrients generally agreed within 5% for SiO_2 and NH_4^+, and within 10% for PO_4^{-3}.

Fluxes of radon and nutrients from sediments were measured directly by using benthic-flux chambers. These chambers were inverted boxes made of plexiglass (25 cm x 25 cm x 15 cm). They were deployed by divers so that the lower 5 cm was below the sediment surface, leaving 10 cm above the surface. Boxes were sampled immediately and at 1-day intervals after deployment through a nylon tube extending to the surface. Occasionally they were sampled 4-6 h after deployment, but changes in nutrients and radon over this period were generally too small to measure accurately. Fresh water was introduced during the sampling by inflow through a check valve as the sample was withdrawn. Measurements on samples drawn from the box were corrected for this inflow by assuming that the inflowing water mixes rapidly with the box water. Chambers were equipped with several types of devices intended to transmit turbulence mechanically from tidal currents to the enclosed water, but observation by divers indicated that these were not successful. Oxygen analyses on a separate aliquot were done by Winkler titration (Carpenter 1965).

RESULTS AND DISCUSSION

Radon in Sediments

To demonstrate the validity of the slurry technique, duplicate cores were collected and sectioned on each of 2 days at station 28 in South San Francisco Bay (Fig. 2). The activity ratios of radon to radium observed in surface samples of these cores are quite consistent and the ratio approaches equilibrium in the 9-12 cm interval (Fig. 3). Below that interval there seems to be a deficiency of a few percent down to about 40 cm, and below that, samples are in equilibrium. The high value at 42-45 cm is unexplained. This radon analysis was done 2 days after collection and any analytical error in radon would be increased by 20% in the decay corrections. It is clear, however, that the deficiency is largest in surface sediments, that it may extend well below the sediment-water interface, and that equilibrium values can be found with this technique.

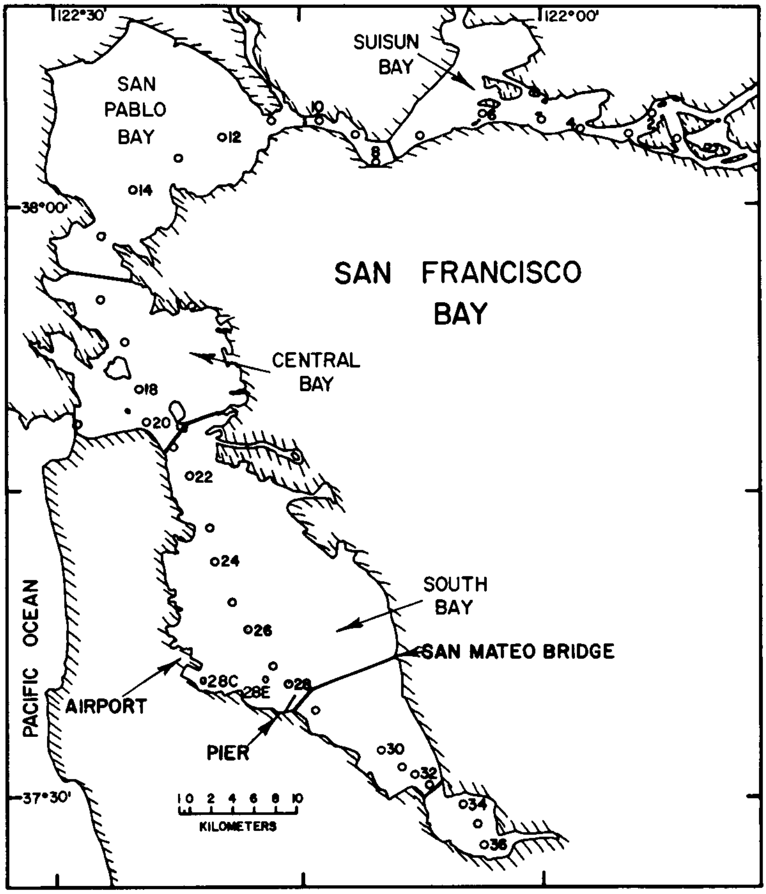

Fig. 2. Location map of San Francisco Bay showing standard U.S.G.S. stations and other stations described in the text.

The data from station 28C (Fig. 2) in a shallow-water (mean depth = 2 m) area in South Bay, show some variation in the supported radon as a function of depth (Fig. 4). The largest source of this error was probably the length of the extruded section. To remove this variation, the radon/radium activity ratio was multiplied by the average radium to yield the values plotted in the figure. The deficiency generally decreases with increasing depth, although some deep minima are observed. The depth of this deficient zone is uncertain because equilibrium samples were not obtained. Data obtained through the year at station 28C and 27 or 28 are listed in Table 1. Integrated deficiencies are also listed, although these are usually lower limits.

Nutrients in Interstitial Waters

Interstitial water data from the duplicate core collected in August 1976 show that all nutrient species have small concentration gradients in the upper 6 cm and much larger gradients below this (Fig. 5). ΣCO_2 shows a small but significant minimum at 3-6 cm. The upper zone correlates well with the zone which is quite deficient in radon. Similar profiles have been observed in cores from this site during other seasons and at other locations (Korosec in press).

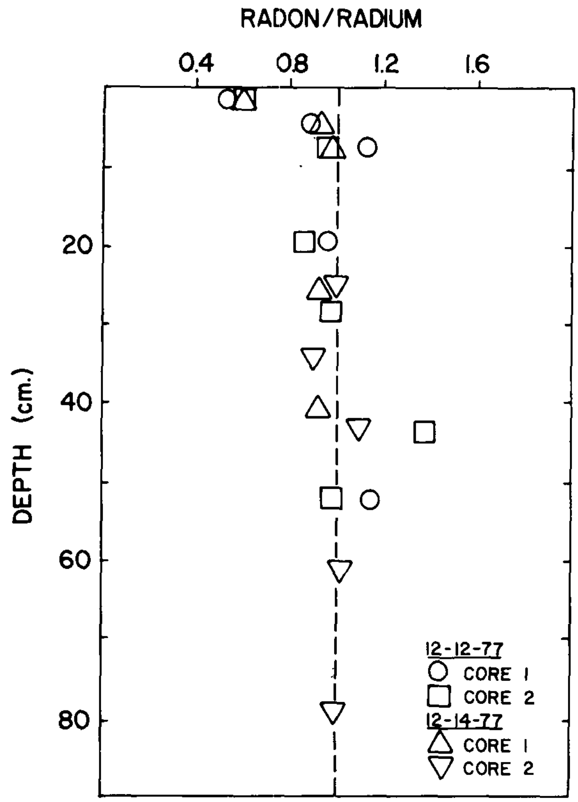

Fig. 3. Radon/Radium vs. Depth at Station 28. The dashed line indicates secular equilibrium. Data to the left of the line indicate radon deficiency.

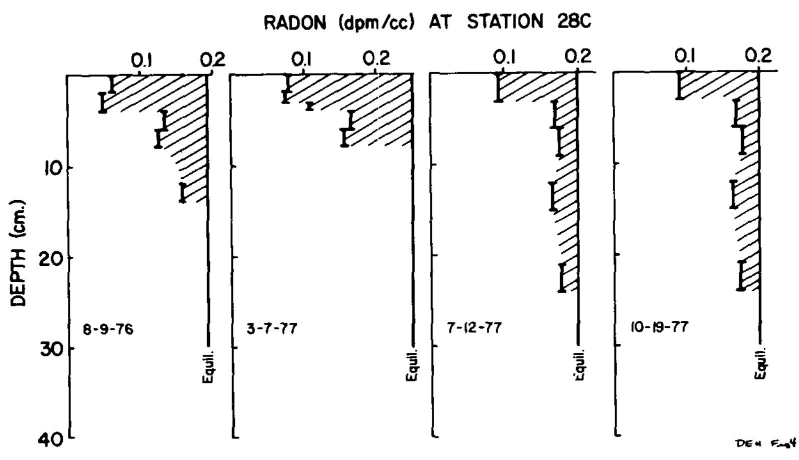

Fig. 4. Radon vs. Depth at Station 28C. Solid lines represent secular equilibrium and dashed areas show deficient zone. This zone may extend below the deepest samples.

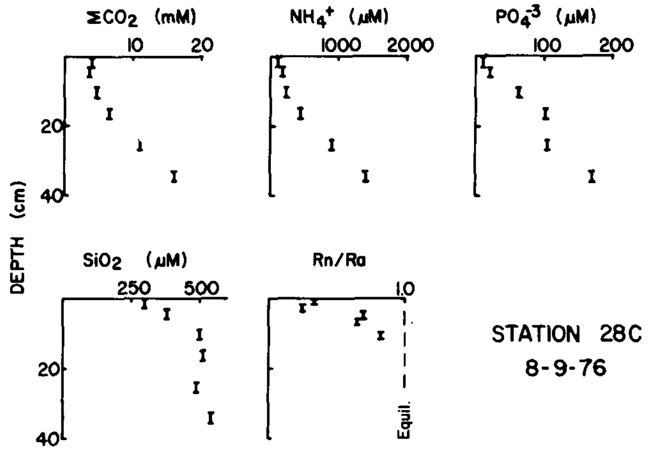

Fig. 5. Interstitial water chemistry at Station 28C. See text for explanation.

Processes which transport dissolved species through interstitial waters and across the sediment-water interface include molecular diffusion (Hammond et al. 1977), irrigation of sediments by benthic organisms (Aller and Yingst 1978) and physical stirring of sediments by wind waves and tidal currents (Krone 1979). Molecular diffusion alone would create a radon deficiency in sediments which decreases exponentially with increasing depth (Hammond et al. 1977). The half-distance of this profile would be about 2 cm. It is clear from the data (Figs. 3, 4, 5) that at least one other mechanism must be important. Physical stirring would create a radon deficiency which decreases monotonically with depth, yet profiles (Figs. 3, 4) are not always monotonic. This suggests that irrigation may be important.

South Bay sediments are inhabited by a number of benthic species which can irrigate sediments as they construct or move about in their burrows. Cores collected at station 28C were always found to contain live specimens of *Asychis elongata,* a large polychaete which builds thick-walled tubes ($\sim$ 3-5 mm ID [see Nichols 1979]); and cores from stations 27 and 28 were always found to contain live specimens of *Heteromastis filiformis,* a smaller polychaete which builds narrower ($\sim$ 2-4 mm ID) soft-walled burrows. These burrows were observed at the sediment-water interface and were often found during sectioning to be open to 40-50 cm in the core. Live worms have also been found close to these depths. Radiographs of cores show worm burrow densities which are typically 0.5-1 burrows$\cdot$cm^{-2} of sediment surface (Korosec in press). Irrigation can enhance the flux of dissolved species across the sediment-water interface and can also produce minima in profiles of dissolved nutrients in interstitial water (Goldhaber et al. 1977). The observations above suggest that irrigation may be of major importance in these sediments and that the polychaete worms are the primary perpetrators, although other unidentified species may also be important. Physical stirring of surface sediments by currents may be occurring, but the surface of these sediments is fairly cohesive and this process is probably not important below the upper 2 cm, if at all. Since any effects of current stirring cannot be distinguished from infaunal irrigation with the techniques discussed here, any effects of this process will be attributed to irrigation.

Past work on interstitial water chemistry has usually treated irrigation as a diffusive process (see Goldhaber et al. 1977). A coefficient of eddy diffusion can be calculated for a substance in the irrigated zone by multiplying the molecular diffusivity times the ratio of the gradient in a deep quiescent zone to the gradient in the irrigated zone. The coefficient determined for one substance can be applied to other substances.

This type of model would not produce a minimum in ΣCO_2, however. A more appropriate model might be an advective pumping model in which worm tubes are a conduit for overlying water to be pumped into the sediments. A minimum in ΣCO_2 or radon could be produced by a localized input. A similar model has been proposed by McCaffrey et al. (in prep.).

In this model (Fig. 6), the sediments can be divided into irrigation zones defined by the stepwise structure of the radon profile. Each zone is assumed to be well mixed. The upper zone

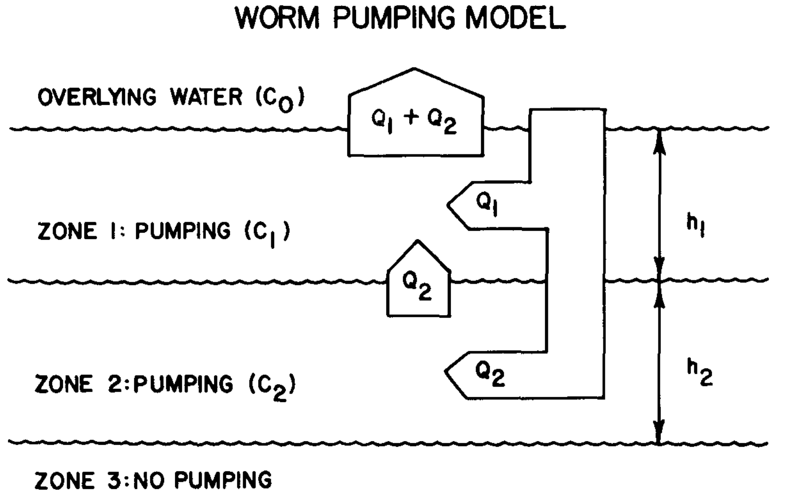

Fig. 6. Worm Pumping Model. The advective flux across the interface is $(Q_1 + Q_2)(C_1 - C_0)$ where Q is the flow rate and C is the concentration in each zone.

receives flow Q_1 directly from the overlying water and Q_2 from the underlying zone. Assuming radon in the water column to be negligible, the radon balance for zone 2 is:

$$\text{Production} = \text{Loss}$$
$$Ph_2A = Q_2C_2 + \lambda h_2AC_2 + J_2A$$

where C_2 = radon concentration in Zone 2 (atoms·vol^{-1})

h_2 = thickness of Zone 2

A = area

P = production rate of radon from radium per unit volume

λ = decay constant for radon

J_2 = net loss by molecular diffusion from Zone 2 per unit area

The balance for Zone 1 is:

$$Ph_1A + Q_2C_2 = (Q_1 + Q_2)C_1 + \lambda h_1AC_1 + J_1A$$

where the subscripted symbols are analogous to those above. These equations can be rearranged so that:

$$\nu C_1 = D - J_D$$

where $D = P(h_1 + h_2) - \lambda (h_2 C_2 + h_1 C_1)$

$= $ integrated radon deficiency

$J_D = J_1 + J_2$

$\nu = (Q_1 + Q_2)/A$

$= $ irrigation velocity in upper zone

Thus irrigation velocities can be calculated from radon, and fluxes of nutrients due to irrigation can be estimated.

Two problems are encountered in using this approach with our data (Fig. 5). The lower limit of radon deficiency was not reached, thus the calculation will yield a lower limit for ν. Also, the net diffusive flux cannot be directly evaluated from these data. If the sample immediately below those collected had an equilibrium amount of radon, the diffusive flux into the irrigated zone from below would approximately equal the diffusive flux across the interface. Thus J_D would be nearly zero because the gradients would be quite similar. If the sample immediately below was deficient, J_D would increase, but so would D. Thus, the major error will arise in the value used for D, and ν will be a lower limit. Defining 0-4 cm as Zone 1 on the basis of radon, taking $D \simeq$ 163 atoms·m^{-2}·s^{-1}, $J_D \simeq 0$, and $C_1 \simeq 5 \times 10^8$ atoms·m^{-3} (Table 1) thus yields $\nu = 3 \times 10^{-7}$ m·s^{-1} $\simeq 3$ cm·d^{-1}. This is the same order of magnitude as the value of 0.7 ± 0.4 cm·d^{-1} observed by McCaffrey et al (in prep.) in laboratory measurements on Narragansett Bay cores.

The fluxes of dissolved nutrients due to irrigation can now be estimated from the expression:

$$\text{Flux} = \nu (C_1 - C_0)$$

where C_0 is the concentration in the overlying water column. These fluxes are listed in Table 2 and are an order of magnitude greater than fluxes which can be attributed to molecular diffusion (Korosec in press). An additional source of uncertainty is introduced in these calculations because water column measurements were not made simultaneously with the core collection. This could be

TABLE 2. CALCULATION OF NUTRIENT FLUXES FROM INTERSTITIAL WATERS[a]

Dissolved Nutrient	C_1 (μM)[b]	C_0 (μM)[c]	F(mmol·m^{-2}·d^{-1})[d]
ΣCO_2	3840	2400	40
NH_4^+	129	6	4
PO_4^{-3}	13.5	12.5	0.03
SiO_2	315	110	6

[a] Data collected at station 28C on 9 August 1976
[b] Weighted average of analyses from 0-4 cm
[c] Values typical for this season
[d] Lower limit, assumes ν = 3 cm·d^{-1}

a major problem for PO_4^{-3}, but not other species. Despite the uncertainties, these estimates should be accurate within a factor of two. The importance of these fluxes in the nutrient balance of the estuary is discussed by Korosec (in press), Peterson (1979) and Conomos et al. (1979).

SAN FRANCISCO BAY

Flux Chambers

The depth-integrated radon deficiency in sediments must equal the flux across the sediment-water interface. This flux was directly measured by placing inverted plexiglass boxes on the sediments and measuring the change in radon. Some difficulties were encountered in sampling as it was difficult to avoid pulling the boxes up by the tubing while sampling on choppy and windy days. About 50% of the deployments were successful and these results are listed in Table 3. Each flux represents a one-day experiment. In one case (box 1, October) the box was left in place for a second day. Substantial variability exists within the experiments at a single station and thus the apparent differences between July and October and between 28C and 28E may not be significant. These measurements can be criticized for two reasons. The failure of the stirring devices to transmit turbulence effectively may allow gradients to build near the interface, reducing fluxes. Also, oxygen in the boxes dropped to nearly zero after one day and this may have reduced irrigation. In either case, these results should represent a lower limit. It is interesting to note that they are within a factor of two of the integrated deficiencies in Table 1. The box experiments and the integrated

TABLE 3. RADON FLUXES ACROSS THE SEDIMENT-WATER INTERFACE MEASURED *IN SITU* WITH BENTHIC CHAMBERS

Station	Sampling period	Box	(atoms·m^{-2}·s^{-1})
28C	July 1977	1	143
		2	123
28C	October 1977	1	198[a]
			280
		3	167
		4	303
		1	296
28E	October 1977	5	127

[a] Mean value of the five observations for station 28C during October, 1977: 249 ± 66.

deficiencies suggest that the flux of radon from South Bay sediments is about 200 ± 70 atoms·m^{-2}·s^{-1}. Molecular diffusion alone would supply radon at a rate:

$$J = \sqrt{\lambda D_S P}$$

where D_S is the effective diffusivity (Hammond et al. 1977). This would be equal to about 80 atoms·m^{-2}·s^{-1} at 15°C, or 40% of the observed flux.

Water Column Analyses

If the rate at which radon escapes to the atmosphere could be predicted, the flux of radon across the sediment-water interface could be obtained by constructing a mass balance for radon in the water column. Thee transects have been made along the Bay axis from station 30 to Rio Vista to collect samples from the water column. All three were similar and one of these is plotted (Fig. 7) to illustrate the uniformity of the distribution. To a first approximation, radon is well-mixed vertically and along the estuary axis. While some variations appear, these are not consistent

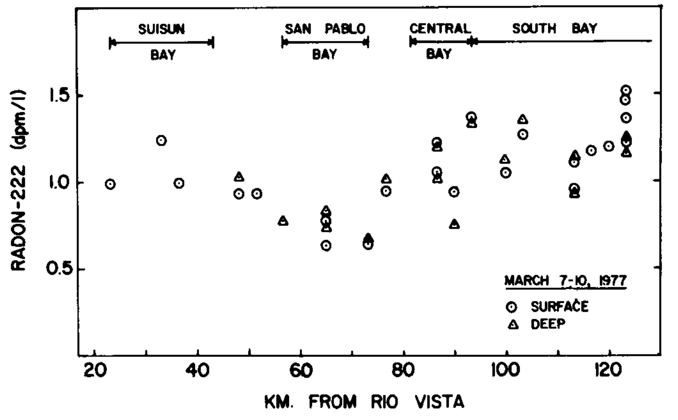

Fig. 7. Radon transect in March 1977. Surface-water samples were collected at 1-m depth and deep-water samples were usually 6-12 m in depth.

spatially or temporally. A few transects have been made perpendicular to the bay axis. These measurements have been similar to channel measurements, although samples collected in shallow (<1 m) water within 200-400 m of shore may have concentrations twice those in channel samples. In the absence of significant horizontal gradients, a box model for the water column can be constructed which ignores horizontal transport. Ground-water can also be ignored because the ratio of water area to recharge area is large. The radon budget for South Bay is computed in Table 4. The decay rate is found by multiplying the average water column concentration by the mean depth. Estimates of radon flux to the atmosphere (evasion) are based on the stagnant film model for gas exchange (Broecker and Peng 1974). This model assumes that film thickness controls exchange rates and an empirical relation between exchange rates and wind speed developed by Emerson (1975) can be used to estimate air-water exchange rates. Radium-226 accounts for the input from dissolved and suspended radium. The input from sediments is used to balance the budget.

If the wind speed-film thickness model is correct, a substantially larger radon flux from sediments is required during periods of high wind than during periods of low wind. Conomos and Peterson (1977) have shown that high winds create waves which resuspend surficial sediments, but this is equivalent to a sediment thickness of only a few millimeters. About 5 cm must be disturbed to supply the extra flux, and the presence of stable benthic communities in surface sediments suggests this does not occur. It is also unlikely that the flux difference in Table 4 would be due to a difference in irrigation because March and January have similar temperatures and are likely to have similar benthic activity. It seems more likely that the calculation of exchange rates from wind speed alone may not be satisfactory.

To test this problem, a sampling station was set up on the end of the San Mateo fishing pier, on the edge of the deep channel in South Bay, about 1.5 km from shore. Surface samples were collected at approximately 1.5-h intervals over a 2-day period (Fig. 8). The average ($\pm$ 1σ) of 29 analyses was 1.17 ± 0.10 dpm·liter^{-1}. Wind speed was measured at the San Francisco International Airport by the National Weather Service and also with a hand-held integrating anemometer (Taylor Inst. Co.) at the end of the pier about 5 m above the water surface. The wind measurements are in fair agreement, although the pier measurements are a little lower during the first day. This may be due to a failure of the pier sitters to orient the anemometer properly or to keep it well away from obstructions on the pier. At high wind speeds, gusts made it difficult to measure speed accurately at the pier. The solid line in Figure 8 was chosen to represent the data. The large diurnal variation

TABLE 4. RADON BUDGET AND ENVIRONMENTAL PARAMETERS FOR SOUTH BAY WATER COLUMN

Date	29-31 Jan 1976	8-11 Aug 1976	7-11 Mar 1976
Environmental Parameters			
T (°C)	10	24	15
Wind ($m \cdot s^{-1}$)	1.5	5	4.5
Film thickness (μ)	500	75	100
Avg. radon ($dpm \cdot liter^{-1}$)	1.49±0.32	1.27±0.22	1.29±0.18
No. samples	10	18	25
Budget ($atoms \cdot m^{-2} \cdot s^{-1}$)			
Losses			
Decay	99±21	85±15	86±12
Evasion	24±12	187±93	122±61
Inputs			
^{226}Ra decay	7±3	7±3	7±3
From sediment[a]	116±24	265±94	201±62

[a] Input from sediment required to balance inputs and losses.

in wind speed during the summer is normal (Conomos 1979). If the flux of radon from sediments is uniform, vertical and horizontal mixing are rapid, and wind speed is the only factor controlling gas exchange, radon in the water column should reflect the diurnal wind variation. In this case, concentration should follow the solid line labeled "model" (Fig. 8). The major features of the model curve are the first minimum and the second maximum. These features should be present because of the large contrast in exchange rates between high wind speed and low wind speed in the model, but neither feature is apparent in the data. Thus, gas exchange in estuarine waters does not seem to be controlled by wind speed alone.

The gas exchange rate per unit area is characterized by a mass transfer coefficient k which has units of velocity:

$$k = J_{atm}/(C_W - C_{atm})$$

where J_{atm} = gas flux/area to the atmosphere

C_W = concentration in the water column

C_{atm} = concentration in water when equilibrated with the atmosphere.

O'Connor and Dobbins (1958) have suggested that flow-generated turbulence may be important in controlling gas exchange rates. On the basis of turbulent velocity fluctuations and scale sizes of vertical eddies, they proposed that the mass transfer coefficient for gas exchange in streams and rivers is approximately:

$$k = (D_m \overline{v}/h)^{1/2}$$

where D_m = molecular diffusivity

$\overline{v}$ = average current velocity

h = water depth

TABLE 5. CALCULATION OF SOUTH BAY GAS EXCHANGE RATE IN OCTOBER 1977

Radon Budget in Water Column (atoms·m^{-2}·s^{-1})	
Average Input	200
Excess Decay	94
Evasion[a]	106
Mass Transfer Coefficient (m·d^{-1})	
Radon	1.0±0.5
O'Connor-Dobbins	1.3

[a] Flux to atmosphere required to balance input and decay.

Applying this model to South San Francisco Bay, we obtain k = 1.3 m·d^{-1}.

The average rate of exchange in October can be calculated by constructing a mass balance for radon in the water column (Table 5). The influx across the sediment-water interface was previously shown to be about 200±70 atoms·m^{-2}·s^{-1}. The depth-integrated decay rate is calculated

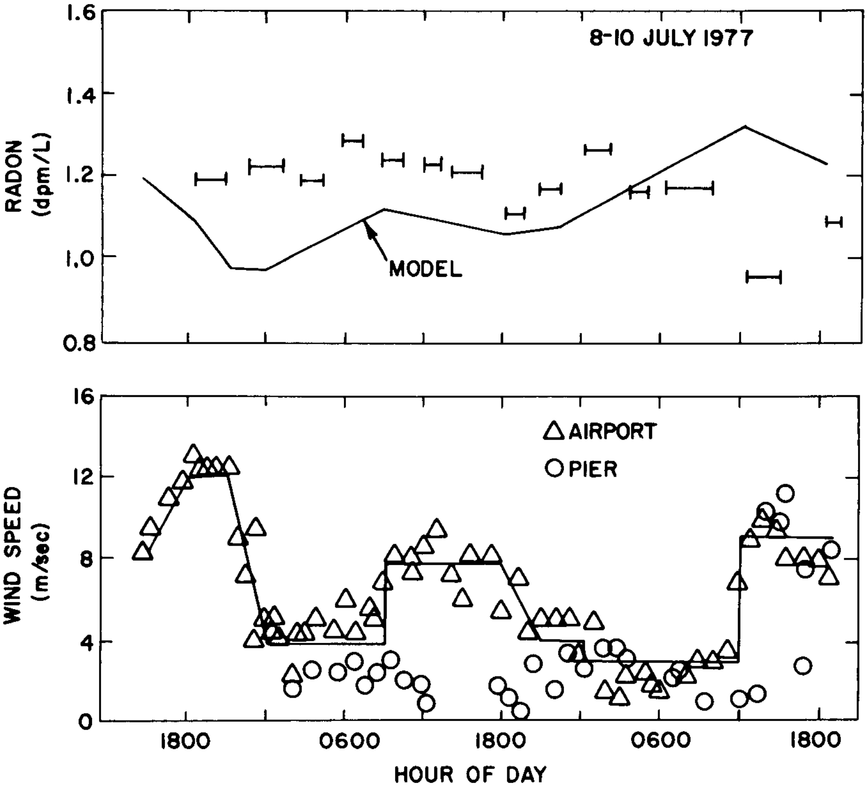

Fig. 8. Radon and wind speed. Data were obtained at the end of the San Mateo fishing pier (Fig. 1). The lower solid line is the average wind speed, the upper solid line is radon expected in the water column. The model curve was calculated assuming a constant decay rate in the water column, a constant input from sediments, and a gas exchange rate which depends on wind speed. Bars show the average of sequential radon analyses.

from the measured concentration in the water column and the mean depth (4 m). The budget is balanced by evasion to the atmosphere which requires k = 1.0±0.5 m·d^{-1}, remarkably close to the O'Connor-Dobbins prediction.

The diurnal field data (Fig. 8) indicate that the gas exchange rate is not closely tied to wind speed, but it is interesting to note that if an average wind speed of 4-6 m·s^{-1} at 10 m above the water surface (the October conditions) is used with the Emerson (1975) wind speed-film thickness relation, the mass transfer coefficient would be 1.5-2.0 m·d^{-1}, fortuitously close to the estimate from the radon mass balance. While the data presented here suggested that gas exchange in estuarine waters is not controlled by wind speed alone, it may play some role. The O'Connor-Dobbins model predicts an exchange rate close to the radon mass balance estimate, but since gas exchange has not been measured over a range of current speeds, the validity of this model cannot be properly assessed from these data. It is clear that further work must be done to elucidate the mechanisms which control gas exchange.

Taking the average mass transfer coefficient to be 1.0 m·d^{-1}, radon budgets can be calculated for different areas of the Bay (Table 6). The difference between fluxes from South Bay and San Pablo Bay sediments may reflect a difference in benthic irrigation. San Pablo Bay has lower densities of these species of deep dwelling polychaetes than South Bay, perhaps because salinity variations are much larger.

The large flux from Central Bay sediments may be due to physical stirring of the sandy sediments by bed-form migration. This does not occur in the fine-grained sediments of South Bay and San Pablo Bay. The remainder of these sediments are medium to coarse sands and would need to supply 445 atoms·m^{-2}·s^{-1} to balance the water column budget. Unfortunately, it is difficult to collect cores in sand and no measurements of radon deficiency have been made in these. Rubin and McCulloch (1979) have shown that sand waves migrate on the Bay floor. Sandy sediments produce radon at a rate of about 1000 atoms·m^{-3}·s^{-1}. Thus, about 40 cm of sand must be continuously stirred to supply the required flux. Alternatively, it may be erosion of bedforms which supplies radon. Assuming sandy sediments to be in secular equilibrium, containing 5 x 10^{8} atoms·m^{-3}, the rate of erosion must be about 8 cm·d^{-1} averaged over the sandy portion. Taking this area to be 100 km^{2}, the volume transport of bedforms should be about 8 x 10^{6} m^{3}·d^{-1}.

TABLE 6. RADON BUDGETS FOR REGIONS IN SAN FRANCISCO BAY (WATER COLUMN)[a]

	South Bay	Central Bay	San Pablo Bay
Mean±1σ(dpm·liter^{-1})	1.32±.24	1.07±.19	0.90±.26
Number of samples	52	22	17
Mean depth (m)	4	14	4
Losses (atoms·m^{-2}·s^{-1})			
Decay	88	250	60
Evasion	123	100	84
Inputs			
Ra^{226} Decay	7	25	7
From Sediments[b]	205	325	137

[a] Based on January, March, and August transects. South Bay includes USGS Sta No. 21-30, Central Bay includes Sta No. 17-20, San Pablo Bay includes Sta No. 11-15 (Fig. 2).

[b] Required to balance inputs and losses.

Vertical Mixing in the Water Column

Surface and deep samples have been collected at 13 stations. The median of top to bottom radon concentration ratios is 1.01, demonstrating that vertical gradients are small. The absence of these vertical gradients can be used to estimate a lower limit for the rate of vertical mixing in South Bay. These estimates can be made by constructing a two-box model (Fig. 9) which divides the water column into a well-mixed surface box of mean thickness h_1 which exchanges with the atmosphere and with a fraction of the sediments, and a well-mixed lower box of mean thickness h_2 which exchanges with the remainder of the sediments. Exchange between the two boxes is characterized by a mixing coefficient K_{12} and exchange between the upper box and the atmosphere is characterized by a mass transfer coefficient K_a. Both K_{12} and K_a have units of velocity.

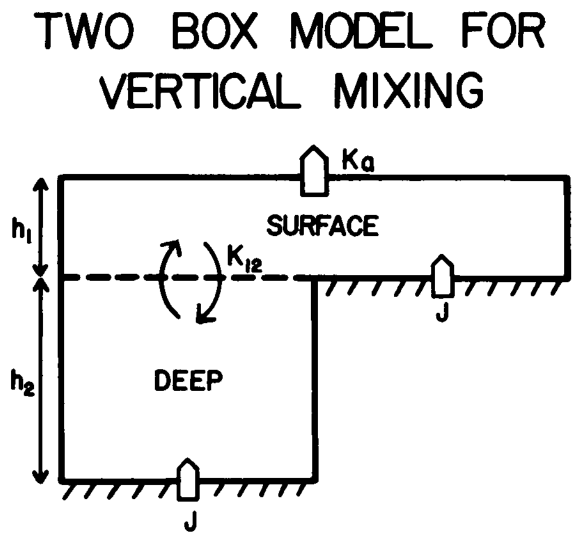

Fig. 9. Two-box model for vertical mixing. See text for explanation.

Input of radon from a unit area of sediment (J) is taken to be constant. The areal fraction of the estuary which is less deep than h_1 is f_1, the fraction which is deeper than h_1 is $1\text{-}f_1$. Assuming a steady state, the mass balance for radon over a unit area in the upper box requires that:

$$Jf_1 + K_{12}\,(1-f_1)(C_2 - C_1) = K_aC_1 + \lambda h_1 C_1$$

In the lower box:

$$J = K_{12}\,(C_2 - C_1) + \lambda h_2 C_2$$

These equations can be solved to calculate the ratio C_1/C_2 in terms of the geometrical characteristics of the system (h_1, h_2, f_1), and the transport coefficients (K_a, K_{12}). A hypsographic curve for South Bay shows that about half the area is quite shallow (<2 m at mid tide) and half the area is a relatively deep channel (Conomos and Peterson 1977). The mean depth of South Bay is 4 m. Taking h_1=2 m, h_2=4 m, f_1=0.50, and K_a=0.8 m·d^{-1}, the ratio of C_1/C_2 can be calculated in terms of K_{12} (Fig. 10). Field data indicate that C_1/C_2 is certainly greater than 0.9 so K_{12} must be greater than 10^{-2} cm·s^{-1}. The model residence time of water in the lower box before it enters the surface box is h_2/K_{12}<$4\text{x}10^4$ or less than 12 h. If the two boxes were separated by a halocline

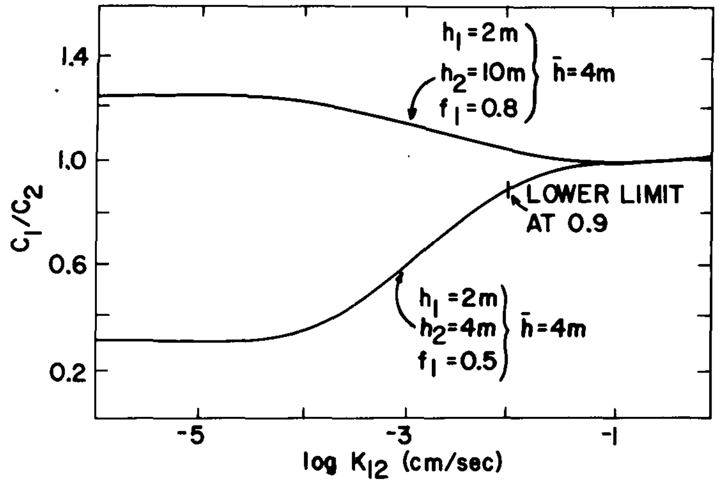

Fig. 10. Surface/deep radon vs. vertical mixing coefficient. If the ratio is greater than 0.9, K_{12} must be greater than 1 x 10^{-2} cm·s^{-1}. The lower curve is drawn for a geometry approximating South Bay; the upper curve is drawn for a hypothetical geometry.

1 m thick, this mixing coefficient would be equivalent to a vertical eddy diffusivity of greater than 1 cm^2·s^{-1}.

It is interesting to note that in an estuary with different geometry, the ratio C_1/C_2 would be quite different. For example, if the mean depth was 4 m and f_1 = 0.80, the concentration ratio could be as great as 1.25 (Fig. 10). Thus, estuaries with very large shoal areas and narrow, deep channels could have concentration ratios well above 1 if vertical mixing was slow.

CONCLUSIONS

(1) Irrigation of sediments by benthic organisms, probably by one or two species of deep-dwelling polychaete worms, creates radon deficiencies in sediments and zones in which concentrations of nutrients in interstitial waters are nearly uniform.

(2) Using a model which treats irrigation as an advective process, fluxes of nutrients across the sediment-water interface due to irrigation can be calculated from radon deficiencies and nutrient measurements. At one station in South Bay, the rate of this transport is an order of magnitude greater than the transport rate which molecular diffusion could accomplish.

(3) Direct measurement of radon fluxes using benthic chambers agrees with fluxes calculated from sediment deficiencies within a factor of two.

(4) The rate of gas exchange across the air-water interface is equivalent to a mass transfer coefficient of 1.0±0.5 m·d^{-1}, in reasonable agreement with the rate predicted by the O'Connor-Dobbins (1958) model. This rate seems to be primarily controlled by flow-generated turbulence rather than by wind-generated turbulence.

(5) A lower limit can be placed on the rate of vertical mixing in South Bay. This limit indicates that vertical mixing is complete in less than 12 hours.

(6) A large flux of radon from the sediments occurs in central San Francisco Bay. If this flux is attributed to the continuous stirring of sandy sediments, a thickness of 40 cm must turn over rapidly. From observations of bedforms, Rubin (pers. comm.) suggests that a thickness of 3 to

several tens of centimeters should turn over on a short time scale, which supports the conclusions from radon measurements.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance and company of Blayne Hartman, Michael Korosec, and Lawrence Miller in field work. T. John Conomos, David H. Peterson, and Frederic H. Nichols of the U. S. Geological Survey have provided shiptime and logistical support as well as invaluable discussion. Stephen W. Hager of the U. S. Geological Survey kindly performed nutrient analyses in the interstitial waters. Richard Ku and T. John Conomos reviewed the manuscript and provided valuable comments.

This research has been supported by National Science Foundation Grant No. OCE76-81154 and NOAA, Office of Sea Grant, Department of Commerce Grant No. 04-7-158-44113.

LITERATURE CITED

Aller, R. C., and J. Y. Yingst. 1978. Biogeochemistry of tube-dwellings: A study of the sedentary polychaete *Amphitrite ornata* (Leidy). J. Mar. Res. 36:201-254.

Broecker, W. S. 1965. The application of natural radon to problems in ocean circulation. Pages 116-145 *in* T. Ichiye, ed. Symposium on Diffusion in Oceans and Fresh Waters. Lamont-Doherty Geological Observatory, Palisades, N.Y.

Broecker, W. S., and T-H. Peng. 1974. Gas exchange rates between sea and air. Tellus 26:21-35.

Carpenter, J. H. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnol. Oceanogr. 10:141-143.

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

Conomos, T. J., and D. H. Peterson. 1977. Suspended particle transport and circulation in San Francisco Bay: An overview. Pages 82-97 *in* L. E. Cronin, ed. Estuarine Processes. Vol. 2. Academic Press, New York.

Emerson, S. R. 1975. Gas exchange rates in small Canadian shield lakes. Limnol. Oceanogr. 20:754-761.

Friedlander, G., J. W. Kennedy, and J. M. Miller. 1964. Nuclear and radiochemistry, 2nd ed. J. Wiley & Sons, New York. 585 pp.

Goldhaber, M. B. et al. 1977. Sulfate reduction, diffusion, and bioturbation in Long Island Sound sediments. Report of the FOAM Group. Amer. J. Sci. 277: 193-237.

Hammond, D. E., H. J. Simpson, and G. Mathieu. 1977. ^{222}Radon distribution and transport across the sediment-water interface in the Hudson River estuary. J. Geophys. Res. 82: 3913-3920.

Key, R. M., N. L. Guinasso, and D. R. Schink. 1977. The release of radon from sediments. Trans. Amer. Geophys. Union 58:421. (Abstr.)

Korosec, M. In press. The effects of biological activity on transport of dissolved species across the sediment-water interface in San Francisco Bay. M. S. Thesis. University of Southern California.

Krone, R. B. 1979. Sedimentation in the San Francisco Bay system. Pages 85-96 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.

Mathieu, G. 1977. Radon-222/radium-226 technique of analysis. Appendix I *in* P. Biscaye, Annual Report to ERDA, Transport and Transfer Rates in the Waters of the Continental Shelf. Contract EY76-S-02-2185. 30 pp.

McCaffrey, R. J., A. C. Myers, E. Davey, G. Morrison, M. Bender, N. Luedtke, D. Cullen,

P. Froehlich, G. Klinkhammer. 1979. Benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island. (Paper submitted to Limnol. Oceanog.)
Nichols, F. H. 1979. Natural and anthropogenic influences on benthic community structure in San Francisco Bay. Pages 409-426 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.
O'Connor, D. J., and W. E. Dobbins. 1958. Mechanism of reaeration in natural streams. Trans. Amer. Soc. Civil. Eng. 123: 641-666.
Peterson, D. H. 1979. Sources and sinks of biologically reactive oxygen, carbon, nitrogen, and silica in northern San Francisco Bay. Pages 175-193 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.
Reeburgh, W. S. 1967. An improved interstitial water sampler. Limnol. Oceanogr. 12:163-165.
Rubin, D. M., and D. S. McCulloch. 1979. The movement and equilibrium of bedforms in central San Francisco Bay. Pages 97-113 *in* T. J. Conomos, ed. San Francisco Bay: The Urbanized Estuary. Pacific Division, Amer. Assoc. Advance. Sci., San Francisco, Calif.