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Methods for measuring benthic nutrient flux on the California Margin: Comparing shipboard core incubations to in situ lander results

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Abstract

The objective of this study was to compare two techniques for estimating benthic fluxes of nutrients (nitrate, phosphate, and silicic acid) and Ge/Si flux ratios. In situ flux chambers were deployed, and cores were collected and incubated at 9 sites along the California margin in July 2001. Both techniques were successful at 8 sites, at depths from 100 to 3300 m. Flux chambers were deployed for 1 to 2 d, and cores were incubated for slightly longer on board the ship in a cold room. In some cases, core incubation flux temperature varied by up to 5°C from in situ temperature, and core incubation results were adjusted for this factor based on the effects of temperature on diffusivities and the adsorption of silicic acid. Sites studied had a range in nutrient fluxes of more than an order of magnitude, based on in situ chambers. The temperature-adjusted core incubation fluxes showed a similar, but slightly smaller range. Both methods had similar precision based on replicates, with uncertainties for high flux stations that were 5% to 20% of the mean. Only phosphate showed significant (95% confidence level) spatial variability in replicate cores; the larger in situ flux chambers had less spatial variability. The two techniques did show some systematic differences that are attributed to several artifacts created by core recovery. Silicic acid fluxes from cores were significantly lower than in situ fluxes at 2 sites; overall averages were about 80% of those for in situ chambers. The differences are attributed to reduced macrofaunal irrigation in incubated cores. Nitrate uptake in core incubations at 5 of 8 stations was significantly lower than in situ uptake; shipboard rates for all sites averaged about 66% of in situ chamber rates. This difference is attributed primarily to decreased denitrification rates in recovered cores in response to altered temperature and pressure. Phosphate fluxes from cores were significantly lower at only one site; overall, results for the two techniques were indistinguishable. Only one site had a significantly different Ge/Si flux ratio.

Establishing the magnitude of benthic fluxes is important for understanding geochemical budgets and for determining the role of sediment diagenesis. Several approaches have been used to estimate fluxes, including use of in situ flux chambers, calculation of fluxes based on gradients measured in porewater profiles, construction of material balances for the water column, and incubation of cores. It is important to establish whether these methods are internally consistent. If two independent methods agree, it is evidence that both are accurate. Considerable efforts have been expended during the past 2 decades to establish the validity of in situ chamber measurements through comparisons with fluxes calculated from porewater profiles or deduced from material balances for solutes in the water column, and results have been generally consistent within the uncertainty of the techniques (Berelson and Hammond 1986; Berelson et al. 1987; Devol 1987; Jahnke and Christiansen 1989; Sayles and Dickinson 1991). However, little has been done to test the accuracy of core incubation methods, except for some comparisons of oxygen fluxes measured with different techniques. The purpose of this experiment is to evaluate whether shipboard core incubations have nutrient fluxes that are consistent with in situ benthic flux chambers. Poten-

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Table 1. Summary of station characteristics

Station/Location	Latitude (N)	Longitude (W)	Collection Date	Depth (m)	BWO_2 (μM)	T (°C) In situ	T (°C) Incubate	Core
1. San Pedro	33°35.72	118°31.98	4 July 2001	897	3	5.2	6.0	A‡§ B‡§
2. Santa Monica	33°44.32	118°47.06	3 July 2001	904	4	5.1	5.5 ± 0.7	A† B
3. Catalina	33°16.37	118°38.96	7 July 2001	1328	17	4.1	6.3 ± 1.0	A§‖¶ B‖
4. Tanner	32°59.12	119°45.46	6 July 2001	1539	21	3.9	6.6 ± 0.9	A B§
6. CC* Morro Bay	35°17.92	120°58.35	9 July 2001	100	112	9.7	4.4 ± 0.5	A‖¶ B‖
7. CC* Morro Bay	35°17.86	121°01.57	9 July 2001	198	64	8.6	4.6 ± 0.4	A‖ B‖
8. CC* O_2 minimum zone	35°26.14	121°24.35	10 July 2001	704	17	4.9	4.6 ± 0.5	A‖ B‖#
9. CC* Slope	35°33.80	122°03.04	11 July 2001	1500	56	2.7	5.2 ± 0.6	A‖** B‖
10. CC* Rise/deep	36°07.35′	122°35.58′	13 July 2001	3444	128	1.6	6.3 ± 0.5	A‖ B

*CC indicates central California sites.
†Irregular stirring.
‡Cores partially frozen at time of last sample.
§Epibenthic fauna.
‖Benthic infauna and/or burrows.
¶Visible fauna swimming in core-top water.
#Core disturbed as piston was inserted.
**Sandy core top with mud below.

tial advantages of the core incubation technique are the ease of core collection, shorter duration of stations, and less investment in capital equipment. However, several artifacts resulting from core collection may influence the results. These include changes in macrofaunal irrigation rates and changes in porewater profiles in response to altered temperature, pressure, or oxygen concentration. Cores that are collected begin with porewater gradients that govern benthic exchange, and the critical issue is whether artifacts created by recovery can change porewater profiles and/or irrigation rates rapidly enough to alter benthic fluxes significantly from in situ rates.

Materials and procedures

Study area and sediment descriptions—Fieldwork was carried out during July 2001. In situ flux chambers were deployed, and cores were collected from 9 study sites near the coast of southern and central California (Table 1; Fig. 1). Many of these sites are described more completely in Berelson et al. (1996). Detailed sedimentological and faunal analyses were not carried out, but several characteristics were obvious from examining cores. Most sediments were fine-grained silts or clays. There was no evidence of infauna in the cores from the nearly anoxic, nearshore basins at station 1 or 2. Both stations had a surficial layer (about 1 cm thick) of slightly reddish sediments; we attributed this color to the presence of ferric iron. Station 1 appeared to have a bacterial mat. Station 3 lacked obvious burrows but had epibenthic forams in stalk-like tubes; core A captured a small copepod. Station 4 had brown, fluffy surficial sediment; core B had foram tubes and a brittle star. Stations 6 and 7 cores (the two shallowest stations) each contained at least 4 to 5 polychaetes; station 6 had by far the greatest number and variety of animals, including a small shrimp, brittle stars, and a jellyfish in the core-top water. Station 8 (704 m), in the oxygen minimum zone, exhibited no visible animals, but did have some deep burrows (to about 15 cm). Sediments were relatively coarse-grained, evidence that they have been subjected to strong currents and winnowing. Station 9 (1500 m) had a sandy surface with some mud; brittle stars, a small shrimp, polychaetes, and a tubeworm were present. At Station 10 (3444 m), core A had an epibenthic foram and a burrow with a worm, but core B lacked visible animals. The activity of recovered animals at all sites was minimal throughout the incubations.

Benthic chamber incubation—A free-vehicle lander (Berelson and Hammond 1986) was used to deploy benthic flux cham-

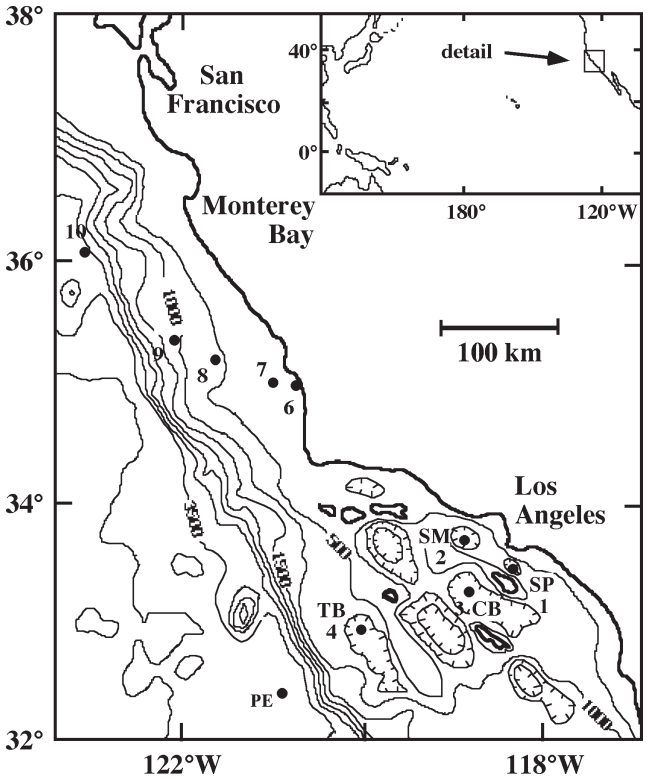

Fig. 1. Map of California Borderland Study Area. Contours indicate depth in meters. Solid dots indicate stations: 1. San Pedro Basin (SP); 2. Santa Monica Basin (SM); 3. Catalina Basin (CB); 4. Tanner Basin (TB); 6. Morro Bay (100 m); 7. Morro Bay (200 m); 8. Oxygen Minimum Zone; 9. Slope (1500 m); 10. Slope (3400 m).

bers for 1 to 2 d at each site. In brief, each lander had 3 cylindrical polyvinyl chloride (PVC) chambers (30 cm i.d.), each identified as blue, red, or yellow, that were embedded in the sediment. A hinged lid (acrylic) then closed, trapping a column of water (about 10 cm high) in contact with a sediment area of 730 cm^2. A paddle (20 cm × 2.5 cm) suspended about 3 cm below the lid stirred the trapped water (2 to 7 rpm). This stir rate should have created a boundary layer of 200 to 400 µm (Berelson et al. 1990). At these study sites, the thickness of this layer was small in comparison with the length scale for porewater gradients, so fluxes should not be strongly dependent on boundary layer thickness. During the deployment, a known volume of trace metal–clean CsBr was injected into each chamber; the dilution of this spike after 1 h was used to determine the volume of trapped water. Six water samples were drawn during the deployment and stored in polyethylene containers until the lander was recovered. Oxygen in the chambers and in ambient bottom water was monitored every 6 minutes, using a pulsed oxygen electrode. At stations 1 and 2, chamber water was essentially anoxic by the conclusion of the experiment. At other stations, chamber water decreased to 30% to 60% of the bottom water value by the conclusion of the deployments. At the end of each deployment, weights were released, and glass floats pulled the lander to the sea surface. Event timing was programmed into a computer (Tattletale model 2B) housed in a pressure case on the lander; this device also logged dissolved oxygen measurements. After recovery, water samples were filtered (0.4 µm) and stored in a refrigerator until analysis.

If two or more of the following were noted, they were interpreted as evidence that the chamber leaked and results were rejected: the calculated chamber volume exceeded the maximum possible volume, the spike was rapidly lost from a chamber, or the dissolved oxygen showed variations with tidal cycles that resemble those in the ambient water. The change in nutrient concentration in these leaky chambers was either negligible or oscillated with tidal cycles. These criteria indicated all chambers leaked at station 8, where sediments were relatively coarse-grained, apparently preventing chambers from being securely embedded. A few chambers at other sites were also rejected as leaky, probably due to an occasional hang-up in the lid releases for some chambers.

Core incubation—Multi-core liners (extruded acrylic tubing, 9.5 cm i.d., 0.3 cm wall) were used to collect the samples for incubation. They were sealed with a PVC plug at the bottom, and a movable PVC piston was inserted at the top and pushed down until it was 10 cm above the sediment. The piston and plug were seated against the acrylic tube with o-rings. The piston had a sample port leading to a length of nylon tubing (1 m × 1/8-inch o.d.) with a 2-way polypropylene stopcock attached at the end, permitting samples to be drawn into a syringe as the piston advanced. A magnetic stir bar (1-inch long, Teflon-coated) sat in a basket bolted to the bottom of the piston. The basket had holes in the bottom and sides to permit water circulation. A 12-volt DC fractional horsepower motor (Hankscraft, 32 RPM) mounted on top of the piston turned a magnet that coupled with the stir bar. Flow visualization experiments with dye showed that this arrangement rapidly mixed the water overlying the core, but did not disturb surficial sediments. The stir rate (32 rpm, 10 cm above the sediment) was selected based on lab experiments to measure alabaster dissolution (Fig. 2). These conditions create a boundary layer of about 120 µm (details in Cummins 2002). This is two to three times smaller than the boundary layer in the benthic chambers, but results will show the difference did not significantly increase fluxes.

Cores were retrieved using a multi-corer and promptly placed in a cold room. Only cores with interfaces that appeared undisturbed and level (<1 cm relief) were selected for incubation. Spot checks (1 to 2 times per day) indicated a relatively constant cold room temperature of 5.5 ± 1.1°C. However, temperature must have varied somewhat more than this, depending on traffic in and out of the cold room and how much the refrigeration unit was adjusted to counter this effect. Evidence for greater temporal and spatial inhomogeneity in the cold room temperature was that both cores from station 1 (incubated next to the cold room wall) had partially frozen overlying water at the end of their incubation. Subsequent experiments

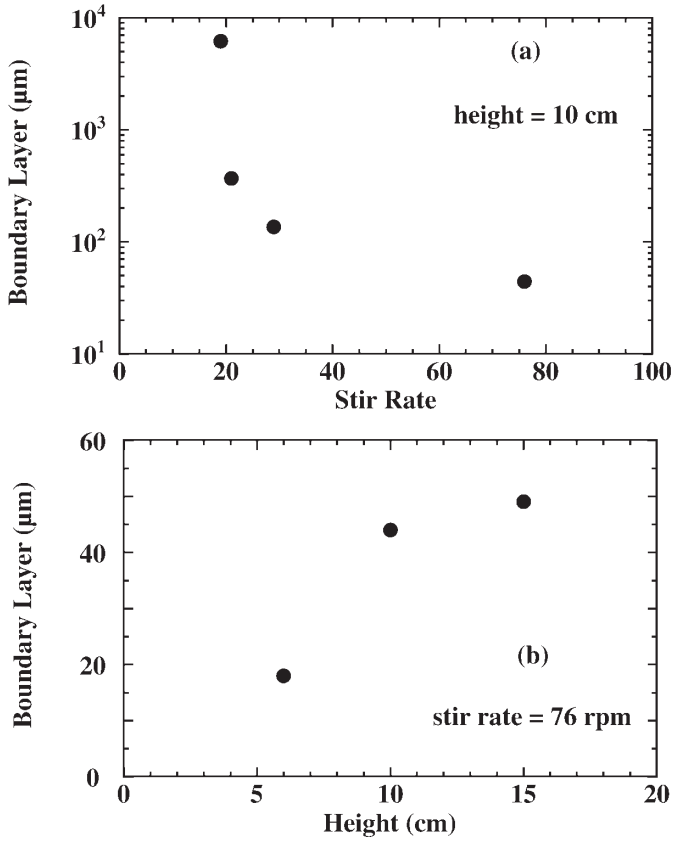

Fig. 2. Dependence of boundary layer on stirring. (a) Thickness versus stir rate; (b) thickness versus height of water. Determinations of boundary layer thickness were made by measuring weight loss of an alabaster plate (gypsum) in deionized water and assuming dissolution rate was limited by diffusion through a stagnant boundary layer.

were positioned further from the wall. Although temperature measurements only varied by about 1°C during the incubation, these were made infrequently; we have assumed a temperature uncertainty of 2°C in calculating the uncertainty in fluxes.

To prepare each core, the spring-loaded arm on the multi-core rack was released, the bottom plug was inserted in the bottom of the core, the multi-core rack was removed, and the piston was inserted into the top of the core, taking care to avoid trapping air bubbles. The piston was advanced until a water column height of about 10 cm remained, and stirring began. Five samples were drawn over a 2-d period. Samples were drawn into Teflon syringes and filtered through a 0.45-μm filter. The first 4 mL of sample were discarded (volume of the nylon tubing). The second 4 mL were used to rinse the syringe prior to drawing the sample. A draw of 30 mL was then taken, filtered, and split to allocate 20 mL for nutrients (PO_4, NO_3, and Si) and 10 mL for Ge and metals (results not reported here). The split for nutrients was stored at 4°C for approximately 2 to 3 wk in nalgene high-density polyethylene 30 mL bottles, and the split for Ge was stored at 4°C for approximately 3 months in acid-washed nalgene high-density polyethylene 15 mL bottles. As the piston was advanced to force water from the core-top into the sample draw syringe, the piston o-ring seal sometimes leaked water. Leakage occurred because the actual size of the multi-core liners varied slightly, so the piston did not always fit as tightly as desired. However, the height of water above the sediment was measured after each draw, so this factor could be used to calculate fluxes. If no leakage occurred, height decreased by 0.5 cm in each draw. In cases where leakage did occur, water sat above the o-ring and prevented any air contact with the core-top water. Oxygen measurements were unsuccessful due to instrumental difficulties. Based on observed in situ oxygen fluxes, core-top water should have been nearly anoxic by the conclusion of most experiments.

Sample analysis—Nutrients (phosphate = PO_4, nitrate + nitrite = NO_3, and silicic acid = Si) were analyzed colorimetrically by flow injection analysis, using a Lachat Instruments QuikChem 4200 and their recommended methods. These methods, along with the precision (±1 sample standard deviation [ssd]) of our replicate analyses, are phosphate method 31-115-01-3-A (±0.1 μM); nitrate (actually N + N) method 31-107-04-1-A (±0.1 μM); silicic acid method 11-114-27-1-A (±0.5 μM). Previous experience has shown nitrite to be an insignificant contribution to the nitrate. Standards for phosphate and nitrate were linear; silicic acid was slightly nonlinear and standard curves were fit with a quadratic function. Any samples exceeding the standard ranges were diluted with artificial seawater. Germanium analysis was done at Oregon State University using the isotope dilution method of Mortlock and Froelich (1996) as modified by Hammond et al. (2000). Precision (±1 ssd) of replicates was ±2.5% or ±3 pM, (whichever is larger).

Flux calculations—The rate of concentration change in the overlying water of a core or chamber depends on the ratio of flux per unit area to effective water height. In the lander chambers, water height remained constant during a deployment and was determined from dilution of the CsBr spike. In most cases, deployment times were sufficiently short that concentration changes were not more than 5% to 25% of the contrast in concentration between bottom waters and that at depth in the porewaters. Because this change was small, the change in concentration gradient across the sediment-water interface during the experiment was modest, and fluxes were relatively constant. Consequently, a linear fit to a plot of concentration versus time provided a good description of the change (a small correction to the chamber measurements was made to account for dilution of lander water with ambient water that enters as each sample is drawn). Further details for data reduction protocols are given in Hammond et al. (1996). Results for one lander deployment are shown in Fig. 3. Although many deployments had substantial concentration changes, curvature was never apparent. Consequently, fluxes were calculated using linear regressions versus time.

During the core incubations, water height changed each time a sample was drawn (by about 5% if no leakage occurred), and this introduces curvature in a plot of concentration versus

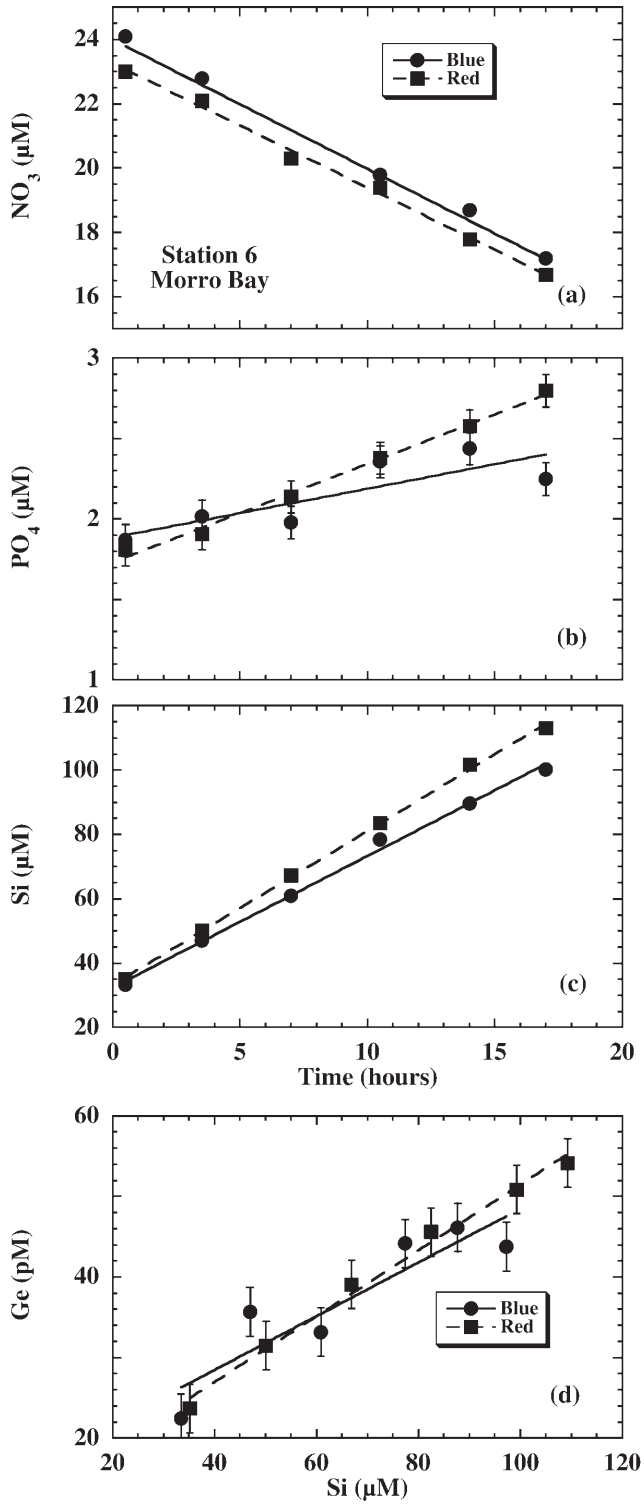

Fig. 3. Example results for in situ flux chambers (Station 6). Results for successful chambers were fit with linear regressions (solid lines for blue chamber and dashed lines for red chamber). Nutrient fluxes were calculated by multiplying slopes by the chamber height (volume/area). Although this station has the largest changes observed in any deployment, nonlinearity was not apparent. For Ge, regressions versus Si for each chamber are shown, although a composite fit was used to obtain results in Table 5.

time. To eliminate this curvature, the ratio of time/height for each sample interval was calculated and the concentration in overlying water was plotted against the sum of elapsed time/height for all preceding intervals (Fig. 4). The slope of this plot is the flux, and the plot should be linear if flux remains constant. Despite this effort to linearize results, curvature was apparent in about half of the experiments, always indicating a decreasing flux with time. Consequently, results were fit with both linear and quadratic functions. For nonlinear fits, the slope at the beginning of the experiment was taken as the best estimate of flux, when perturbations should be least important. Uncertainties for each incubation were calculated from the uncertainties in the initial slopes. To calculate Ge/Si flux ratios, regressions of Ge versus Si were used.

Assessment

Landers—Fluxes for each chamber are presented in Table 2. Incubation results for each core are in Table 3. Station averages for both techniques are summarized in Table 4. The variability for replicate chambers at each site was quite similar to that expected from the uncertainties for individual chambers, indicating that at these sites, spatial variability in flux on length scales of 30 cm (the separation of adjacent chambers) is modest. Exceptions to this pattern were at station 4, where one chamber had fluxes of NO_3 and Si that were about 50% greater than the other 2 chambers, and at station 6, where PO_4 in the two chambers differed from the mean by about 30%. NO_3 fluxes were into the sediments, reflecting denitrification, and the means (Table 4) were determined with uncertainties of 5% to 20% at all but the two deepest stations. For PO_4, fluxes at near-shore sites were out of the sediments and sufficiently large to measure readily. At sites below 1000 m, PO_4 fluxes were very small, essentially at their limit of detection for these experiments. For Si, fluxes were sufficient to determine averages for each station with uncertainties of 5% to 15%. Si fluxes generally decrease with depth, except for station 10, which was significantly greater than station 9.

Core incubation—Curvature was apparent in some core incubations (Fig. 4), although it was not apparent for in situ flux chamber results (Fig. 3). For each incubation, a decision about the extent of nonlinearity and the best choice for a fitting function was based on the magnitude of the change in concentration during the experiment and on the quality of the fit. If the change during the incubation was less than three times analytical uncertainty, a linear function was used because any curvature that might exist would not be accurately constrained. Otherwise, both functions were fit and the reduced chi square statistic (RCS) was calculated (Taylor 1997). If RCS for the linear fit was less than 2, this function was chosen as a satisfactory description of the results. If not, and if RCS for the quadratic function was more than two times smaller than for the linear fit, the quadratic fit was used. If curvature was large, fluxes calculated for the quadratic fits were substantially larger than results for linear fits (Table 3). Results for two cores were

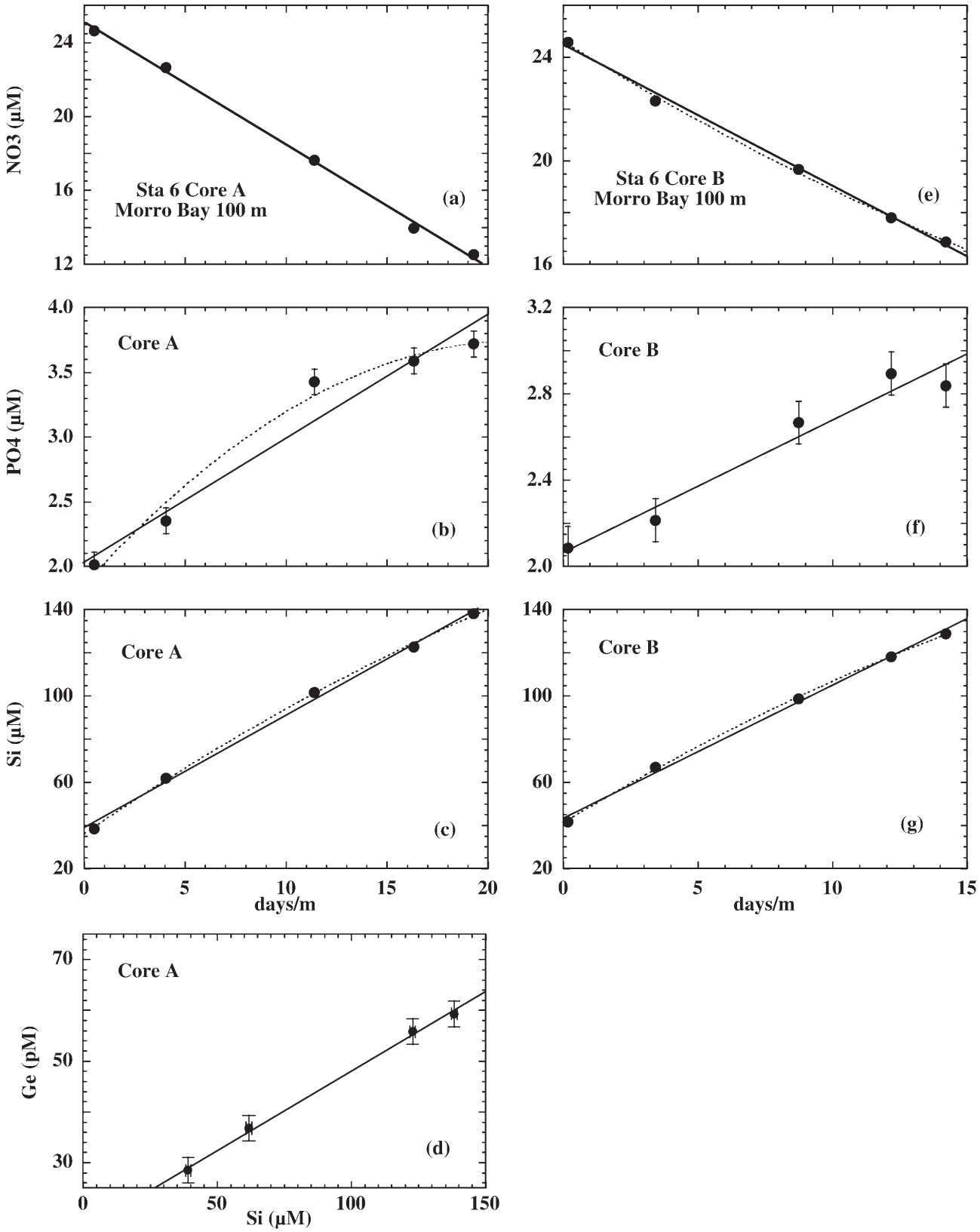

Fig. 4. Example results for core incubations (Station 6). The abscissa is the integral of time/height for replicate cores, except for the panel showing Ge results. Only one core was analyzed for Ge. Solid lines indicate linear regressions, and dashed lines indicate nonlinear regressions if these were better fits.

Table 2. In situ benthic chamber flux measurements (mmol m^{-2} d^{-1})*

Station	Δt†	chamber‡	RPM§	NO_3 flux	PO_4 flux	Si flux
1	33.5	Blue	6	–1.20 ± 0.08	0.088 ± 0.012	2.82 ± 0.25
		Red	5	–1.27 ± 0.09	0.060 ± 0.016	2.91 ± 0.23
		Yellow	2	–1.24 ± 0.07	0.131 ± 0.027	2.74 ± 0.34
2	34.5	Blue	6	–1.29 ± 0.13	0.111 ± 0.021	2.17 ± 0.31
		Red	6	–1.54 ± 0.09	0.147 ± 0.028	2.35 ± 0.26
		Yellow	2	–1.17 ± 0.18	0.111 ± 0.017	2.01 ± 0.23
3	31.5	Red	5	–0.38 ± 0.05	0.001 ± 0.005	0.97 ± 0.46
		Yellow	2	–0.38 ± 0.06	0.018 ± 0.008	0.96 ± 0.29
4	34.0	Blue	6	–0.67 ± 0.08	0.009 ± 0.005	2.77 ± 0.23
		Red	7	–0.38 ± 0.06	–0.007 ± 0.004	2.07 ± 0.24
		Yellow	2	–0.34 ± 0.13	0.013 ± 0.014	1.88 ± 0.21
6	17.5	Blue	7	–1.29 ± 0.13	0.099 ± 0.032	13.2 ± 0.8
		Red	8	–1.16 ± 0.10	0.185 ± 0.011	14.3 ± 0.7
7	29.0	Yellow	7	–1.34 ± 0.08	0.114 ± 0.015	9.2 ± 0.6
9	42.0	Blue	6	–0.12 ± 0.05	0.000 ± 0.005	1.80 ± 0.24
		Red	7	–0.17 ± 0.05	0.002 ± 0.005	2.28 ± 0.50
10	31.0	Blue	6	–0.18 ± 0.05	0.025 ± 0.005	3.13 ± 0.26
		Yellow	7	–0.24 ± 0.05	0.019 ± 0.005	3.13 ± 0.31

*Uncertainties are given as the larger of the uncertainty predicted from analytical precision or the uncertainty based on the fit of a linear regression to data. These also include a contribution from the uncertainty in chamber height.
†Incubation time is given in hours.
‡Each lander has 3 chambers (colors).
§RPM indicates stirring speed.

rejected: stirring for core 2A was intermittent because of magnet alignment difficulties, and core 8B was disturbed and probably aerated as it was being set up for incubation. For other cores, results for replicates were averaged and the uncertainty for the station was taken as the larger of (a) the observed standard deviation of the mean (SDOM) for results from replicate cores, or (b) the expected SDOM calculated from the uncertainties of the two results for replicates (formulas in notes to Table 3). In a few cases, the observed SDOM (a) exceeded the expected SDOM (b) by more than a factor of two, and this is evidence that spatial variation among cores exceeds variation attributable to analytical procedures.

The factors influencing curvature were considered. In the case of stations 1 and 2, curvature is present for almost all nutrients and is probably a result of cooling during the latter portion of the experiment, although cooling was not directly measured. As noted above, some ice formed in cores from station 1 at the end of the experiment. Station 2 incubations occurred simultaneously and also may have been influenced by cooling. At stations other than 1 and 2, the greatest nonlinearity occurred in experiments that had the greatest change in the overlying water composition. This would reduce the interfacial concentration gradient during the latter part of the experiment and reduce the flux, and the correlation between nonlinearity and concentration change suggests this factor is important. Core incubations were more susceptible to this than in situ chambers, because they had smaller water column heights (<10 cm) and longer durations (about 2 d). Curvature could also reflect decreases in reaction rate or macrofaunal activity with time, or effects of decreasing oxygen (not measured during the core incubation). These factors were probably not major for PO_4 and Si. For NO_3, only two cores other than those at stations 1 and 2 exhibited nonlinear behavior: core 3A did not have a very good fit, and core 6B was only slightly nonlinear. The concentration change in these cores was not particularly large, so the cause of their nonlinearity is not obvious. It may be that cores with larger changes in NO_3 were influenced by two factors that acted oppositely. A declining NO_3 in the core-top water should reduce NO_3 flux, but declining oxygen concentration in the core-top water should reduce the depth at which denitrification could take place and may have compensated for this factor. In any case, a linear fit for NO_3 was usually adequate.

The patterns of fluxes observed with cores were very similar to those in the lander. NO_3 fluxes in most cores show removal (negative flux) from the water column, reflecting denitrification. The exception is the deepest station (10), which shows a small positive flux, although the uncertainty exceeds the average flux. The observed SDOM for NO_3 is similar to the expected SDOM, indicating spatial variability is small on the length scale defined by replicate cores (Table 3).

Most PO_4 fluxes were positive from the sediments into the water column. The exception was station 3 (Catalina Basin), which had a small but significant flux (–0.008 ± 0.002) from the water column into the sediments. This result indicates

Table 3. Core incubation flux results (mmol m^{-2} d^{-1})*

Nutrient	Core	Linear fit	Quadratic fit	Best†	Average	Observed SDOM‡	ExpectedSDOM‡
NO_3	1A	–0.64 ± 0.10	–1.06 ± 0.40	Q	–0.95	0.12	0.21
	1B	–0.55 ± 0.05	–0.83 ± 0.14	Q			
	2A	(–0.52 ± 0.05)	(–0.83 ± 0.01)	Q	–0.93		0.16
	2B	–0.50 ± 0.07	–0.93 ± 0.16	Q			
	3A	–0.23 ± 0.04	–0.45 ± 0.12	Q	–0.36	0.10	0.06
	3B	–0.26 ± 0.02	–0.27 ± 0.11	L			
	4A	–0.25 ± 0.02	–0.19 ± 0.13	L	–0.24	0.01	0.02
	4B	–0.23 ± 0.03	–0.38 ± 0.16	L			
	6A	–0.66 ± 0.02	–0.65 ± 0.09	L	–0.66	0.00	0.03
	6B	–0.54 ± 0.02	–0.65 ± 0.06	Q			
	7A	–0.62 ± 0.02	–0.54 ± 0.08	L	–0.73	0.11	0.10
	7B	–0.84 ± 0.19	–1.38 ± 0.85	L			
	8A	–0.73 ± 0.03	–0.85 ± 0.12	L	–0.73		0.03
	8B	(–0.76 ± 0.06)	(–0.39 ± 0.12)	Q			
	9A	–0.04 ± 0.04		L	–0.08	0.04	0.05
	9B	–0.12 ± 0.10		L			
	10A	0.02 ± 0.02		L	0.01	0.01	0.01
	10B	0.00 ± 0.02		L			
PO_4	1A	0.089 ± 0.024	0.204 ± 0.090	Q	0.122	0.082	0.045
	1B	0.040 ± 0.005	0.069 ± 0.004	L			
	2A	(0.029 ± 0.002)	(0.038 ± 0.008)	L	0.072		0.016
	2B	0.051 ± 0.004	0.072 ± 0.016	Q			
	3A	–0.008 ± 0.003	–0.020 ± 0.009	L	–0.008	0.001	0.002
	3B	–0.007 ± 0.002	–0.012 ± 0.010	L			
	4A	–0.009 ± 0.006		L	0.000	**0.009**	**0.003**
	4B	0.009 ± 0.002		L			
	6A	0.096 ± 0.013	0.174 ± 0.038	Q	0.118	**0.057**	**0.019**
	6B	0.061 ± 0.008	0.085 ± 0.035	L			
	7A	0.103 ± 0.027	0.257 ± 0.083	Q	0.197	0.060	0.046
	7B	0.137 ± 0.038	0.243 ± 0.177	L			
	8A	0.007 ± 0.003		L	0.007		0.003
	8B	(–0.018 ± 0.005)	(0.010 ± 0.014)	L			
	9A	0.014 ± 0.005		L	0.010	0.004	0.004
	9B	0.006 ± 0.006		L			
	10A	0.045 ± 0.007		L	0.024	**0.021**	**0.007**
	10B	0.003 ± 0.011		L			
Si	1A	1.59 ± 0.24	2.91 ± 0.48	Q	2.63	0.28	0.29
	1B	1.33 ± 0.18	2.35 ± 0.33	Q			
	2A	(0.99 ± 0.07)	(1.43 ± 0.08)	Q	1.67		0.19
	2B	1.13 ± 0.09	1.67 ± 0.19	Q			
	3A	0.82 ± 0.02	0.77 ± 0.07	L	0.75	**0.07**	**0.02**
	3B	0.68 ± 0.02	0.76 ± 0.10	L			
	4A	2.04 ± 0.06	2.44 ± 0.23	Q	2.38	0.06	0.12
	4B	2.32 ± 0.03	2.52 ± 0.14	L			
	6A	5.23 ± 0.18	6.40 ± 0.46	Q	6.99	0.59	0.31
	6B	6.13 ± 0.22	7.58 ± 0.41	Q			
	7A	4.90 ± 0.10	5.28 ± 0.43	L	6.00	**1.10**	**0.10**
	7B	6.04 ± 0.15	7.09 ± 0.18	Q			
	8A	3.99 ± 0.11	4.67 ± 0.08	Q	4.67		0.08
	8B	(2.79 ± 0.02)	(2.93 ± 0.02)	L			
	9A	2.24 ± 0.06	2.61 ± 0.06	Q	2.72	0.11	0.08
	9B	2.18 ± 0.11	2.83 ± 0.14	Q			
	10A	2.27 ± 0.11	2.90 ± 0.22	Q	2.76	0.14	0.11
	10B	2.29 ± 0.06	2.61 ± 0.06	Q			

*Negative values represent fluxes into the sediment. Data are not corrected for temperature. As noted in the text, a quadratic fit was selected as better if the flux uncertainty was significantly reduced, based on reduced chi squares. Values in parentheses have been rejected for reasons discussed in the text.
†Q, quadratic; L, linear.
‡SDOM is standard deviation of the mean of replicate cores based on observed differences or differences expected based on uncertainty of each measurement. Observed SDOM = sample standard deviation/$\sqrt{n}$, where n = number of experiments, and

expected SDOM = $\frac{\sqrt{\partial A^2 + \partial B^2}}{n}$, where δA and δB are uncertainties in flux measurements for cores A and B. Results in bold indicate where observed SDOM for replicate cores was two times more than expected.

Table 4. Comparison of core incubation and in situ nutrient fluxes (mmol m^{-2} d^{-1})

	NO_3 Flux*		PO_4 Flux*		Silicic Acid Flux*	
Station/Location	**Core†**	**In situ‡**	**Core†**	**In situ‡**	**Core†**	**In situ‡**
1. San Pedro	–0.92 ± 0.22	–1.24 ± 0.05	0.12 ± 0.08	0.09 ± 0.02	2.50 ± 0.41	2.82 ± 0.16
2. Santa Monica	**–0.93 ± 0.16**	**–1.34 ± 0.11**	**0.07 ± 0.02**	**0.12 ± 0.01**	1.63 ± 0.27	2.16 ± 0.16
3. Catalina	–0.33 ± 0.09	–0.38 ± 0.04	–0.01 ± 0.00	0.01 ± 0.01	0.66 ± 0.10	0.97 ± 0.26
4. Tanner	**–0.22 ± 0.02**	**–0.47 ± 0.10**	0.00 ± 0.01	0.01 ± 0.01	1.99 ± 0.26	2.24 ± 0.27
6. Morro Bay	**–0.78 ± 0.07**	**–1.23 ± 0.08**	0.14 ± 0.07	0.14 ± 0.04	**9.66 ± 1.58**	**13.75 ± 0.59**
7. Morro Bay	**–0.83 ± 0.14**	**–1.34 ± 0.08**	0.22 ± 0.07	0.11 ± 0.02	7.72 ± 1.78	9.25 ± 0.60
8. O_2 minimum zone	–0.74 ± 0.05		0.01 ± 0.00		4.75 ± 0.58	
9. Slope	–0.07 ± 0.05	–0.15 ± 0.04	0.01 ± 0.00	0.00 ± 0.00	2.31 ± 0.29	2.04 ± 0.56
10. Rise/Deep	**0.01 ± 0.01**	**–0.21 ± 0.03**	0.02 ± 0.02	0.02 ± 0.00	**1.98 ± 0.26**	**3.13 ± 0.20**

*Bold type indicates where core incubation and in situ results are significantly different (95% confidence level, indicated if difference > $2\sqrt{\partial \text{core}^2 + \partial \text{in situ}^2}$ where δ indicates uncertainty in each estimate).

†Core incubation results are from Table 3 and have been adjusted for the difference between shipboard and in situ temperatures (6% C^{-1} for Si and 2.5% C^{-1} for NO_3 and PO_4).

‡In situ incubation results are station averages from Table 2.

there was PO_4 uptake at this site. The highest fluxes were observed at shallow water sites near Morro Bay (stations 6 and 7) and near-shore sites in San Pedro and Santa Monica basins. The observed SDOM for replicate cores is often 50% of the mean, much larger than for NO_3 and frequently 2 to 3 times larger than the expected SDOM. This indicates that on small scales (dimensions of 10 to 50 cm), PO_4 may have significant spatial heterogeneity in benthic flux.

Si fluxes are all positive, from the sediments into the water column. The largest fluxes are from the shallow water sites. Replicate cores are generally within 5% to 10% of the mean. As for NO_3, the observed and expected variabilities are similar, except for stations 3 and 7, which show a modest spatial variability of 15% from the mean.

Some spatial heterogeneity was observed in the macrofaunal abundances and burrow densities in replicate cores from the same location. This was greatest at the shallow sites. However, this heterogeneity did not obviously correlate with the spatial variability in the fluxes observed in replicate cores from each site.

Adjusting for temperature artifacts—Core incubation temperatures sometimes differed from those in situ (Table 1). The largest differences were at stations 6, 7, and 10, with incubation temperatures too cold by about 5°C at the first two, and too warm by 5°C at station 10. This was a limitation imposed by using the cold room for temperature control and simultaneously incubating cores from stations with different in situ temperatures. A lower limit for the influence of temperature can be made for each nutrient. For temperatures in the range of 0°C to 10°C, molecular diffusivity changes by about 3.5%°C^{-1} (Li and Gregory 1974). A temperature change also systematically changes porewater Si by 2.5%°C^{-1} due to rapid adsorption/desorption (McManus et al. 1995). Flux is proportional to both diffusivity and concentration gradient, so these effects should be additive. If we assume that temperature changes do not have any influence on length scales for porewater gradients, the temperature artifact should be 3.5%°C^{-1} for NO_3 and PO_4, and 6.0%°C^{-1} for Si. This introduces little effect for the majority of the stations, but incubation fluxes at stations 6 and 7 should be at least 15% to 30% too small, and at station 10 they should be high by an equal amount.

If reaction rates are temperature dependent, a greater effect may occur if sufficient time elapses for the porewater profile to adjust to the altered kinetics and diffusivities. The time required to adjust to a changed reaction rate is addressed in the next section. For nitrate and phosphate, we are uncertain about the relationship between reaction kinetics and temperate, and did not make any adjustments. For Si, the temperature dependence of opal dissolution has been measured and is characterized by an activation energy of 50 kJ mol^{-1} (Van Cappellen 1996) This indicates that opal dissolution should have a temperature dependence of 7.2%°C^{-1}, similar to the value of 6%°C^{-1} based on diffusivity and adsorption/desorption. If Si porewater gradients can respond quickly to changes in reaction rates, the altered reaction rates would control the fluxes, and the opal dissolution temperature dependence should provide a more accurate correction factor. As will be shown later, Si porewater profiles from cores at these two shallow sites should respond very quickly to changes in reaction rates, and the higher value for Si temperature dependence should be appropriate at those sites. Measurements in Table 3 were corrected for temperature effects and results are shown in Table 4.

Evaluating effects of oxygen—During the core incubations, the oxygen concentration decreased with time. This could affect fluxes in two ways, by influencing bio-irrigation activity or by influencing porewater profiles of redox-sensitive solutes. If either effect was significant, a change in flux during the experiment should occur. The rather linear character of most experiments suggests that this factor had little effect. Where nonlin-

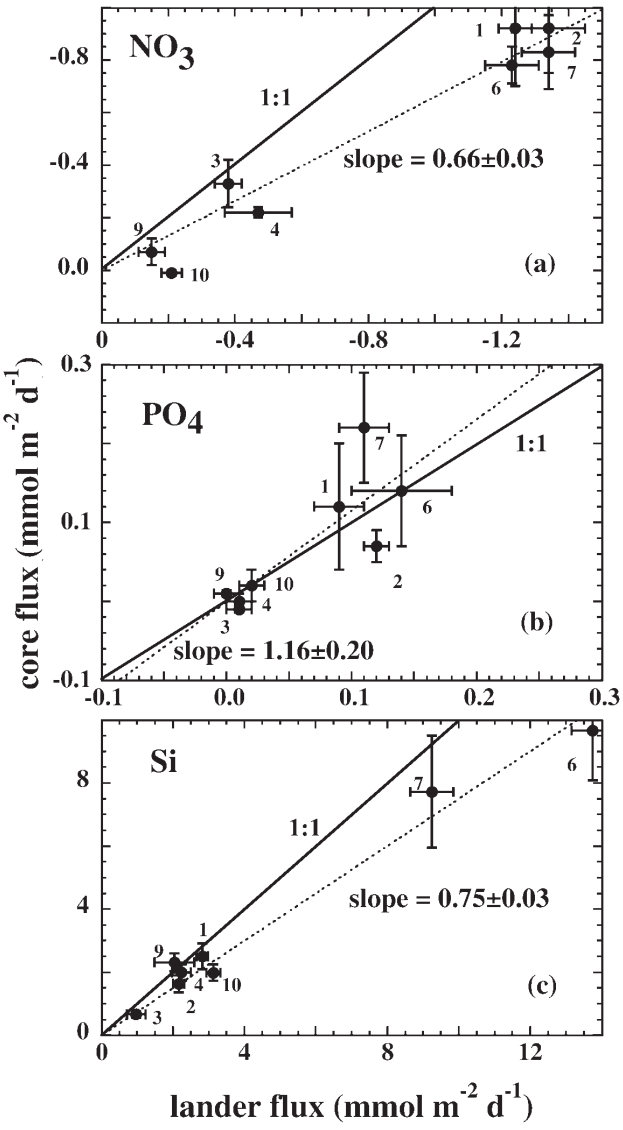

Fig. 5. Core incubation fluxes versus in situ chamber fluxes. Core incubation results have been adjusted for known temperature effects. Solid lines represent 1:1 correspondence of methods. Dashed lines indicate linear regressions through the origin. Note that axes for NO_3 have been reversed. Numbers identify stations.

ear behavior was observed, using the initial slope should minimize any influence of oxygen decrease. Alternatively, it is possible that some oxygenation of cores occurred during handling. Addition of oxygen might initially suppress nitrate uptake. It could also suppress phosphate release due to enhanced coprecipitation of iron oxyhydroxides in surficial sediments. However, it seems unlikely that oxygenation occurred because the core top water surface was exposed to the atmosphere for less than 1 minute while the upper piston was inserted, and no bubbles were observed after the piston was inserted. The exception to this was core 8B, which had a large bubble introduced when the bottom piston was inserted. Its nitrate flux was much lower, its phosphate flux went from positive to negative, and it has been ignored in the compilation.

Comparison of shipboard and in situ nutrient fluxes—Results from benthic landers (in situ) and core incubations (adjusted for estimated temperature artifacts) are compared in Table 4 and plotted in Fig. 5. If both methods are equivalent, results should lie near the 1:1 lines. Because in situ results should be free of artifacts due to pressure and temperature changes, and because previous work has indicated the reliability of this approach, these were taken as the standard for comparison. In general, the core incubation fluxes were rather similar to in situ results. However, differences were sometimes significant at the 95% confidence level (boldface comparisons in Table 4 have differences twice the uncertainties). PO_4 fluxes were in good agreement at all but one site, and the two techniques did not show any significant systematic difference. However, the large uncertainties limited sensitivity to discern differences at some sites, and systematic effects up to 20% could exist. Si fluxes were significantly different at 2 of the 8 stations (6 and 10). The overall pattern (Fig. 5) suggests that Si incubation fluxes were systematically low by 25%. This interpretation is heavily influenced by the results at the shallow sites, which lie farthest from the origin and had the largest temperature correction. A simple average of the ratios of Si core fluxes to in situ fluxes for all stations yields 0.81 ± 0.07 (±1 SDOM), indicating a systematic effect of about 20%. NO_3 uptake is consistently low in the incubated cores, as 5 of the 8 stations show significant differences, typically differing by 34%. The average ratio of core/in situ for the 6 stations with substantial fluxes is 0.67 ± 0.06 (±1 SDOM).

Comparison of Germanium fluxes—The biogeochemical cycle of Ge in the water column is closely linked to that of Si, but diagenesis appears to decouple these two solutes in iron-rich, reducing sediments (Hammond et al. 2000; King et al. 2000). The Ge/Si flux ratio expected from congruent dissolution of opal is 0.7 μmol/mol, but in this data set, all of the stations except station 4 had iron-rich porewaters in the upper 2 cm of sediment; therefore smaller Ge/Si flux ratios were expected (McManus et al. 2003). Flux ratios were obtained from regressions of Ge versus Si (Table 5). Temperature changes should cause both solutes to have similar changes in diffusivity and adsorption, and we do not expect large effects of pressure on either solute. Consequently, no adjustments to the measured ratios were made. The Ge versus Si regression was slightly nonlinear for the core at station 7, but was linear at other sites. The linearity indicates that oxygen changes during incubations did not systematically alter one solute more than another. There is a general correspondence between the ratios obtained for the two techniques, as sites with low ratios for lander observations also have low ratios in the core incubations. Only one station (station 4) had a significant difference. However, the core incubation results may be systematically smaller than the lander results. A regression of ratios from core incubations versus in situ results yields a slope of 0.7 ± 0.1, if con-

Table 5. Ge/Si flux ratios (μmol/mol)

	Ge/Si*	
Station/Location	**Core**	**In situ†**
1. San Pedro	0.31 ± 0.13	0.32 ± 0.04
2. Santa Monica	0.16 ± 0.10	0.29 ± 0.11
3. Catalina	0.54 ± 0.05	0.68 ± 0.34
4. Tanner	**0.70 ± 0.07**	**1.09 ± 0.17**
6. Morro Bay	0.31 ± 0.01	0.38 ± 0.04
7. Morro Bay	0.50 ± 0.08‡	0.35 ± 0.04
8. O_2 minimum zone	0.48 ± 0.04	
	(0.32 ± 0.02)§	
9. Slope	0.50 ± 0.07	0.68 ± 0.18
10. Rise/deep	0.32 ± 0.14	0.75 ± 0.42

*The Ge/Si ratio expected for congruent opal dissolution is 0.70. Only one core incubation and 1 to 2 in situ chambers were analyzed for Ge, except at station 8. The result in bold is significantly different at the 95% confidence level.
†In situ ratios are based on a single regression of Ge versus Si for all samples (may be multiple chambers) taken at a given site.
‡Result from nonlinear fit. Linear fit was 0.28 ± 0.04.
§Core B was disturbed, so this result is questionable.

strained to pass through the origin and the highly uncertain result for station 10 is ignored. If the surprisingly large in situ ratio for station 4 is also ignored, a regression yields a slope of 0.8 ± 0.1, at the limit of reasonable consistency. The large uncertainties in the in situ fluxes, reflecting the relatively small Ge changes during deployments, limit our sensitivity in comparing the techniques to 10% to 30% of the flux ratio.

Discussion

The two methods for estimating flux are consistent for PO_4. For Si, fluxes are consistent at most sites, although core incubation fluxes appear to be systematically reduced by about 20%. For NO_3, significant differences exist at many sites, and core incubations fluxes show an overall decrease of about 34% from in situ fluxes. The systematic differences cannot be only a temperature artifact, because incubation temperature was sometimes greater, sometimes lower, and sometimes unchanged (Table 1). They cannot reflect a difference in stirring, because core incubations had a thinner boundary layer than in situ chambers. Furthermore, in situ chamber fluxes did not vary significantly with stirring rate (Table 2). This leaves three other factors to be considered as possible causes for the differences, including (1) spatial variability in fluxes, (2) a reduction of irrigation by macrofauna in recovered cores, and (3) alteration of porewater profiles due to changes in temperature and pressure for the incubated cores. It is unlikely that factor (1) can account for differences in benthic flux, because the good agreement of replicate cores and in situ chambers indicates spatial variability in NO_3 and Si fluxes is small. Factor (2) may be quite significant at the shallowest stations (6 and 7) where macrofauna were most abundant. In each core from these sites, 4 to 5 polychaetes came out of their burrows and did not appear to move much during incubations. Although we lack in situ observations of their activity for comparison, reduced irrigation may account for the lower Si fluxes and partially account for the lower NO_3 fluxes at stations 6 and 7. It is unclear if the organisms responded to the physical disturbance, reduced temperature, and/or reduced pressure. In any case, the average decrease in silicic acid flux was modest (15% to 30%). Nearly all other cores, except those from stations 1 and 2, also had burrows (Table 1). If reduced irrigation also reduced their effective surface area for exchange by 10% to 15%, the systematic Si offset would disappear, and the NO_3 offset would be partially explained. PO_4 measurements would also be affected, but they are much less precise, and a 10% to 15% difference would not be detectable. The remaining differences are attributed to factor (3).

Changes in porewaters after core retrieval—Benthic fluxes are driven by porewater gradients, and if porewater gradients are altered by core recovery, fluxes must change. Changes in pressure do not appear to alter Si and NO_3 profiles, as fluxes calculated from porewater profiles in cores are in reasonable agreement with in situ flux measurements, even with core retrieval from 4.5 km (e.g., McManus et al. 1995; Hammond et al. 1996). However, PO_4 flux is a potential problem, because Jahnke et al. (1982) have shown that PO_4 is lost from porewaters of carbonate-rich equatorial Pacific sediments as cores are retrieved. An artifact of this sort would certainly reduce fluxes, but would only be apparent at a high flux sites; our high flux sites have little carbonate and are less than 1 km depth. The effect of temperature on Si adsorption has already been considered, but temperature changes may also alter diagenetic reaction rates. If core incubation is of sufficiently short duration, the in situ porewater profile should not be greatly altered and incubation should provide a good estimate of flux. However, if incubation is long compared to the time scale for porewater response, the flux may change significantly. The rate at which flux can respond to a change in reaction kinetics must depend on the length scale that initially characterized the solute porewater gradient, as well as on the change in reaction rate for the solute in question.

As an illustration of this concept, we consider a steady state solute profile that exponentially approaches zero at depth (an analogous argument can be made for any function that exponentially approaches an asymptote at depth:

$$C = C_o \exp\left(-\frac{z}{a}\right) \quad (1)$$

where C = concentration, z = depth, a = the length scale for the porewater gradient, and the subscript zero indicates the sediment-water interface. The flux can be found by applying Fick's first law, so that

$$J = -\Phi D_s\left(\frac{\partial C}{\partial z}\right) = \frac{\Phi D_s C}{a} \quad (2)$$

where J = flux, Φ = porosity, and D_s is molecular diffusivity corrected for tortuosity. If the reaction creating the porewater gradient suddenly ceased, the time constant τ for the flux to respond can be estimated by

$$\frac{1}{\tau} = \left(\frac{1}{J}\right)\left(\frac{\partial J}{\partial t}\right) = \left(\frac{1}{C}\right)\left(\frac{\partial C}{\partial t}\right) - \left(\frac{1}{a}\right)\left(\frac{\partial a}{\partial t}\right) \quad (3)$$

If we assume that the length scale for diagenetic reactions is dictated by the distribution of reactive biogenic particles, the corresponding solute length scale (= a) should not change. Substituting Fick's second law for a solute that can be adsorbed leads to

$$\frac{1}{\tau} = \left(\frac{D_s}{C}\right)\left(\frac{\partial^2 C}{\partial z^2}\right) = \frac{D_s}{(1+K)a^2} \quad (4)$$

where K is the partition coefficient (adsorbed/dissolved) for the solute. The length scales and response times depend on the particular solute and station, and they can be estimated from the benthic flux (J_o) and the contrast between the overlying water concentration and the concentration at depth (C_o):

$$a = \frac{\Phi D_s C_o}{J_o} \quad (5)$$

Based on previous measurements of porewater profiles at many of these sites (Berelson et al. 1987; Hammond et al. 2000; J. McManus unpubl. data unref.), length scales for Si should be 0.5 to 1 cm. We have not measured K for these sediments, but a likely value is 0.5 to 1, based on unpublished work at other sites. Therefore, at all stations except 6 and 7, time constants should be 0.9 to 4 d, and a change in reaction kinetics after core recovery should not affect the measured fluxes very much. The high lander Si fluxes at the two shallowest stations (6 and 7) indicate length scales of 2 to 3 mm and time constants of 1 to 4 h. Si fluxes at these sites should quickly relax to a steady state dictated by the new kinetics, justifying our earlier use of opal dissolution activation energy to estimate the temperature effect on flux at these sites. Length scales for PO_4 are several centimeters (McManus et al. 1997), so time constants are several days or longer at all stations. Unless other artifacts influence the core incubations, the two methods should give similar results, and this was observed at the high flux stations. While the factors governing NO_3 profiles are complex and a simple exponential function may not provide an ideal fit, this treatment should still provide an approximation for response time. Length scales for NO_3 are only a few millimeters, it should not be adsorbed, and time constants are <2 h at stations 1, 2, 6, 7, and 8; about 12 to 18 h at stations 3 and 4, and >2 d at stations 9 and 10. This indicates that most cores should have adjusted to new steady state values prior to or in the early stages of incubations. The relatively low NO_3 fluxes are probably attributable to a lower denitrification rate in the core incubations. At the shallow stations, the reduction in rate is probably due to the temperature reduction from in situ. At deeper stations, incubation temperatures were rather similar to in situ temperatures, and the reduction in denitrification rate is probably due to a reduction in pressure.

Pressure effects on metabolism—When cores are removed from their in situ environment to the surface of the ocean, the pressure difference may alter the metabolism of any organisms present. A few studies have done shipboard incubations and in situ flux measurements of oxygen fluxes at the same stations. Studies of shallow water sites (most <100 m) in the Adriatic Sea, indicated reasonable agreement (±30% with no systematic bias) between O_2 fluxes measured with incubated cores and in situ landers (Tahey et al. 1996; Giordani et al. 1999). However, Rowe et al. (1997) observed a shipboard oxygen consumption that was two times greater than in situ consumption on the Greenland shelf, suggesting that shipboard incubations overestimate fluxes. It should be noted that the depths of their cores were relatively shallow (less than 500 m). Wijsman (2001), compiled a summary of deck incubations that were also a factor of 2 higher than in situ incubations, at depths greater than 1500 m. However, comparisons were not from simultaneous samplings. By contrast, others have observed that reducing pressure can significantly decrease metabolic activity of bacteria in sediments from depths of 800 to 1500 m, as indicated by ^{3}H-thymidine uptake to measure bacterial productivity (Tholosan et al. 1999; Deming and Colwell 1985). Effects were quite variable on different expeditions, but typically showed a 20% to 70% decrease. This decrease was not strongly depth dependent. In summary, conflicting results exist for the comparison of bacterial metabolism based on comparison of shipboard core incubations and in situ oxygen flux measurements. No literature has been found that actually compares shipboard incubation and in situ fluxes for nutrients with simultaneous sampling, as was done in this study. The NO_3 behavior in this study suggests that denitrification rates are decreased from in situ values as a result of a reduction in pressure and/or temperature in some cases.

Comments and recommendations

Nutrient fluxes from incubated cores have been compared to fluxes measured with in situ chambers at 8 sites from 100 to 3300 m depth on the California Margin. If in situ measurement is not feasible, the core incubation technique provides flux estimates that are similar to in situ flux chambers. However, artifacts are evident, as incubation results are about 65% to 100% of in situ fluxes. Results are best for phosphate and silicic acid, and less satisfactory for nitrate. Further comparisons must be done to determine whether core incubations are equally satisfactory at sites with much lower or higher fluxes. Macrofaunal irrigation in cores was probably reduced from in situ rates at our sites, and this factor apparently reduced benthic fluxes of nutrients from incubated cores by an average of 10% to 15%. The importance of irriga-

tion probably varies from one site to another. Good temperature control is important. Estimates of the effect of temperature were made for cases where incubation and in situ temperatures differed. These adjustments brought shipboard and in situ measurements into better, but not always satisfactory agreement. The temperature adjustment used was probably not satisfactory for nitrate, because nitrate profiles in porewaters of incubated cores from organic-rich sites should respond rapidly to changes in microbial metabolism, and we have not quantified the effect of temperature on metabolism at our sites. For cores from depths of 900 m and more, pressure reduction appears to significantly reduce denitrification rates. Similar Ge/Si flux ratios were observed with both techniques, but analytical uncertainties limit the confidence with which their correspondence can be evaluated to about 20% of the ratios measured.

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