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Organic matter diagenesis in the sediments of the San Pedro Shelf along a transect affected by sewage effluent

W.M. Berelson^{a,*}, K. Johnson^b, K. Coale^c, H.-C. Li^a

^a *Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089-0740, USA*

^b *Monterey Bay Aquarium Research Institute, 7700 Sandholt Road, Moss Landing, CA 95039, USA*

^c *Moss Landing Marine Labs, P.O. Box 450, Moss Landing, CA 95039, USA*

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Abstract

A study was conducted to examine the rate of organic matter degradation within the sediments adjacent to the Whites Point Los Angeles County sewage outfall system on the San Pedro Shelf. Benthic chamber deployments were made at three stations in a transect away from the outfall pipe during three cruise periods (October 1990, February and October 1991). The fluxes of phosphate, silicate and radon-222 showed the most significant difference (factor of 3) between stations proximal and distal to the sewage effluent outfall pipe; the fluxes of nitrate, ammonia, alkalinity and TCO₂ showed some gradient (a factor of 1.5–2) and the uptake of oxygen showed no variability between sites. Carbon oxidation in these sediments is driven primarily by net oxygen consumption and secondarily by net sulfate reduction. Net sulfate reduction accounts for about 30% of the carbon oxidation near the outfall pipe and 10–15% at the distal sites. Measurements of radon-222 fluxes and radon emanation rates from sediments indicate that the intensity of bio-irrigation is greater by a factor of 2 at sites away from the outfall pipe, but also shows that bio-irrigation does take place at the site adjacent to the pipe. The total amount of particulate organic carbon (POC) oxidized in the sediments around the outfall is $\sim 2 \times 10^7$ g C/d. An estimate of carbon burial in this region is 4×10^7 g C/d. The outfall system could supply $\sim 3 \times 10^7$ g C/d of which 12–20% is estimated to have been deposited in the region. Hence, effluent-derived POC, although it may be a part of the total organic carbon pool undergoing diagenesis and burial on the sea floor, is not likely the only source of carbon to this system. Primary productivity in the surface ocean could supply $9\text{--}13 \times 10^7$ g C/d to the sea floor. A balanced carbon budget requires that half the primary production is exported to the sea floor, although this budget does not account for other sources of POC to the region. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The fate of pollutants buried within the sediments of the San Pedro continental shelf off the Los Angeles County sewage effluent outfall pipe has been a concern of scientists and policy makers

for more than 25 years (Bruland et al., 1974; Sweeney et al., 1980; Stull and Baird, 1985). Although the input of DDT and a number of trace metals has declined significantly since maximum discharge in 1971, there is still concern over the fate and potential transport of these buried compounds. At present, the maximum concentration of DDT and trace metals within the sediments lies 25–50 cm below the sediment–water interface.

*Corresponding author. Fax: +1-213-740-5828.

E-mail address: berelson@earth.usc.edu (W.M. Berelson).

The point source input of particles and solutes has generated a strong gradient in sediment deposition and composition with respect to the outfall location. One of the important questions pertaining to effluent discharge has been to determine the fate of particles which exit the outfall pipe at Whites Point, Palos Verdes (Fig. 1). A number of studies have utilized chemical tracers (stable isotopes and trace metals) to establish the fraction of effluent particles that are retained in the sediments surrounding the outfall (Sweeney and Kaplan, 1980; Sweeney et al., 1980; Huh et al., 1992 and others). In this study a budgetary approach is utilized to examine the fate of outfall particulate carbon. We derive a budget for organic carbon (C_{org}) burial and remineralization within the sediment column and compare these values to rates of nutrient and particulate C_{org} input via the sewage outfall pipe. There is also an important question as to whether the particles deposited on

the shelf undergo diagenesis in situ, or if they are mixed by sediment infauna and bottom water turbulence and transported into the water column and out of the region. The importance of both processes have been demonstrated by research groups in support of different sides of a major lawsuit (Drake et al., 1994; Quensen et al., 1998; Santschi et al., 2001a,b).

The research presented in this paper gives information about the diagenetic reactions occurring within the sediments of the outfall region and the rate of chemical solute exchange between the sea bed and the overlying water column. We examine processes controlling pore water–overlying water exchange and the stoichiometry of reactions involving organic matter diagenesis.

The study makes use of free-vehicle benthic chamber devices (landers) and the ability to derive a flux value from a time series of samples collected from an incubation chamber (Berelson and

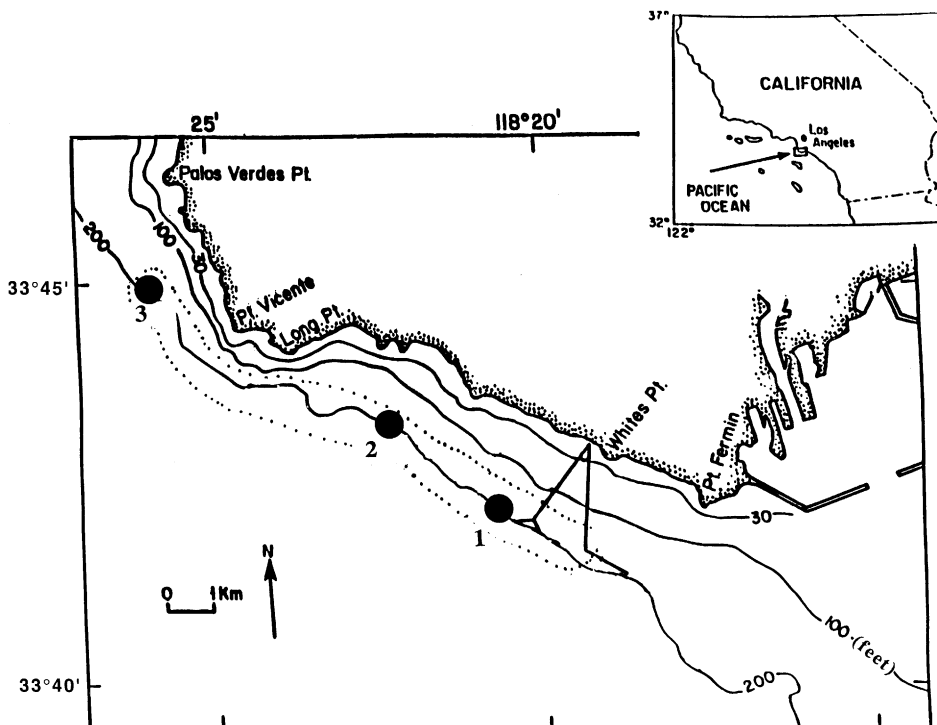


Fig. 1. Study area, the San Pedro Shelf. The L.A. County Whites Point Wastewater outfall is indicated by the bifurcated line directed offshore from Whites Point to a depth of 200 ft. The station locations are indicated by the solid points. The area enclosed by a dotted line indicates the general distribution of sewage-impacted sediments in the region.

Hammond, 1986). The outfall pipe opening lies on a muddy sea bed at a depth of 60 m where temperatures are 11–14°C. The benefit of in situ chamber incubation is that there is minimal alteration of the natural environment, thus fluxes are considered representative of ambient solute exchange rates. The fluxes of oxygen, ammonia, nitrate, phosphate, silicic acid, alkalinity, TCO₂ and radon-222 were measured utilizing flux chamber devices. Multiple measurements were made at three sites in a transect away from the outfall pipe in the direction of predominant current flow, to the northwest (Fig. 1). Average fluxes were determined and diagenetic patterns and processes were described for each site. The amount of organic carbon which undergoes oxidation within the sediment bed, the use of various oxidants and the depth distribution and solute transport mechanisms are all important to the solubilization or retention of particulate trace metals (Shaw et al., 1990; Thamdrup et al., 1994; Gobeil et al., 1997) and to the fate of DDT (Quensen et al., 1998). Thus, a major objective of this study was to define rates and pathways of organic matter degradation along a sewage-impacted gradient.

2. Methods

Benthic chamber free-vehicle devices were deployed at three sites during field work conducted in October 1990, February and October 1991 (Table 1). The lander operation has been described previously (Berelson and Hammond, 1986) but a brief description follows.

Each lander deployed is released from a research vessel and following free-fall, sits on the sea floor for 6–8 h before chambers are deployed. At a programmed time, three cylindrical chambers are released from within the lander frame and embed partially into the sea floor sediments. Hours later, lids seal to the top of the chambers, thereby initiating three incubation experiments. The chambers capture ~7 l of water in contact with 0.073 m² of sea bed. Six samples (250 ml each) were removed from each chamber to sample vessels during the incubation period (12–20 h). A CsCl spike was injected early in the incubation and the observed dilution of this spike in successive sample draws was used to calculate chamber volume and verify that the chamber was not leaking. The chambers were stirred by a rotating paddle such that the diffusive boundary layer within the chamber was 200–400 µm. The oxygen concentration within the chamber and in the ambient bottom water was monitored by a pulsed electrode with readings made every 6 min. Following the final sample draw, a pinching apparatus closed off all the sample tubes and ballast weights released. Glass flotation allows the device to surface where the ship is waiting to recover.

Samples collected from the device were immediately filtered (0.45 µm) except for 2 splits, one on which pH was measured and a second for radon analyses. Ammonium, nitrate, nitrite, phosphate and silicate were analyzed by colorimetric auto-analyzer techniques with replicate precisions of 0.2, 0.1, 0.01, 0.05, and 1 µM, respectively. Alkalinity was determined on a 5 ml sample split to a precision of 10 µeq/l and TCO₂ was calculated

Table 1
Site information

Station	Latitude (N)	Longitude	Depth (m)	BW O ₂ (µM)	# chambers	Sediment		
						Mass accum ^a (g/cm ² yr)	Average wt% ^b	
							C	S
1	33°42.1	118°20.7	67	152	10	1.1	4	0.5
2	33°43.1	118°22.8	63	166	6	1.0	3	0.2
3	33°45.0	118°26.4	64	175	8	0.8	4	0.2

^a These rates represent accumulation between the early 1970s and the mid 1980s and utilize porosities of between 0.8 and 0.7.

^b Sediment from 2–6 cm.

from alkalinity and pH (standardized to NBS buffers, ± 0.02 units) to a reproducibility of $12 \mu\text{M}$. Radon activity was measured on a 100 ml sample using vacuum extraction techniques and scintillation counting methods (Berelson et al., 1987). Cesium was measured by flame emission techniques to a precision of $\pm 10\%$. The oxygen electrodes were calibrated in the lab and in the field to measurements of oxygen concentration using the Winkler technique. All analyses were completed within a few days of recovery.

All chamber concentrations were corrected for the successive dilution that occurs when a sample is drawn and ambient water replenishes the chamber volume. Fluxes were calculated as the product of the slope (concentration vs. incubation time) and chamber height. The slope was determined only from the linear portion of the concentration vs. time plots at the beginning of the incubation period. For some chemical solutes, the change in concentration vs. incubation time was decidedly non-linear; for other constituents, the flux appears constant for the entire incubation period. The uncertainty in the concentration vs. time slope was attributed to both the uncertainty in the analytical precision and in the fit of the data to a linear function. The uncertainty in the flux accounts for both the uncertainty in this slope and in the determination of chamber heights (about 10–15%). Generally, chamber fluxes have an uncertainty of 15–50%. All the chamber fluxes measured at a site were averaged to generate a mean flux with a standard error of the mean also reported (Table 2).

Sediment box cores were collected at each site and subcores were extracted for analyses of radon emanation. Two centimeter sections were incubated in glass jars containing 64 ml of sea water. The radon emanation from this slurry was measured 4–6 weeks after sealing the jars and following sampling, the jar was refilled and incubated for another 4–6 weeks. Three to four emanation measurements were made from a single jar and the average value was used for calculation. The incubated sediment was weighed and radon flux calculations were made assuming that radon emanation rates followed a linear function of sediment depth (Hammond and Fuller, 1979).

Samples from a separate subcore were used to measure sediment porosity and the average porosity for the 0–4 cm interval was applied to the calculation of diffusive radon flux. Sediment splits were also analyzed for total weight percent C and S using a Perkin–Elmer CNS analyzer.

3. Results

Variability in chamber flux estimates may be attributable to a number of factors: uncertainties in the flux determination, heterogeneity on the scale of chamber separation (< 1 m), heterogeneity on the scale of lander separation (10 m), and temporal variability in fluxes (Table 2). Although the variability in chamber fluxes can be quite large (e.g. phosphate fluxes at Station 2 in February 1991), generally the agreement in fluxes between chambers is better than 50%, which is the same magnitude of variability between lander deployments. There was some variability in fluxes corresponding to the different cruise dates, although only the radon fluxes were systematically related to season at all three stations. Average station flux values were determined from no less than 3 and as many as 10 chamber experiments. Generally, the average flux value for a given constituent at a given station was known to better than 30%.

Flux chamber data are shown in Fig. 2 for the chambers deployed in October 1991. Although the individual chamber data are not differentiated, it is clear that generally, all the nutrient concentrations increased in a monotonic trend with incubation time. The data from different stations are distinguished by different symbols and a few station-to-station trends are recognizable. Phosphate fluxes are greater from the sediments adjacent to the outfall pipe relative to the other stations and the flux of silicic acid is lower at this proximal site. Oxygen uptake also produced a monotonic decline in oxygen concentration within the chamber from ambient concentrations of about $160 \mu\text{M}$ to values approaching $20 \mu\text{M}$. The portion of the oxygen uptake profile utilized in the flux calculations was limited to the linear region of change in oxygen concentration vs. time.

Table 2
Whites Point Outfall benthic flux summary

Station chamber	Date	Ch. Ht. (cm)	Oxygen	Ammonia	Nitrate	Phosphate	Silica	Alkalinity	TCO ₂	Radon
1-Y	10/2/90	10.0	-22	3.7	—	0.58	2.2	—	—	90
R		9.2	-15	2.6	—	0.24	1.5	—	—	62
B		8.5	-21	3.3	—	0.51	1.9	—	—	—
1-Y	2/13/91	11.0	-15	—	—	—	—	—	—	—
R		11.0	-42	—	—	—	—	—	—	—
B		11.0	-17	—	—	—	—	—	—	—
1-B	2/14/91	10.7	-13	2.0	—	0.50	1.3	—	—	67
1-Y	10/3/91	9.1	-26	3.6	-0.9	1.33	2.0	15	31	221
R		10.9	-14	3.5	-1.1	2.35	1.3	40	48	177
B		10.2	-21	4.5	-1.0	1.71	2.6	37	44	263
	Mean 1		-21	3.3	-1.0	1.03	1.8	31	41	147
	±SE		3	0.3	0.1	0.33	0.2	10	6	39
2-Y	2/13/91	9.7	-14	3.0	—	0.50	4.3	11	20	—
R		13.3	-16	1.2	—	0.04	1.7	7	14	—
B		10.3	-17	2.1	—	0.21	2.3	—	—	113
2-Y	10/2/91	9.0	-23	5.6	-0.6	0.86	5.2	33	55	462
R		8.0	-25	3.1	-0.4	0.24	2.6	7	22	226
B		9.9	-24	4.8	-1.1	0.62	4.7	23	39	404
	Mean 2		-20	3.3	-0.7	0.41	3.5	16	30	301
	±SE		2	0.7	0.2	0.14	0.6	6	9	95
3-Y	2/15/91	12.3	-22	0.4	—	—	2.6	6	12	203
R		13.0	-26	1.0	—	—	3.7	14	31	341
B		12.0	-20	1.7	—	—	3.0	—	—	254
3-Y	9/30/91	7.2	-21	2.2	-0.4	0.20	3.6	11	21	324
R		9.8	-27	3.7	-0.7	0.34	5.4	14	29	538
B		8.5	-20	2.3	-0.4	0.31	4.4	15	25	430
3-Y	10/1/91	9.7	-24	2.6	-0.3	0.27	4.9	17	32	429
B		9.6	-21	2.6	-0.7	0.22	4.4	14	31	465
		Mean 3		-23	2.1	-0.5	0.27	4.0	13	26
	±SE		2	0.4	0.1	0.03	0.4	2	3	43
	Mean all		-21	2.8	-0.7	0.61	3.1	19	32	282

Fluxes in mmol/m²d except alkalinity (meq/m²d) and radon (atoms/m²s). Negative fluxes imply uptake by the sediments.

A summary of fluxes for all the chamber deployments in the outfall region indicate a strong regional trend in flux values for three of the chemicals measured: phosphate, silicic acid and radon (Table 2). The phosphate flux at Station 1 was three times greater than the flux at Station 3, the silicic acid flux was 2–3 times smaller at Station 1 than Station 3 and the radon-222 flux was 2.5 times smaller at Station 1 compared to Station 3. Fluxes for these constituents were intermediate at Station 2. The fluxes of TCO₂, alkalinity and ammonia were slightly greater at the proximal station relative to Stations 2 and 3 and the uptake

of nitrate also shows a trend towards greatest values at Station 1. There was virtually no difference in the rate of oxygen uptake between the three sites.

4. Discussion

4.1. Early diagenesis

Inferences about the diagenetic pathways in sediments may be made by assuming stoichiometric relationships between oxidants and

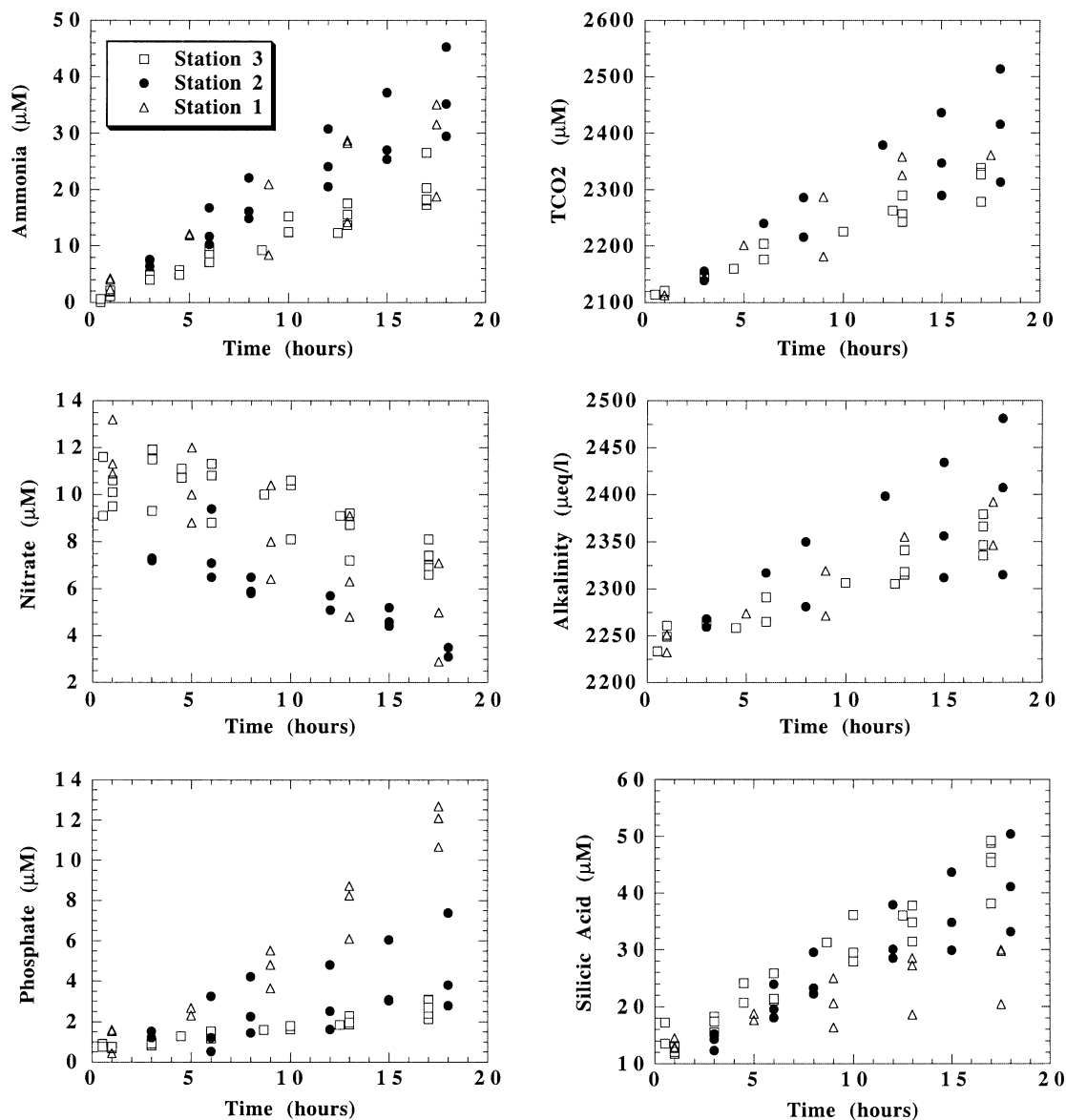


Fig. 2. Flux chamber data from deployments in October 1991. The data indicate the increase or decrease in chamber concentration as a function of incubation time. The different symbols represent chambers deployed at the different stations. Initial ambient bottom water concentrations are: 0 μM for ammonia, 11 μM for nitrate, 0.3 μM for phosphate, 2100 μM for TCO₂, 2225 $\mu\text{eq/l}$ for alkalinity and 11 μM for dissolved Si.

products of organic matter degradation. Chambers integrate the net product of sedimentary diagenesis, therefore the diagenetic and stoichiometric arguments presented will consider reactions which occur both at the sediment–water interface and centimeters below this surface. In order to use

stoichiometric relationships it is necessary to identify which fluxes are produced by which reactions. For example, an alkalinity flux may be produced by: (a) the release of ammonium, (b) denitrification, (c) sulfate reduction and the reaction of sulfide with iron oxyhydroxides, and (d)

dissolution of calcium carbonate. Alkalinity may be consumed by a range of reactions as well (Berelson et al., 1998; Hammond et al., 1999). The net flux of alkalinity into or out of a chamber will reflect the integration of all reactions, production and consumption. That the net flux of alkalinity is always positive, out of the sediments, suggests that reactions (a)–(d) are greater than reactions involving alkalinity consumption.

Fluxes of alkalinity and TCO_2 provide a critical part of the organic carbon diagenetic picture for the outfall region (Table 3). In order to distinguish TCO_2 flux derived from organic carbon oxidation from TCO_2 flux derived from mineral dissolution, a number of corrections and assumptions about the alkalinity flux are made. The station-averaged total alkalinity flux is adjusted for the contribution of ammonium flux and nitrate reduction (Berelson et al., 1998; Hammond et al., 1999). This residual alkalinity flux, Alk_{corr} , primarily reflects the contribution of reactions (c) and (d) given above. The total CO_2 flux measured may represent a combination of oxidized organic carbon (C_{ox}) and carbonate ion from calcium carbonate dissolution. If all the Alk_{corr} is attributed to carbonate dissolution because the mineral form is undersaturated, the CO_2 flux gets reduced by the CaCO_3 dissolution flux resulting in the column in Table 3 labeled Minimum C_{ox} . However, if all the Alk_{corr} is attributable to sulfate reduction, the total CO_2 flux measured is also the measure of organic carbon oxidized (Max C_{ox}). As an upper limit, if sulfate reduction is the source of all the Alk_{corr} , 50% of the carbon oxidized at Station 1 occurs via net sulfate reduction and this pathway accounts for 33% of the carbon oxidized at Stations 2 and 3. This argument does not indicate the amount of total sulfate reduction, rather it accounts for net

sulfate reduction, which is identified by the amount of iron-oxyhydroxide which is reduced to pyrite or other iron-sulfide minerals.

Both carbonate dissolution and sulfate reduction are quite likely to occur within these sediments. An average value for C_{ox} between the minimum and maximum estimate is within $\pm 20\%$ of the upper and lower limit estimates of organic carbon oxidation and thus is probably a reasonable representation of the mean value. Organic carbon diagenesis at the proximal station likely includes the effect of oxygen consumption and sulfate reduction and the contribution of sulfate reduction to total carbon oxidized is greater for Station 1 than for Stations 2 and 3. It is clear that although bottom water oxygen concentrations are $> 100 \mu\text{M}$, the sediments are reducing enough such that nitrate reduction occurs at all sites. However, neither nitrate reduction nor metal oxide reduction can be a major oxidant of organic carbon relative to oxygen and sulfate consumption (Fig. 3).

Solid phase sulfur accumulation rate measurements from these sediments serve as a check on the stoichiometric balances presented above. Assuming that net sulfate reduction involves a reaction with organic carbon and iron-oxyhydroxides ($\text{Fe}(\text{OH})_3$) and results in the formation of pyrite (FeS_2), a measure of S accumulation provides a measure of net sulfate reduction (Leslie et al., 1990; Hammond et al., 1999). Sediment accumulation rates in the vicinity of the outfall pipe multiplied by the weight percent S in sediments (Table 1) yield estimates of net S accumulation rates. Sulfur accumulation rates are converted to sulfate reduction rates and this rate is $4.7 \text{ mmol SO}_4/\text{m}^2 \text{ d}$ for Station 1, $1.7 \text{ mmol SO}_4/\text{m}^2 \text{ d}$ for Station 2 and for Station 3 the rate is $1.5 \text{ mmol SO}_4/\text{m}^2 \text{ d}$. These rates of sulfate reduction could

Table 3
Summary of chamber flux measurements used to understand carbon diagenesis

Station	Oxygen	Meas. alkalinity	Alk_{corr}	Max CaCO_3 dissolution	Max C_{ox} by SO_4	Meas. $\text{TCO}_2 = \text{Max C}_{\text{ox}} - \text{Min C}_{\text{ox}}$	Ave. C_{ox}
1	–21	31	27	13	22	41	28
2	–20	16	12	6	10	30	24
3	–23	13	10	5	9	26	23

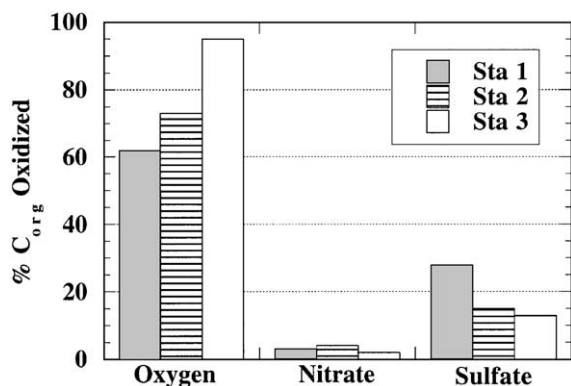


Fig. 3. A comparison of the total organic carbon oxidized by reactions with oxygen, nitrate and sulfate. Reactions with sulfate that involve reoxidation of sulfide by oxygen are considered a part of the oxygen budget. Sulfate reduction, for the purposes of this comparison, are only those reactions which involve C_{org} , SO_4 and Fe and result in net production of solid sulfide minerals.

oxidize 9, 4 and 3 mmol C/m^2d , which is consistent with, but lower than the maximum sulfate reduction rates determined by chamber budgets of alkalinity and TCO_2 (Table 3). The S burial rate calculations suggest that half of the Alk_{corr} is due to sulfate reduction and half due to carbonate dissolution. Hence, the sediment solid phase S data supports the conclusion that net sulfate reduction is responsible for about 30% of the carbon oxidized at Station 1 and 10–15% of the carbon oxidized at Stations 2 and 3.

Identifying the source of the organic matter undergoing diagenesis in this region is of interest as flux ratios may reflect breakdown of sewage-derived particulate organic carbon (POC) or phytoplankton which has rained to the sea bed. The Redfield ratio of C:N:P in marine phytoplankton, 106:16:1, may be used to decipher the sources of the organic matter undergoing diagenesis in this region. For example, the phosphate efflux at Station 3, 0.27 mmol/ m^2d multiplied by 106 suggests that 29 mmol/ m^2d of phytoplankton carbon should be oxidized to balance the phosphate flux. The measured TCO_2 flux for Station 3 is 26 mmol/ m^2d , extremely close to this calculated value. However, at Station 1 the average phosphate flux, 1.03 mmol/ m^2d predicts a carbon oxidation flux of 109 mmol C/m^2d , whereas the

measured flux is 41 mmol C/m^2d . Even given the uncertainties in the fluxes, this large imbalance suggests that: (a) the organic matter undergoing diagenesis at Station 1 is enriched in P by a factor of 3 over the Redfield ratio, (b) diagenesis at Station 1 is causing the liberation of inorganically bound P (Ruttenberg and Berner, 1993), or (c) P is preferentially released from decomposing organic matter. The particles arriving on the sea floor in the vicinity of Station 1 are more impacted by sewage effluent than the particles sedimenting at Station 3 (Sweeney et al, 1980; Stull and Baird, 1985; Eganhouse and Kaplan, 1988) and it appears that the efflux of phosphate is enhanced as a function of proximity to sewage particle loading. The agreement between C:P efflux ratios at Station 3 and the Redfield ratio suggests that typical marine phytoplankton is the main source of organic carbon undergoing diagenesis at this site. However, C:P measurements in buried organic matter are necessary to test this hypothesis.

The C:N molar ratio in marine phytoplankton, ~ 7 , is roughly half the C:N ratio in sewage effluent (Sweeney and Kaplan, 1980). Hence the ratio of N-to-C fluxes may be impacted by the proportion of sewage-derived organic matter undergoing oxidation. However, the oxidation of ammonia and coupled denitrification which may occur in these sediments makes the interpretation of total N fluxes more difficult to relate to organic carbon diagenesis. The C:N efflux ratio is elevated at Stations 1 and 3 (the molar ratio is 12) relative to Station 2, where the molar ratio is 9. Either more denitrification is occurring at the end-member stations relative to the middle station or the organic matter undergoing diagenesis at the end-member stations has a greater fraction of sewage-derived particles. It seems reasonable that denitrification dominates at Station 3 and the degradation of effluent particles is more important at Station 1.

There are distinct stoichiometric differences in the diagenesis of organic carbon, nitrogen and phosphorus at the three stations studied. This is most apparent in the efflux of P which is enhanced near the outfall pipe by a factor of 3 over fluxes elsewhere. The difference in C_{ox} along this sewage effluent gradient is only 40%. The efflux of

phosphate and TCO₂ at Stations 2 and 3 could be consistent with a marine phytoplankton source of the degrading organic matter. The highly reducing nature of these sediments (nitrate uptake in the presence of high bottom water oxygen concentrations) suggests that net sulfate reduction plays an important role in carbon oxidation at all three sites, but is most important at the proximal station.

4.2. Bio-irrigation gradients

One of the more striking features of the flux chamber data (Table 2) is the consistent gradient in radon flux between the three stations. Radon-222, produced by Ra-226 within the sediment column, is not biologically active, hence its flux is dependent on sediment source strength and transport mechanism (Hammond and Fuller, 1979;

Martens et al., 1980). The diffusive flux of radon can be predicted from measurements of Ra-226 in sediment cores from the outfall region (Hammond and Fuller, 1979; Berelson et al., 1982) and a summary of these measurements and calculations appears in Table 4. The predicted diffusive flux is 2–3 times less than the average measured radon flux. Bio-irrigation is typically invoked as an important transport mechanism in most shallow marine sediments (Hammond et al. 1985; Callender and Hammond, 1982; Emerson et al., 1984) and it appears that bio-irrigation is important to solute transport in these San Pedro Shelf sediments. The gradient in bio-irrigation strength is qualitatively reflected in the radon flux ratio, the degree to which the observed flux is enhanced over the diffusive flux. Bio-irrigation occurs at all stations, but to a greater degree at sites away from the outfall pipe.

Table 4

Sediment radon emanation from Radium-226 in sediments from the San Pedro Shelf in the vicinity of the Whites Point sewage outfall

Station ID	Depth interval (cm)	Ra activity (dpm/cm ³ wet)	Porosity	Diff. flux (atoms/m ² s)	Chamber flux/ diff. flux
1-1	0-2	0.195	0.82	69	
	2-4	0.208			
	4-6	0.196			
1-2	0-2	0.271	0.82	95	
	2-4	0.273			
	4-6	0.181			
Mean station 1				82	1.8
2-1	0-2	0.283	0.71	89	
	2-4	0.259			
	4-6	0.321			
2-2	0-2	0.244	0.71	95	
	2-4	0.335			
	4-6	0.522			
Mean station 2				92	3.3
3-1	0-2	0.224	0.75	76	
	2-4	0.232			
	4-6	0.256			
3-2	0-2	0.487	0.75	168	
	2-4	0.540			
	4-6	0.520			
Mean station 3				122	3.1

Cores designated -1 were collected in February 1991; cores designated -2 were collected in October 1991. The diffusive flux of radon is estimated from the radium activity data using the formulation described by Berelson et al. (1982). The ratio of chamber flux to diffusive flux is calculated from the average of the chamber fluxes (Table 2) and the mean diffusive flux.

A study by Wheatcroft and Martin (1996) has shown a gradient in bioturbation intensity, as defined by the mixing of a particle tracer, within the region of the chamber flux study. They found that bio-diffusivities, solid sediment mixing coefficients, were lowest adjacent to the outfall pipe and increased with distance away from the outfall up to 10 km. Bioturbation and bio-irrigation are not necessarily generated by the same sediment in-fauna, although they both require the activities of macrofauna. Our results are consistent with those of Wheatcroft and Martin (1996) which suggest that the activity of macrofauna, both as irrigators and sediment mixers is inhibited proximal to the outfall pipe relative to regions 5–10 km away.

The increase in bio-irrigation with distance from the outfall pipe may impact the efflux of dissolved silica. Because opal dissolution is thought to have a longer time constant than organic carbon degradation, silica flux may be more impacted by irrigation than other diagenetic constituents (Aller, 1984; McManus et al., 1995). It has been noted in other studies that the flux of dissolved silica correlates well with the radon enhancement ratio (Hammond et al., 1985; Berelson et al., 1998). This relationship is observed in this region as well (Fig. 4). The silica flux gradient could also reflect a gradient in the opal rain to the sea bed and dissolution in the vicinity of the outfall pipe. However, the tight correlation of silica flux with radon flux suggests that this gradient is related to the gradient in irrigation efficiency. Thus, it would be expected that sediments in the proximal vicinity of the outfall pipe would accumulate more opal than sediments at the distal sites.

The average radon flux into benthic chambers was about 2 times lower during the February 1991 field season compared to the October 1991 data. This pattern was consistent for all three stations and thus there must be some environmental control on bio-irrigation which is seasonal and capable of affecting biological activities at 60 m water depth.

4.3. Chemical budgets

The outfall pipe is a point source of dissolved chemicals to the water column and particulate

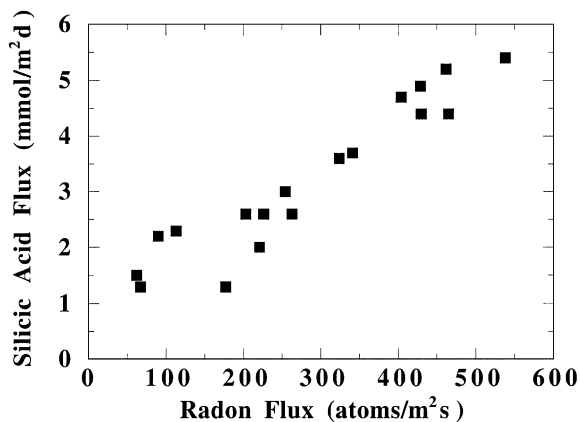


Fig. 4. Relationship between silicic acid flux into benthic chambers and the measured flux of radon-222. The strong linear correlation implies that bio-irrigation has a strong control on opal dissolution.

matter to the sediments of the adjacent shelf. Measurements of chemical fluxes from the outfall pipe have been made for many years and sediment profiles of trace metal concentrations are consistent with the changes in outfall chemical burdens over the last 30 years (Huh et al., 1992). One objective of this study was to compare recycling rates to particulate and dissolved inputs from the sewage outfall pipe. A report of effluent constituent concentrations for 1989 (SCCWRP, 1991) was used to compare benthic recycling sources to outfall inputs. Outfall inputs have changed with time and we have tried to minimize temporal discrepancies by comparing benthic recycling rates measured in 1990 and 1991, outfall discharge for the late 1980s and sediment accumulation rates which average over the period between 1971 and 1985.

The benthic fluxes reported in Table 2 were averaged to a single value deemed representative of the entire region between Stations 1 and 3. Huh et al. (1992) divided the outfall-impacted region into 11 sub-areas, and the Stations discussed in this report lie in their zones VIII, IX and X. These three zones cover $\sim 20 \text{ km}^2$ whereas the entire region mapped by Huh et al. (1992) and impacted by effluent covers 45 km^2 . It is assumed that the fluxes measured during this study are generally representative of all the zones impacted by sewage

effluent, and thus mean fluxes are multiplied by 45 km^2 in order to relate average daily effluent input to sediment flux.

The mean daily sedimentary efflux of N (as ammonia) during the chamber study period was $2 \times 10^6 \text{ g N/d}$. The P (as phosphate) efflux was $8.5 \times 10^5 \text{ g P/d}$, and C (as DIC) was $1.7 \times 10^7 \text{ g C/d}$. In 1989, the input of dissolved N (as ammonia) from the Whites Point outfall pipe was $5.5 \times 10^7 \text{ g N/d}$ and the input of dissolved P was $1.1 \times 10^7 \text{ g P/d}$. This means that the sediments in the region of the outfall system recycle to the water column approximately 4% and 8% of the N and P (respectively) contributed by the effluent outflow. Other sources of nutrients to this region may include advection by horizontal current flow and vertical mixing of water from depths $> 60 \text{ m}$. The magnitude of these sources relative to effluent and sediment recycling is not known; however, there is negligible ammonia in surface or deep waters in the region adjacent to the outfall. Thus, effluent and sedimentary sources of ammonium must be rapidly mixed with low ammonia water, oxidized to nitrate, and/or utilized for phytoplankton growth to account for the absence of ammonia in these shelf waters.

It is interesting to note that the sediments are a larger net sink for nitrate ($4.4 \times 10^5 \text{ g N/d}$) than the outfall is a source ($1.7 \times 10^5 \text{ g N/d}$) and that nitrate is a trivial fraction of the total dissolved N coming from the effluent pipe. The sedimentary sink of nitrate is indicated by the uptake of nitrate from bottom water. Bottom water on the shelf has nitrate concentrations of $10\text{--}14 \mu\text{M}$ (Fig. 2) and this inventory of fixed N could not be supported by effluent nitrate sources.

The total amount of organic carbon oxidized within the sediments of this region must be supported by one or two sources, input of particulate carbon from the sewage outfall pipe, or phytoplankton rain from the surface ocean. The regionally averaged rate of organic carbon oxidation in the sediments of San Pedro Shelf in the vicinity of the effluent-impacted area is $1.7 \times 10^7 \text{ g C/d}$. An estimate of the total outflow of POC from the sewage pipe in 1989 was $\sim 3 \times 10^7 \text{ g C/d}$. This value was established from the suspended solid concentration in effluent (SCCWRP, 1991), the

flow rate, and assuming effluent suspended solids were 30 wt% organic carbon (Sweeney et al., 1980; Eganhouse and Kaplan, 1988). This estimate is probably accurate to $\pm 25\%$. Estimates of the fraction of sewage-derived particles that rain to the sea floor in the vicinity of the outfall pipe (within 45 km^2) vary, but Huh et al. (1992) assign this fraction a value of 12–20%. Hence, it appears that sources of POC, other than that derived directly from the outfall pipe, are responsible for the remineralization occurring in the sediments of this region.

Measurements of primary productivity at a site near the Hyperion outfall system in Santa Monica Bay indicate rates of $2\text{--}3 \text{ g C/m}^2 \text{ d}$ (Eppley et al., 1979) which are consistent with rates measured by B. Jones (pers. comm.) in the Whites Point outfall region. This rate of primary production translates into $9\text{--}13 \times 10^7 \text{ g C/d}$ when normalized to a patch of seafloor 45 km^2 . It is likely that phytoplankton growth in this region is limited by the availability of fixed N (B. Jones, pers. comm.). If primary productivity in the region were 'fed' by outfall-derived ammonia, this source of N could account for a production of $30 \times 10^7 \text{ g C/d}$. Hence the outfall source of fixed N could generate 2–3 times the amount of organic C produced by phytoplankton growth. It is not likely that all the ammonia output from the sewage effluent is converted to fixed C_{org} within the 45 km^2 region. The actual fraction of outfall ammonia which generates primary production in the outfall region is unknown. This value will depend on light penetration depth, sewage plume buoyancy, horizontal and vertical mixing rates and the availability of P. It is clear that primary productivity rates are sufficient to supply the region with ample POC given the measured rates of organic carbon oxidation on the sea floor.

The source of organic carbon to the sea floor must equal the amount of carbon buried in the sediments plus the amount oxidized and returned to the overlying water as CO_2 (Fig. 5). Closure of this budget is achieved by converting sediment accumulation rate measurements to C_{org} accumulation rate values. Sediment accumulation rates vary with distance from the outfall pipe and were determined by measuring the depth between the

interface and the trace metal maximum, which is assumed to represent the year 1971 (Stull et al., 1986). By this method, sediment accumulation rates for this region varied between 1 and 2 cm/yr or 0.8–1.1 g dry sediment/cm²yr. These rate determinations were made from data presented by Stull et al. (1986), using sediment porosity values of 0.8 for the proximal station and 0.7 for the distal station, and assuming a sediment grain density of 2.5 g/cm³. This range of accumulation rates represents conditions between the early 1970s and the late-1980s. To approximate organic carbon burial rates for the early 1990s, and recognizing that accumulation rates have been declining since the 1970s (Santschi et al., 2001b), we utilize the lower range of mass flux estimates (0.8 g/cm²yr) to represent the average accumulation rate in this region. The weight percent organic carbon in sediments at a depth of 4 cm below the surface, determined from cores collected at Stations 1–3, is 3.5% (Table 1). Hence, an estimate for organic carbon burial in this region representing the time period of the study is 4×10^7 g C/d. This value probably has an uncertainty of about 40%, due to the uncertainty in assigning a sediment accumulation rate for the region for the time

period of our study and other uncertainties in the calculation.

The sum of C_{org} recycling and C_{org} burial estimates for the outfall region total about 6×10^7 g C/d. This is more than that could be provided by effluent C_{org} particles discharged at the outfall. Even if 100% of the particulate carbon exiting the outfall pipe arrives on the seafloor in the study area, 3×10^7 g C/d must be provided by other sources. Regardless of the source of the fixed N for primary production, a regional carbon balance demands that roughly half of the primary production on the shelf falls to the sea bed, given the assumption that 20% of the particulate carbon exiting the outfall pipe falls to the sediments in the region described.

Other sources of C to this region may be important to the overall carbon budget, particularly the input of sediment transported into the region (Santschi et al., 2001a). The budget presented here takes no account of sources of C other than via the outfall pipe and water column production. If horizontal transport is a significant contributor of organic carbon to this region, the conclusions regarding the sources of that carbon do not change; it still appears as though a large

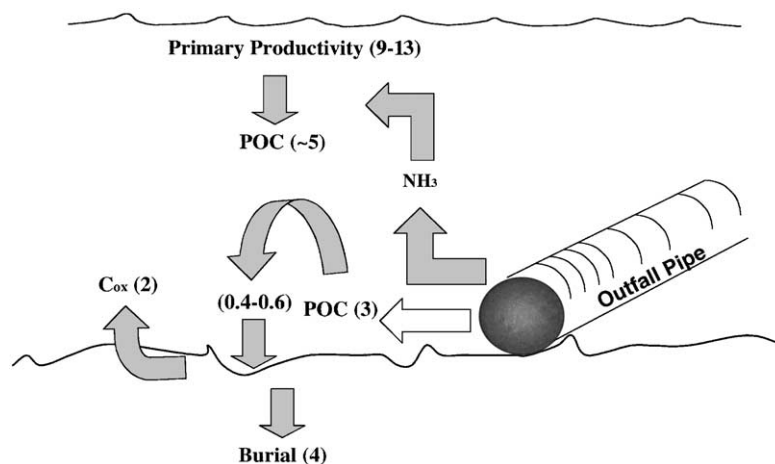


Fig. 5. A schematic representing carbon ($\times 10^7$ g/d) loading in the Whites Point Outfall region for the time period around 1990. At the sea floor, $2 (\times 10^7$ g C/d) units of carbon are oxidized and 4 are buried. POC is supplied by the outfall effluent at a rate of 3 units, of which only 12–20% is thought to fall to the sea floor (0.4–0.6). The ammonia flux from the outfall could supply 30 units of carbon via productivity; measured rates of primary production are about $9\text{--}13 \times 10^7$ g C/d. A steady state budget of C_{org} is achieved when ~ 5 units of POC rain from the upper ocean to the sea floor.

fraction of the organic matter buried and undergoing degradation within the sediments of this region is derived from phytoplankton production in the water column.

5. Conclusions

A series of benthic chamber deployments on the San Pedro continental shelf adjacent to the Whites Point sewage outfall system has helped define diagenetic processes taking place in these sediments. Measurements were made during three cruise periods at three stations in a transect away from the outfall pipe.

- (1) The fluxes of phosphate, silicate, and radon-222 showed the most significant difference (factor of 3) between stations proximal and distal to the sewage effluent outfall pipe; the fluxes of nitrate, ammonia, alkalinity and TCO_2 showed some gradient (a factor of 2) and the uptake of oxygen showed no variability between sites.
- (2) Net sulfate reduction contributes to the oxidation of organic matter at all three sites, but to a greater extent (30%) at the station proximal to the outfall pipe relative to the distal stations (10–15%). These results are suggested both by budget calculations utilizing benthic chamber data and by sediment solid phase S measurements. This conclusion is important given recent studies which indicate that reducing conditions within the sediments are necessary for the degradation of DDT to non-hazardous byproducts (Quensen et al., 1998). Oxygen is the primary oxidant of organic carbon at all three stations; nitrate reduction plays a minor role in the overall carbon budget for this region.
- (3) There is a gradient in the activity of bio-irrigators with distance from the outfall pipe; there is less bio-irrigation near the outfall. Our results are consistent with those of Wheatcroft and Martin (1996) and suggest that the activities of macrofauna (mixing and irrigation) are suppressed proximal to the outfall pipe. The gradient in bio-irrigation may result

in less opal dissolution around the outfall region relative to distal sites on the shelf.

- (4) The sediments are a source of ammonia (N) and phosphate (P) to the overlying shelf water (2×10^6 g N/d; 8.5×10^5 g P/d) but sediment recycling contributes only 4% and 8% of the N and P contributed by the outfall effluent. The sediments are a larger sink for nitrate (4.4×10^5 g N/d) than the outfall input (1.7×10^5 g N/d).
- (5) The total amount of carbon oxidized in the region around the outfall is about 2×10^7 g C/d. An estimate of carbon burial in this region is $\sim 4 \times 10^7$ g C/d. The outfall system supplied $\sim 3 \times 10^7$ g C/d of which 12–20% is estimated to have been deposited in the region. Hence, effluent-derived POC, although it may be a part of the total organic carbon pool undergoing diagenesis and burial on the sea floor, cannot be the only source of carbon to this system. Dissolved ammonia and nitrate contributed by the outfall effluent, when converted to organic carbon by productivity in the upper water column, could contribute 30×10^7 g C/d. Thus the 6×10^7 g C/d hitting the sea floor in this region could be completely accounted for by the POC produced by conversion of the outfall ammonia, although it is likely that the organic carbon raining to the sediments of this region is derived from a combination of sources. Primary productivity measurements in the surface ocean indicate production of $9\text{--}13 \times 10^7$ g C/d in the region. A balanced carbon budget requires that half the primary production is exported to the sea floor, although this budget does not account for lateral sources of POC to the region.

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