

YALE PEABODY MUSEUM

P.O. BOX 208118 | NEW HAVEN CT 06520-8118 USA | PEABODY.YALE. EDU

JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research*, one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at <https://elischolar.library.yale.edu/>.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research*.

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.



This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License.
<https://creativecommons.org/licenses/by-nc-sa/4.0/>



Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific

by Allan H. Devol¹ and John P. Christensen²

ABSTRACT

The exchange of O_2 , N_2 , NO_3^- , NH_4^+ , $Si(OH)_4$, and PO_4^{3-} between the sediments and the overlying water (benthic flux) was determined at 18 locations on the Washington State continental margin using an *in situ* benthic tripod. Oxygen consumption by the sediments ranged from $21.2 \mu\text{mole cm}^{-2} \text{ s}^{-1}$ on the shelf to $2.85 \mu\text{mole cm}^{-2} \text{ s}^{-1}$ on the slope. Nitrogen gas fluxes were from the sediments to the overlying water. They varied 5.5 to $1.2 \mu\text{mole-N cm}^{-2} \text{ s}^{-1}$ and were always greater than the corresponding NO_3^- flux into the sediments. A nitrogen mass balance indicated that the difference between the N_2 flux out and the NO_3^- flux in could be accounted for by oxidation of NH_4^+ produced during aerobic and anaerobic carbon remineralization to NO_3^- and subsequent denitrification to N_2 . Comparison of the benthic fluxes of O_2 , NO_3^- and $Si(OH)_4$ with the fluxes predicted from molecular diffusion across the sediment water interface showed that for all three solutes the benthic fluxes were up to three times greater than the molecular fluxes and indicated the importance of macrobenthic irrigation in these sediments. However, several existing empirical irrigation models were not able to describe all three solutes. The overall carbon oxidation rate, as estimated from the sum of the O_2 flux, the N_2 flux and the measured SO_4^{2-} reduction rate, could be fit with a normalized power function; i.e., carbon oxidation rate ($\text{gC m}^{-2} \text{ y}^{-1}$) = $110 \cdot (z/100)^{-0.91}$. The exponent describing the rate of attenuation with depth (-0.91) was similar to the carbon rain rate attenuation coefficient determined from sediment traps in the pelagic, eastern North Pacific.

1. Introduction

On the order of 30% to 50% of marine primary production takes place in waters overlying sediments of the continental margins (shelf-slope-rise; Romankevich, 1984; Walsh, 1988, 1991). Because of proximity to shore and its importance with respect to commercial fisheries, the primary productivity of many margin waters has been relatively well studied. However, the ultimate fate of the majority of this production and the location of either burial or oxidation is not nearly as well documented. Because of the higher primary productivity in waters overlying margin sediments, the higher proportional carbon rain rate through the shallower water column and the fact that terrestrial carbon inputs enter the ocean here, shelf sediments have a relatively high carbon content, 0.7% (w/w) and slope sediments are

1. School of Oceanography WB-10, University of Washington, Seattle, Washington, 98195, U.S.A.

2. Oceanic Associates, P.O. Box 151, Brunswick, Maine, 04011, U.S.A.

even more enriched, 1.3% (Premuzic *et al.*, 1982; Romankevich, 1984). Indeed, fully 50% of the total oxidizable (1000 yr time scale) sedimentary organic matter is thought to reside in shelf and slope sediments (Emerson *et al.*, 1987; Emerson and Hedges, 1988). This fact alone implies that continental margin sediments are important, if not the dominant, site of cycling for the biogenically active elements.

Continental margin sediments are important areas of organic carbon oxidation and also, it has been hypothesized, depocenters for organic carbon burial (Grant *et al.*, 1987; Walsh, 1991; Walsh *et al.*, 1985). Based on mass balances, it has been suggested that a significant fraction of the carbon rain rate to slope and rise sediments derives from primary production on the continental shelf (Walsh *et al.*, 1985; Christensen, 1989; Jahnke *et al.*, 1990). Due to the various pathways by which organic matter can be oxidized margin sediments are also important areas for the biogeochemical cycling of other elements, e.g., N, S, Fe, Mn, P, Si (Bender *et al.*, 1989; Jahnke, 1990; Berelson *et al.*, 1987). In fact, continental margin sediments have been suggested as the single largest sink term in the marine combined nitrogen budget (Codispoti and Christensen, 1985; Codispoti, 1989; Devol, 1991).

Despite the obvious importance of margin sediments in the global cycles of many elements, there have been few studies of elemental cycling in these sediments. This is especially true of continental shelf sediments where determination of rates from pore water profiles is complicated by macrobenthic irrigation (Aller, 1980) and resuspension of bottom sediments renders sediment trap results questionable. In this report we present the results of a study of oxygen consumption, denitrification and sulfate reduction in sediments of the Washington State shelf and slope. The specific questions addressed are (1) quantitatively, what are the rates of the different oxidation reactions, (2) how important is macrobenthic irrigation versus molecular diffusion in supplying oxidizing agents for organic matter mineralization, (3) what are the dominant nitrogen cycle processes, and (4) are these various processes correlated with physical variables such as depth, oxygen concentration and distance from shore?

2. Methods

a. Study area. Measurements were made in continental shelf and slope sediments off Washington State. The Washington shelf is a classical, eastern boundary current region. Its high production results from wind-driven coastal upwelling primarily during the summer months (Hickey, 1989). Nearshore sediments consist of sands with carbon concentrations less than 1% by weight. The mid-shelf silt deposit and upper slope sediments contain more carbon, between 1% and 2%, and the highest carbon concentrations, > 2%, are found in the mid- and lower slope regions (Gross *et al.*, 1972; Carpenter and Peterson, 1989). Despite the presence of a major river, the Columbia, sedimentary organic carbon is primarily of marine origin (Hedges and Mann, 1979; Praul and Carpenter, 1984; Carpenter and Peterson, 1989). A signifi-

Table 1. Station locations and water depth for stations occupied during R/V *New Horizon* cruise 88-8 (NH-prefix) and R/V *Wecoma* cruise WE9106A (WE- prefix).

Station	Latitude	Longitude	Depth
NH01	46°48.60'	124°35.35'	115
NH02	46°50.15'	124°49.70'	161
NH03	46°52.88'	124°29.57'	85
NH06	46°43.70'	124°15.01'	42
NH07	46°50.28'	124°52.70'	225
NH10	46°48.90'	124°57.10'	465
NH12	46°48.28'	125°03.23'	630
NH14	47°05.75'	124°45.83'	114
NH16	46°36.74'	124°28.94'	122
NH17	46°21.69'	124°29.42'	124
NH18	46°09.55'	124°32.70'	146
NH19	46°49.74'	123°42.03'	98
WE101	46°45.66'	124°33.45'	106
WE102	46°17.85'	124°20.80'	122
WE103	46°46.24'	124°42.95'	140
WE104	47°31.92'	124°52.69'	137
WE105	46°44.71'	124°51.27'	323
WE107	46°44.63'	124°50.38'	239
WE108	46°47.93'	124°16.57'	43

cant feature of the eastern North Pacific is the relatively intense oxygen minimum found there, which results in oxygen depletions to concentrations as low as 40 μM at about 800 m in the study area (Stefansson and Richards, 1964).

Benthic flux measurements were made at a total of 18 locations (Table 1) over the course of two cruises, cruise 88-8 of the R/V *New Horizon* during June–July 1988 and cruise WE9106A of the R/V *Wecoma* during June of 1991. Stations were located primarily along two transects (Fig. 1). The major transect ran nearly east-west perpendicular to the coastline out to about the 1000 m isobath, while the secondary transect ran, generally, north-south along about the 100 m isobath. Along the primary section depth increased more or less uniformly from the shore to the shelf break, about 200 m, and again more or less uniformly but at a greater rate from the shelf break to at least 1000 m (McManus, 1972). In addition to benthic flux measurements, cores were collected at each station in order to determine pore water chemistry, organic carbon content and sulfate reduction rate.

b. Benthic flux measurement. At each of the 18 stations, benthic fluxes of oxygen, nitrogen, nitrate, nitrite, ammonium, silicate and phosphate were routinely determined using the *in situ* benthic tripod described by Devol (1987). The tripod contains two stainless steel flux chambers (412 cm² each) attached to a moveable tray. Because of the relatively shallow depth on the Washington shelf and slope the tripod

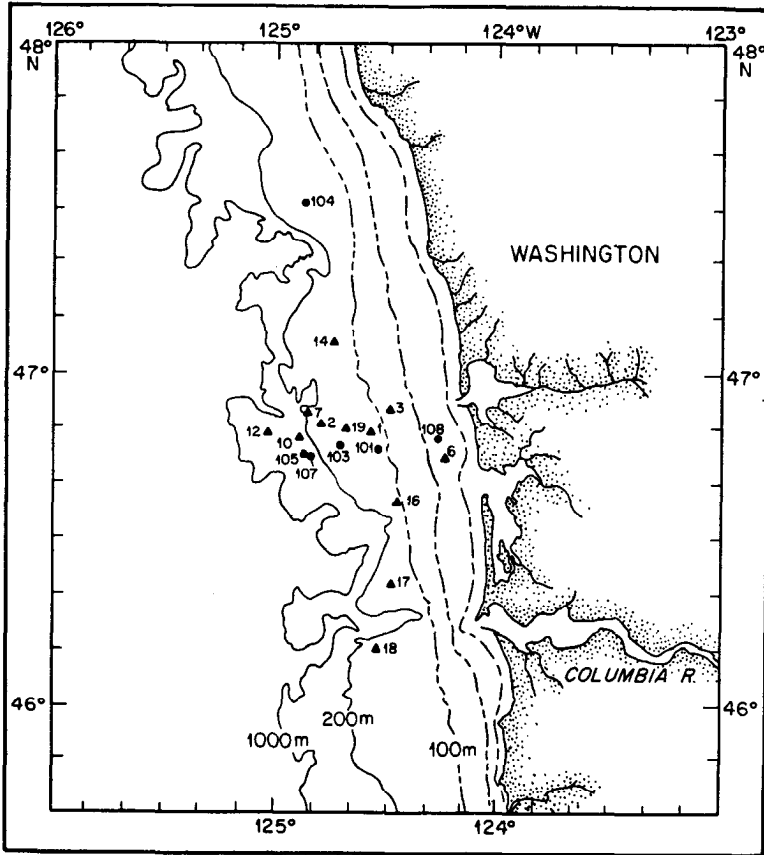


Figure 1. Location of stations where benthic flux measurements were made during cruise 88-8 of the *R/V New Horizon* (filled circles) and cruise WE9106A of the *R/V Wecoma* (filled triangles).

was lowered to the bottom on its own line and subsequently tethered to a free-floating buoy during operation. When the tripod approached the bottom the descent speed was reduced to about 5 m min^{-1} , thereby insuring minimal disturbance to the surrounding sediments. Once on the bottom the flux chambers were implanted in the sediments. During this operation both the bottoms and the tops of the chambers were open. The flux chamber lids were then closed and spring actuated syringes were used to take 8 samples of overlying water as a function of time. The syringe samples were first drawn through 5 ml sample loops that were subsequently used for dissolved gas analysis. Replacement water for the water removed as samples (10% to 15% of the total volume) was drawn from the external bottom water through a 25 cm section of $\frac{1}{8}$ inch i.d nylon tubing. During operation the flux chambers were continuously stirred. Both to check for leaks and to verify the volume of water enclosed, tritiated water was injected into the flux chambers at the beginning of each deployment.

Deployment times varied from 12 to 36 h, with chamber implantation, lid closure, tritium injection and sampling times programmable and accomplished by electro-deplating links.

Benthic fluxes were calculated from the changes in concentration observed in the flux chamber time series samples. However, enclosure of water in the flux chamber results in a non-steady state environment and, as solute concentrations increase or are depleted, gradients and therefore fluxes diverge from their undisturbed values (Devol, 1987; Bender *et al.*, 1989; Jahnke, 1990). To minimize the effect of this artifact, whenever possible only the first 3 time series points were used in the flux calculation.

On the 1988 cruise a microelectrode oxygen profiler was also mounted on the flux tripod to determine pore water oxygen profiles *in situ*. Profiler design and operation is described in Archer and Devol (1992) and Archer *et al.* (1989).

c. Sediment sampling. Sediment samples were obtained using either a Soutar box core during the 1988 or a MK III box corer (Ocean Instruments, San Diego CA.) during the 1991 cruise. The box core was lowered at speeds less than 5 m min^{-1} through the bottom 10 m of the water column to insure minimal disturbance of the overlying water. Upon retrieval each core was visually inspected and those that evidenced disturbance to the "fluff layer" were discarded. Box cores were subsampled using 5 cm, 7.5 cm and 10 cm diameter subcores. The 10 cm subcores were sectioned under a nitrogen atmosphere into 0.5, 1.0 and 2.0 cm thick sections that were packed into centrifuge tubes and centrifuged at 10,000 RPM for 20 min to separate the pore waters from the bulk sediments. To minimize temperature effects, core sectioning and centrifugation were done in a cold room at *in situ* temperature ($\sim 8^\circ\text{C}$). The samples were then filtered through $0.2 \mu\text{m}$ Nucleopore filters.

In addition to the centrifuged samples, high resolution pore water profiles were obtained using a whole-core squeezing technique similar to that described by Bender *et al.* (1987). During the 1988 cruise these samples were analyzed for nitrate and nitrite only using a non-segmented flow method (see below). During the 1991 cruise a temperature controlled sampling chamber (total volume $\sim 70 \mu\text{l}$) containing a Radiometer oxygen electrode was mounted in line with the squeezer to obtain pore water oxygen profiles.

d. Chemical analyses. Samples for dissolved gas analysis were run immediately after tripod retrieval. Oxygen and nitrogen were stripped from the 5 ml sample with helium, dried over silica gel and introduced into a Varian gas chromatograph equipped with a 2 m, molecular sieve 5A column and Carle thermoconductivity detectors. The determination was standardized with air, as described by Grundmanis and Murray (1982). Using this method an analytical precision of about $\pm 3\%$ was obtained (Devol, 1991).

On the 1988 cruise nutrient analyses (nitrate, nitrite, phosphate, ammonium and silicate) were done on a Technicon Autoanalyzer using the methods described by Whitedge *et al.* (1981). During the 1991 cruise phosphate and silicate concentrations were determined manually by the methods outlined in Strickland and Parsons (1972). Nitrate and nitrite were determined on 1 ml of sample by a non-segmented flow version of the cadmium reduction method of Armstrong *et al.* (1967) as described by Lambourn *et al.* (1991), while ammonium was determined utilizing a gas permeable membrane technique (Willason and Johnson, 1986).

e. Sulfate reduction rate. Sulfate reduction rates were measured utilizing the $^{35}\text{SO}_4$ technique (Devol *et al.*, 1984; Christensen, 1989). In general, samples were taken about every 3 cm down to a depth of about 30 cm. During the 1988 cruise, only the acid volatile portion of the reduced sulfate was recovered. Total sulfate reduction rates for this period were calculated using the relationship between the total sulfate reduction rate and the acid volatile fraction presented by Christensen (1989). In 1991 the total sulfate reduction rate was estimated as the sum of the acid volatile and chromium reducible fractions (Fossing and Jorgensen, 1990). Total sulfate reduction rates from the two cruises showed good agreement.

f. Solid phases. Sediment porosity was determined by water loss after drying to constant temperature. Organic carbon and nitrogen were determined on the dried samples using a Carlo Erba C-H-N elemental analyzer (model 1100) by the method described in Hedges and Stern (1984).

3. Results

a. Benthic fluxes. The results of a typical deployment are shown in Figure 2. Within the flux chambers oxygen concentrations always decreased as expected. Because oxygen concentrations in the waters in contact with the Washington shelf and, especially, slope are relatively low to begin with, a significant fraction of the oxygen was frequently removed. This resulted in significant changes in the pore water-overlying water O_2 gradient during the deployment and was probably the principal cause of the curvature in the time series (Devol, 1987; Bender *et al.*, 1989). Nitrate fluxes were also from the overlying water to the sediment during all deployments and reflected intense sedimentary denitrification. The nitrogen gas flux out of the sediments confirmed that the nitrate flux in was, indeed, being consumed in denitrification rather than by some other process. Nitrite fluxes (not shown) were frequently zero, but when there was a flux it was out of the sediments and it was small relative to the nitrate flux. In contrast, but as expected, the sediments were strong sources of $\text{Si}(\text{OH})_4$. Phosphate and NH_4^+ fluxes were also generally from the sediments to the overlying water as shown in Figure 2, however, for both solutes, there were several instances in which the initial flux was zero.

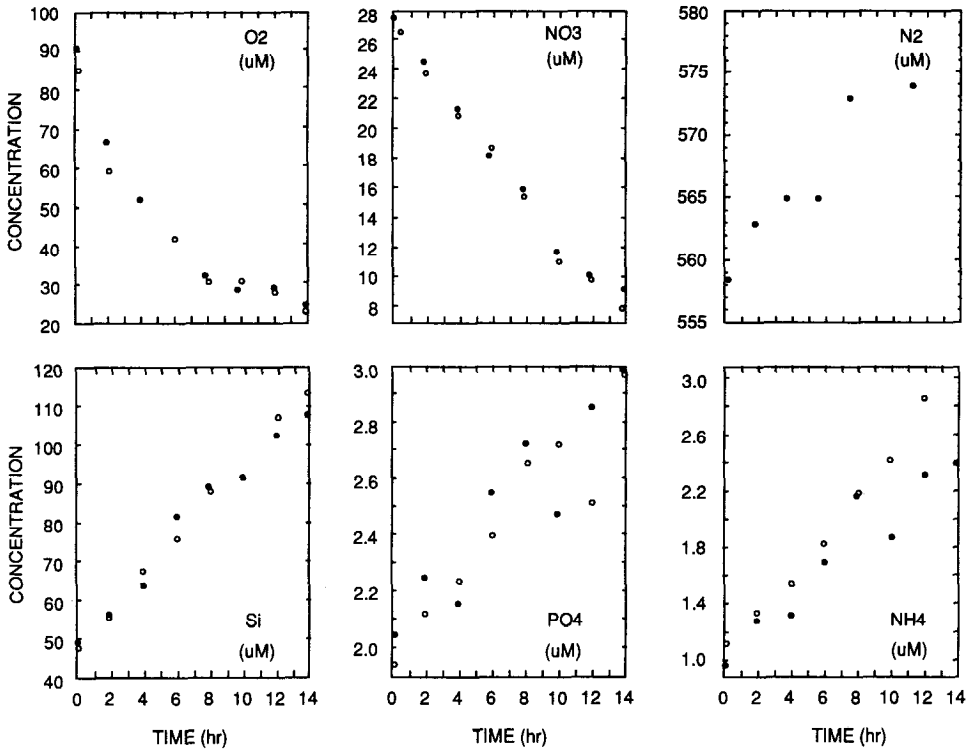


Figure 2. Typical changes in concentration with time in samples from the benthic flux tripod. Different symbols represent the two replicate chambers. Data is from station NH02.

The values of the fluxes measured at each station are listed in Table 2 along with the overlying water oxygen content, integrated sulfate reduction rate and percent organic carbon and nitrogen. Among the shelf stations (< 200 m) oxygen fluxes varied from a high of $21.2 \text{ } \mu\text{mole cm}^{-2} \text{ s}^{-1}$ in the midshelf silt deposit (station NH14) to a low of $6.0 \text{ } \mu\text{mole cm}^{-2} \text{ s}^{-1}$ in the nearshore sands (station WE08). Oxygen consumption by slope sediments was lower. Of the 5 slope stations, 4 had oxygen fluxes of $5 \text{ } \mu\text{mole cm}^{-2} \text{ s}^{-1}$ or less while a single station (WE07) had an oxygen consumption rate of $10 \text{ } \mu\text{mole cm}^{-2} \text{ s}^{-1}$.

At all stations the nitrate flux was from the overlying water to the sediments and was used to support suboxic, organic matter oxidation via denitrification. However, unlike oxygen, which varied by an order of magnitude overall, the nitrate flux only varied by about a factor of 2.3 overall, from $2.8 \text{ } \mu\text{mole cm}^{-2} \text{ s}^{-1}$ (station NH17) to $0.9 \text{ } \mu\text{mole cm}^{-2} \text{ s}^{-1}$ (station NH12). In contrast, the nitrogen gas flux out of the sediments resulting from denitrification varied from $0.96 \text{ } \mu\text{mole-N cm}^{-2} \text{ s}^{-1}$ to $5.5 \text{ } \mu\text{mole-N cm}^{-2} \text{ s}^{-1}$, or more than a factor of 5. Note that the nitrogen gas fluxes are presented in units of $\mu\text{mole-N}$, where N refers to mono-atomic nitrogen and is

Table 2. Benthic fluxes of O_2 , N_2 , NO_3^- , NH_4^+ , PO_4^{3-} , $Si(OH)_4$, sulfate reduction rate (SO_4^{2-} -R), bottom water oxygen content, percent C and N of surface sediments (upper cm) and surface sediment porosity (v/v) for stations on the Washington continental margin (Fig. 1). Stations taken during R/V *New Horizon* cruise 88-8 are designated with the prefix NH, while those taken during R/V *Wecoma* cruise WE9106A have the prefix WE. The station name suffix, A or B, designates one of the two flux chambers on the tripod. The bulk sediment measurements, SO_4^{2-} -R, %C, %N and porosity, were made using sediments obtained with a box core at the same location at which the tripod was deployed. Benthic fluxes are in $\mu\text{mole cm}^{-2} \text{ s}^{-1}$ except for N_2 which is in $\mu\text{mole-N cm}^{-2} \text{ s}^{-1}$, i.e. $\mu\text{g-atom cm}^{-2} \text{ s}^{-1}$. Sulfate reduction rate is likewise in $\mu\text{mole cm}^{-2} \text{ s}^{-1}$ and oxygen concentration is in μM . Negative values indicate uptake by the sediments, i.e. flux into the sediments.

Station	O_2	O_2 Flux	N_2 Flux	NO_3^- Flux	NO_2^- Flux	NH_4^+ Flux	$Si(OH)_4$	PO_4^{3-} Flux	SO_4^{2-} -R	%C	%N	Porosity
NH01A	100	-11.4		-1.6	0.13	0.91	11.8	0.00	2.5	1.60	0.11	0.72
NH01B	100	-13.2		-1.4	0.10	0.76	10.2	0.00				
NH02A	113	-13.2	2.6	-1.4	0.02	0.26	5.1	0.11	2.7			0.59
NH02B	113	-10.6		-1.2	0.01	0.20	3.9	0.078				
NH03A	86	-8.3		-1.3	0.00	0.68	5.3	0.00	7.2	0.76	0.08	0.63
NH03B	86	-6.9		-1.8	0.02	0.56	3.4	0.00				
NH06A	113	-10.5			0.00	0.97	5.4	0.00				
NH06B	113	-6.8		-1.6	0.00	0.47	4.1	0.00				
NH07A	104	-5.8		-0.66	0.01	0.00	2.2	0.05	5.8	0.64	0.08	
NH07B	104	-5.5		-1.0	0.01	0.00	2.6	0.036				
NH10A	47	-3.7		-0.70	0.00	0.002	4.4	0.040	1.5	1.56	0.18	0.81
NH10B	47	-2.2		-0.92	0.00	0.006	4.9	0.049				
NH12A	38	-2.6	1.1	-0.90	0.02	0.12	3.1	0.025	0.76	1.35		0.83
NH12B	38	-2.4	1.0	-0.76	0.04	0.034	2.5	0.017				
NH14A	127	-21.2	5.4	-1.9	0.00	0.56	16.6	0.032	3.5			0.69
NH16A	96	-17.8	3.6	-1.3	0.01	0.34	8.7	0.00				0.61
NH16B	96	-6.9		-1.3	0.09	0.93	9.4	0.095				
NH17A	112	-17.7	4.6	-2.3	0.01	1.14	14.0	0.042	4.5			
NH17B	112	-15.6	4.9	-1.5	0.09	0.71	13.7	0.10				
NH18A	106	-19.2	3.6	-2.0	0.00	0.053	4.2	0.086	2.7			0.57
NH18B	106	-14.6		-1.4	0.01	0.76	5.1	0.051				
NH19A	97	-10.9	3.5	-1.8	0.03	0.036	6.6	0.022		0.59	0.07	

Table 2. (Continued)

Station	O ₂	O ₂ Flux	N ₂ Flux	NO ₃ ⁻ Flux	NO ₂ ⁻ Flux	NH ₄ ⁺ Flux	Si(OH) ₄	PO ₄ ⁻³ Flux	SO ₄ ⁻² -R	%C	%N	Porosity
WE101A	78	-6.1		-1.2	0.21	0.16	6.6	0.021	8.7	1.80	0.11	0.76
WE103A	68-	-18.5	3.2	-1.3	0.38	0.66	13.6	0.072	3.2	1.33	0.10	0.73
WE103B	68	-15.4		-1.4	0.43	0.56	15.8	0.061				
WE104A	109	-9.9	3.7	-2.4	0.16	1.33	20.4		4.8	1.47	0.10	0.73
WE104B	109	-10.8	4.2	-4	0.05	1.78	35.6	0.055				
WE105A	58			-0.90	0.07		5.6	0.045		0.58	0.06	
WE105B	58	-2.9	1.2	-1.0	0.04	0.16	6.3	0.042	1.7			0.61
WE107A	108	-11.1	2.2	-1.9	0.25	0.78	31.0	0.022	3.1	0.59	0.08	0.63
WE107B	108	-10.4	2.1	-1.9	0.11	0.78	22.0	0.017				
WE108A	66	-6.6	2.6	-1.5	0.04	0.00	11.8	0.10				
WE108B	66	-7.0	2.7	-1.5	0.01	0.00	9.6	0.083				

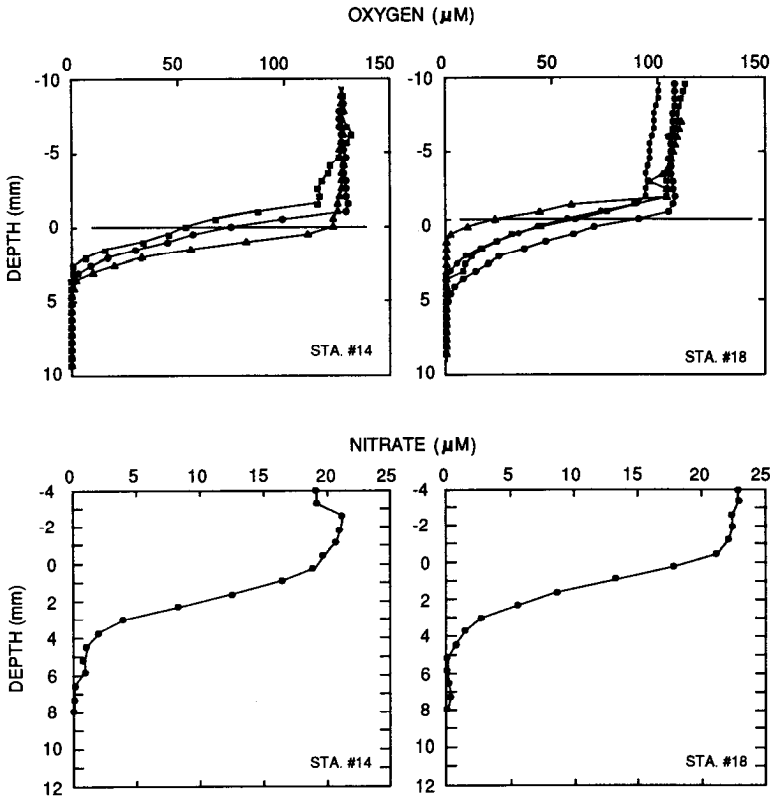


Figure 3. Representative profiles of dissolved oxygen (upper, redrawn from Archer and Devol, 1992) and nitrate (lower) across the sediment-water interface in Washington shelf sediments. The sediment-water interface for oxygen was determined *in situ* by resistivity change. The interface depth for nitrate was determined visually and is only approximate.

equivalent to 1 pg-atom. With these units nitrogen gas fluxes are directly comparable to fluxes of combined nitrogen species.

Silicate fluxes displayed a range similar to that of oxygen but in the opposite direction, i.e., from the sediments to the overlying water. The highest silica flux was observed in the mid-shelf silt deposit at station WE04, $17.8 \text{ pmole cm}^{-2} \text{ s}^{-1}$, while the lowest flux was again recorded from the slope sediments, $2.48 \text{ pmole cm}^{-2} \text{ s}^{-1}$ at station NH12. Ammonia and PO_4^{-3} fluxes were, in general, much smaller and at times were unmeasurable; they varied from 0 to $1.14 \text{ pmole cm}^{-2} \text{ s}^{-1}$ and 0 to $0.22 \text{ pmole cm}^{-2} \text{ s}^{-1}$, respectively.

b. Pore waters. Typical pore water profiles for oxygen and nitrate are shown in Figure 3 for shelf sediments. (The complete suite of pore water oxygen data is presented by Archer and Devol, 1992.) Both oxygen and nitrate decrease rapidly with sediment depth and reach zero values within several millimeters of the sediment

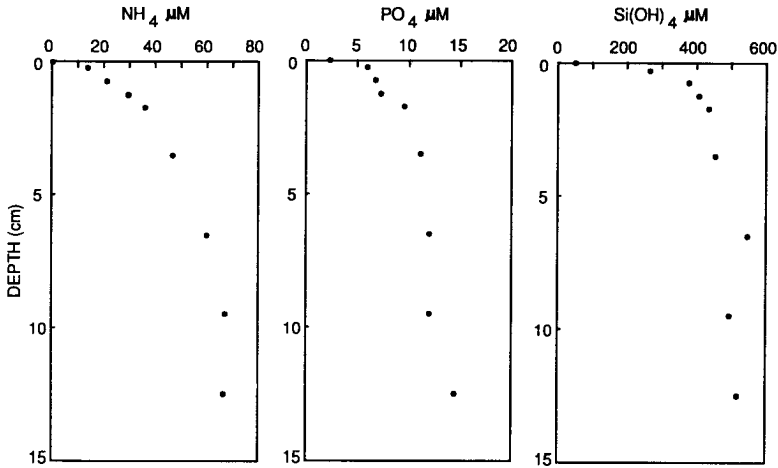


Figure 4. Representative pore water profiles for NH_4^+ , PO_4^{3-} , and $\text{Si}(\text{OH})_4$ for Washington shelf sediments. Data are from station NH14.

surface. In slope sediments oxygen gradients were not as steep as those on the shelf even though the penetration depths were about the same because overlying water concentrations were lower. The opposite was true for nitrate.

In shelf sediments pore water ammonium concentrations generally increased asymptotically to values between 60 and 80 μM at about 15 cm (Fig. 4). Pore water phosphate values also generally increased, with 15 cm values most commonly approaching values of about 15 μM . However, there were frequently significant exceptions to this trend. For example, at station 14 a subsurface maximum of about 30 μM was observed at about 5 cm depth below which concentrations decreased to about 15 μM at 15 cm. Silicate concentrations increased rapidly down core to between 500 and 600 μM at about 5 cm and, generally, remained constant thereafter. In slope sediments the silicate profiles were similar but ammonium and phosphate were not. Ammonium profiles were more linear and only increased to between 30 and 40 μM at 15 cm depth. Phosphate profiles also had much less curvature and concentrations at 15 cm did not exceed 8 μM . For all solutes, many of the pore water profiles contained local maxima and minima similar to those reported for other areas (Grundmanis and Murray, 1977), where they were attributed to deep macrofaunal irrigation.

c. Sedimentary carbon and nitrogen and sulfate reduction rate. The % organic carbon content of the sediments at the tripod deployment locations ranged from 0.58% to 1.85% and followed the general patterns observed previously for the Washington Margin (Carpenter and Peterson, 1989; Gross *et al.*, 1972) with the exception that sediments in the 200 m to 300 m depth range had consistently lower %C, 0.5% to 0.6%. Sulfate reduction rates varied from a low of 1.8 $\text{pmole cm}^{-2} \text{s}^{-1}$ up to 8.1 pmole

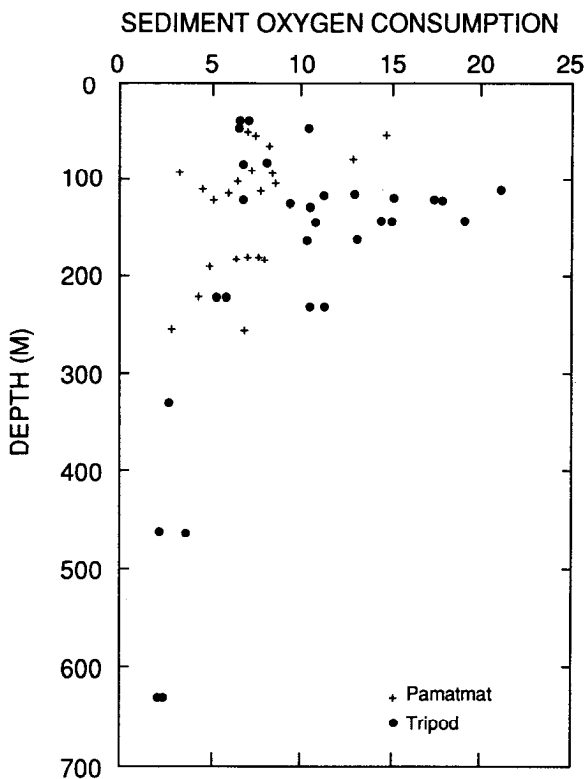


Figure 5. Benthic flux of oxygen into the sediments of the Washington continental margin ($\mu\text{mole cm}^{-2} \text{s}^{-1}$). Filled circles are estimates from the *in situ* flux tripod deployments while crosses represent on deck incubation measurements (Pamatmat, 1973). All individual flux chambers are plotted.

$\text{cm}^{-2} \text{s}^{-1}$. When only the shelf sediments are considered, the average sulfate reduction rate was $4.8 \mu\text{mole cm}^{-2} \text{s}^{-1}$. This value is very similar to the value for the mid-shelf silt deposit of $5.1 \mu\text{mole cm}^{-2} \text{s}^{-1}$ observed by Christensen (1989).

4. Discussion

a. Benthic fluxes. Benthic oxygen flux varied by an order of magnitude (Fig. 5), from $2.4 \mu\text{mole cm}^{-2} \text{s}^{-1}$ (at 462 m) to $21.2 \mu\text{mole cm}^{-2} \text{s}^{-1}$ (at 114 m). However, when only the shelf values were considered the variation was only from 6.0 to $21.2 \mu\text{mole cm}^{-2} \text{s}^{-1}$ or about a factor of 3 to 4. These shelf values are in general agreement with estimates from other open shelf areas (Florek and Rowe, 1983; Rowe *et al.*, 1988; Grebmeier and McRoy, 1989). The tripod-measured O_2 fluxes are, however, greater than values reported for the Washington shelf nearly two decades earlier by Pamatmat (1973) as determined by shipboard core incubation (Fig. 5). The average

benthic oxygen uptake on the shelf, 12.1 ± 4.3 (SD) $\mu\text{mole cm}^{-2} \text{s}^{-1}$ was nearly twice that of Pamatmat, $6.8 \pm 2.1 \mu\text{mole cm}^{-2} \text{s}^{-1}$. The main discrepancy between the two studies occurs in the 100 m to 170 m depth zone. This is the midshelf silt deposit and it contains higher organic carbon and greater populations of benthic macroorganisms than the rest of the shelf (Gross *et al.*, 1972; Nittrouer *et al.*, 1979; Carpenter *et al.*, 1981). We speculate that much of the difference between the two estimates is due to more representative inclusion of macrobenthic irrigation in our large (412 cm^2) chambers than in Pamatmat's smaller (20 cm^2) cores.

Benthic oxygen fluxes have been previously shown to be related to such variables as depth, distance from shore and macrofaunal abundance (Jahnke *et al.*, 1990; Smith, 1987). For a basin scale transect extending from Southern California to almost north of Hawaii, Smith (1987) found significant correlations between all three variables and benthic oxygen flux. In an independent study of benthic oxygen flux Smith *et al.* (1989) found a significant inverse depth dependence when sediment oxygen demand on the tops of two seamounts at different depths was compared. Our data also are significantly correlated with depth. A power curve regression results in the relationship, $d\text{O}_2/dz = 14.4 \cdot (z/100)^{-0.916}$, where $d\text{O}_2/dz$ is in $\mu\text{mole cm}^{-2} \text{s}^{-1}$ (regression correlation coefficient [*rcc*] = 0.76, *df* = 13). It should be pointed out, however, that in the study region depth, distance from shore and dissolved oxygen concentration are all intercorrelated, albeit nonlinearly, such that the oxygen flux is related to the other variables as well.

All the other benthic fluxes are plotted against water depth in Figure 6 along with the depth integrated sulfate reduction rate. As was the case for oxygen, both the N_2 flux and the sulfate reduction rate decrease as a power function of depth, presumably reflecting the dependence of denitrification and sulfate reduction on carbon rain rate to the sediments ($d\text{N}_2/dz = 5.94 \cdot (z/100)^{-0.892}$, *rcc* = 0.90, *df* = 13; $d(\text{SO}_4\text{-R})/dz = 5.67 \cdot (z/100)^{-0.919}$, *rcc* = 0.80, *df* = 12). Although all other fluxes also decrease with depth, none is well fit by a power function or other relationship. Ammonium, PO_4^{-3} and NO_2^- all vary over a wide range on the continental shelf and for each variable there are frequent measurements of zero fluxes. For all benthic fluxes the highest degree of variance occurs in the mid shelf silt deposit and probably results, in part, from varying degrees of bioturbation. Among the benthic fluxes, there were significant positive relationships between O_2 flux and N_2 flux ($\text{N}_2 = 0.17 \cdot \text{O}_2 + 1.01$, *rcc* = 0.81) and the N_2 flux and the NO_3^- flux ($\text{N}_2 = 1.96 \cdot \text{NO}_3^- + 0.4$, *rcc* = 0.63). There was also a weak but statistically significant correlation between Si flux and O_2 flux. As we will show in a following section, oxygen, silica and nitrate fluxes all displayed similar responses to macrofaunal irrigation and this probably accounts for a significant amount of the correlation among them. For reasons discussed below the total combined nitrogen flux was always into the sediments and thus N and P fluxes were not necessarily stoichiometrically related.

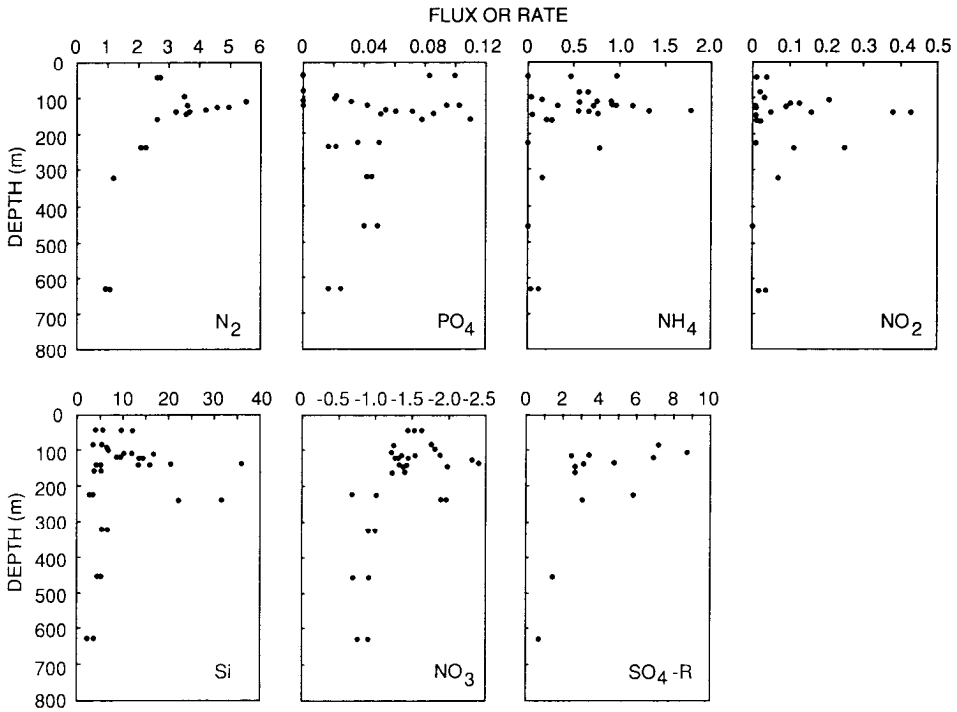


Figure 6. Benthic fluxes of N_2 , PO_4^{-3} , NH_4^+ , NO_2^- , $Si(OH)_4$, NO_3^- and sulfate reduction rate (SO_4^-R) versus depth for stations on the Washington continental margin. All units are in $\mu\text{mole cm}^{-2} \text{s}^{-1}$ except N_2 which is in $\mu\text{mole-N cm}^{-2} \text{s}^{-1}$.

b. Nitrogen cycling. In general, shelf and slope sediments have been suggested as a large, if not the largest, sink in the marine combined nitrogen budget (Bender *et al.*, 1989; Christensen *et al.*, 1987a; Codispoti, 1989; Devol, 1991; Jahnke, 1990). However, much of the evidence results from models rather than direct measurement and only relatively few shelf and slope areas have been studied. Most of the models to date require that a significant fraction of all of the NH_4^+ regenerated during organic carbon oxidation be oxidized to N_2 , either directly by NO_3^- (Bender *et al.*, 1989) or indirectly through coupled nitrification and subsequent denitrification (Christensen *et al.*, 1987a, Seitzinger, 1988).

As indicated by the magnitudes and directions of the nitrogen fluxes, nitrogen cycling in Washington margin sediments is dominated by denitrification. The actual rate of denitrification is best estimated by the flux of nitrogen gas out of the sediments. Nitrogen gas fluxes varied from $0.96 \mu\text{mole-N cm}^{-2} \text{s}^{-1}$ to $5.5 \mu\text{mole-N cm}^{-2} \text{s}^{-1}$ with an average of $3.7 \mu\text{mole-N cm}^{-2} \text{s}^{-1}$. While the intensity of the denitrification is indicated by the consistent flux of nitrate from the overlying waters to the sediments, this varied only from 0.7 to $1.9 \mu\text{mole cm}^{-2} \text{s}^{-1}$ and averaged only $1.5 \mu\text{mole cm}^{-2} \text{s}^{-1}$. Thus, the magnitude of the nitrogen flux out of the sediments was

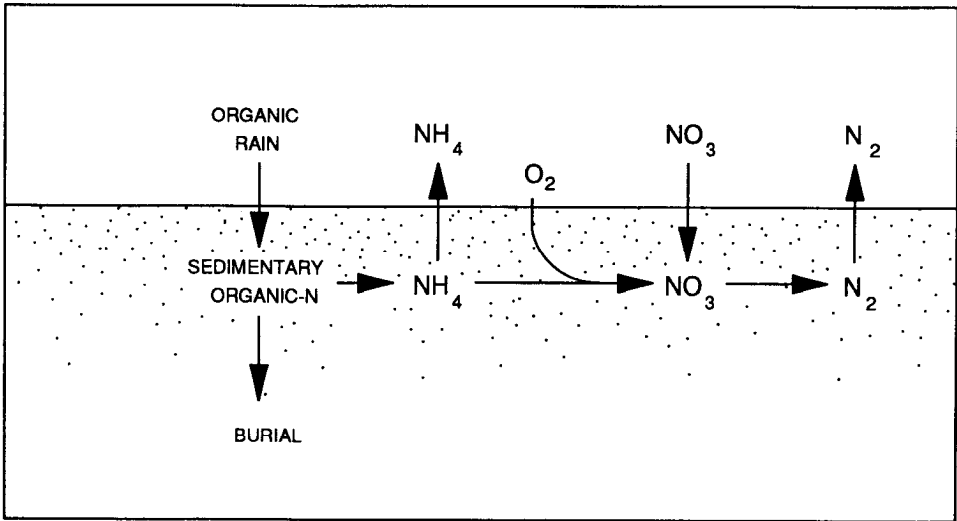


Figure 7. Proposed nitrogen cycle for Washington margin sediments.

about 2.5 times the nitrogen flux into the sediments and indicated that only about 40% of the overall denitrification could be supported from nitrate supplied from the overlying waters. This result strongly supports the hypothesis that a significant fraction of the regenerated NH_4^+ is ultimately converted to N_2 and suggests the nitrogen cycling scheme shown in Figure 7.

If the proposed nitrogen cycle Washington margin sediments (Fig. 7) is correct then the observed combined nitrogen flux out of the sediments, which in these sediments is essentially the NH_4^+ flux, should be significantly less than the stoichiometric flux predicted from the measured sediment oxygen consumption rate and sulfate reduction rate. The nitrogen mass balances for stations on the shelf and slope are given in Table 3. The NO_3^- , NH_4^+ and N_2 fluxes are the averages of those that were measured (Table 2; we have neglected the NO_2^- flux because it is small relative to the other fluxes). The flux labeled N-Reg SO_4 is the expected NH_4^+ regeneration rate that would result from the measured sulfate reduction rate assuming a stoichiometry of 53:16 ($\Delta\text{SO}_4^-:\Delta\text{NH}_4^+$; Froelich *et al.*, 1979). The flux labeled N-Reg O_2 is the expected amount of regenerated nitrogen resulting from aerobic, organic matter oxidation as calculated from the average observed oxygen flux after downward correction by an amount sufficient to oxidize the NH_4^+ produced during sulfate reduction. A stoichiometry of 138:16 was used for oxygen consumed to nitrogen regenerated (Froelich *et al.*, 1979). This stoichiometry is for the oxidation of "Redfield" organic matter in which all regenerated NH_4^+ is oxidized to NO_3^- . As nitrate diffusion out of the sediments was never observed, the implicit assumption is that nitrification is coupled to denitrification. Addition of the two regenerated nitrogen fluxes results in $\Sigma\text{Reg-N}$, that is, the flux of combined nitrogen out of the sediments expected in the absence of

Table 3. Nitrogen mass balances for sediments of the Washington continental margin. The NO_3^- and NH_4^+ fluxes are the averages of those reported in Table 1. The flux labeled N-Reg $_{\text{SO}_4}$ is NH_4^+ regeneration rate that would result from the measured sulfate reduction rate assuming a stoichiometry of 53:16 ($\text{SO}_4^{2-}:\text{NH}_4^+$). The flux N-Reg $_{\text{O}_2}$ is the amount of regenerated nitrogen expected from aerobic respiration. It was calculated by first correcting the average oxygen flux by the amount required to oxidize the NH_4^+ produced during sulfate reduction to NO_3^- ($\text{NH}_3 + 2\text{O}_2 + \text{OH}^- \rightarrow \text{NO}_3^- + 2\text{H}_2\text{O}$). The flux of regenerated nitrogen was then calculated from the remaining oxygen flux by assuming a stoichiometry of 138:16 ($\text{O}_2:\text{NO}_3^-$). The sum of N-Reg $_{\text{SO}_4}$ and N-Reg $_{\text{O}_2}$ is the quantity $\Sigma\text{N-Reg}$. N $_2$ -Exp is the predicted flux of N_2 gas out of the sediments as calculated by $\Sigma\text{N-Reg} - \text{NH}_4^+$ flux - (NO_3^- flux \cdot 1.16), where 1.16 is the ratio of N_2 produced to NO_3^- consumed during denitrification. (Note that mathematically we subtract the observed NO_3^- flux, which is itself negative, so that the overall term is a positive addition to the expected flux of N_2 out of the sediments.) N $_2$ -obs is the average measured flux out of the sediments. For station WE08 a value of 0.9 was assumed for N-Reg $_{\text{SO}_4}$, the approximate average for the midshelf silt deposit.

Station	NO_3^- Flux	NH_4^+ Flux	N-Reg $_{\text{SO}_4}$	N-Reg $_{\text{O}_2}$	$\Sigma\text{N-Reg}$	N $_2$ -Exp	N $_2$ -obs
NH02	-1.3	0.23	0.80	1.4	2.2	3.3	2.6
NH12	-0.83	0.075	0.23	0.29	0.52	1.4	1.1
NH14	-1.9	0.56	1.0	2.5	3.5	4.9	5.4
NH16	-1.3	0.63	1.4	2.1	3.5	3.9	3.6
NH17	-1.9	0.93	1.4	1.9	3.3	4.2	4.8
NH18	-1.6	0.41	0.82	2.0	2.8	4.1	3.6
WE03	-1.4	0.61	0.95	1.9	2.9	3.7	3.2
WE04	-2.4	1.6	1.4	1.2	2.6	3.5	4.0
WE05	-0.95	0.08	0.52	0.17	0.68	1.6	1.2
WE07	-1.9	0.78	0.58	1.3	1.8	3.2	2.2
WE08	-1.5	0.00	0.90	0.79	0.79	3.4	2.7

any sedimentary denitrification. Subtraction of the average observed NH_4^+ flux out of sediments and addition of the average observed NO_3^- flux into the sediments multiplied by 1.16 ($\Delta\text{N}_2:\text{NO}_3^-$ during denitrification; Froelich *et al.*, 1979) results in N $_2$ -Exp, the expected N_2 flux out of the sediments assuming denitrification is the only other nitrogen transformation taking place.

Strictly speaking, at least some NH_4^+ produced during carbon oxidation is not oxidized to NO_3^- as evidenced by the NH_4^+ flux out of the sediments. However, even in the case of the largest NH_4^+ flux, station 17, this would only alter the N $_2$ -Exp value by about 5%. Also, although Fe and Mn can serve as oxidizing agents for organic matter, it appears that these reactions typically account for less than 1% of the total in margin sediments (Archer and Devol, 1992; Christensen and Rowe, 1984; Reimers *et al.*, 1992). Given the uncertainty in the actual pathway of N_2 production from NH_4^+ this correction was not made. Finally, in some sediments a significant fraction of the O_2 flux is used to reoxidize sulfide produced during sulfate reduction (Jorgensen, 1982). Both Christensen *et al.* (1987b) and Archer and Devol (1992) argue that sulfide oxidation is not a major oxygen consumption mechanism in

Washington shelf sediments. Archer and Devol (1992) demonstrate that about half the oxygen flux is due to gradient driven diffusion across the sediment surface within the upper few mm (Fig. 3) and the other half is supplied by macrobenthic irrigation (see also Section c—The importance of macrobenthic irrigation). For the surface O_2 flux it can be argued that any sulfide consumed during sulfide oxidation would have to be supplied by *in situ* production within the upper few mm because there is no free sulfide, i.e. no diffusible sulfide, within the sediment pore waters. As measured sulfate reduction rates in the 0–1 cm interval are only about 1% to 5% of the measured O_2 flux, it appears that most of the surface diffusive oxygen flux was used for some process other than sulfide oxidation, presumably organic matter oxidation. Although it is difficult to estimate the fraction of the O_2 flux supplied by irrigation that is used for the oxidation of sulfide, even if the entire amount was used for sulfide oxidation it would only reduce the N_2 -Exp value by about 15% to 20%. Consequently, we assume that the N budgets presented in Table 3 are a reasonable representation of the *in situ* processes.

In general, the agreement between the N_2 -Exp and the observed N_2 flux is good and supports the proposed nitrogen cycle (Fig. 7) a large fraction of the N_2 flux out of the sediments is derived from organic nitrogen. Indeed, when all the stations are averaged, fully 75% of the NH_4^+ produced during organic matter remineralization is oxidized to nitrate and subsequently denitrified to N_2 . Others have examined the importance of the conversion of remineralized NH_4^+ to N_2 either through models of coupled nitrification-denitrification (Billen, 1982; Aller *et al.*, 1980; Christensen and Rowe, 1984) or through discrepancies in flux budgets (Bender *et al.*, 1989; Berelson *et al.*, 1987; Jahnke, 1990; Kemp *et al.*, 1990). However, in most of these previous studies alternate explanations, such as oxidation of organic matter with high C:N ratio or fluxes of dissolved organic nitrogen, could not be ruled out. The direct flux measurements presented here clearly require a significant within-sediment source of N_2 to balance the observed flux, with the most probable N_2 production mechanism being oxidation of NH_4^+ to nitrogen oxides that are subsequently denitrified. The data also indicate that NO_3^- reduction beyond N_2 to NH_4^+ , as has been proposed for several other environments (Jorgensen and Sorensen, 1985; Smith, 1982; Koike and Sorensen, 1988) is not important in Washington state margin sediments and is probably not important in similar open, exposed continental shelf and slope sediments.

Although sediments have frequently been suggested as important sites of nutrient regeneration (Rowe *et al.*, 1988; Blackburn and Henrikson, 1983; Kelley and Nixon, 1984), recent studies of the California Borderland Basins have shown that, at least for nitrogen, these sediments are net sinks rather than sources (Berelson *et al.*, 1987; Bender *et al.*, 1989; Jahnke, 1990). On the Washington shelf and slope the flux of NO_3^- into the sediments always greatly exceeded the flux of NH_4^+ out. Assuming that any fluxes of dissolved organic nitrogen were small relative to NO_3^- , it appears that

these sediments, which are probably more typical of margin sediments in general, also are nitrogen sinks. However, in contrast to the borderland studies in which no NH_4^+ escaped the sediments, small NH_4^+ fluxes from the sediments to the overlying water were commonly observed from Washington margin sediments. Though the cause of this difference is not easily determined from the existing data, it may be linked to macrobenthic irrigation. As discussed below, irrigation is an important mechanism for flux enhancement on the Washington shelf and it is from these sediments that significant NH_4^+ fluxes were observed. In slope sediments irrigation was not an important flux enhancement mechanism and NH_4^+ fluxes were very low or zero (Table 2). Likewise, irrigation was not important in the California borderland basins and NH_4^+ fluxes out of those sediments were not detectable.

c. The importance of macrobenthic irrigation. Although the importance of macrobenthic fauna in enhancing benthic exchange is well documented (Aller, 1985; Aller, 1990; Christensen *et al.*, 1987b; Hammond *et al.*, 1985; Martin and Sayles, 1987; Andersen and Helder, 1987) most of the direct evidence is derived from sediments of coastal embayments; little data are available from more typical, open continental shelf and slope areas. As indicated by the oxygen flux and also the nitrate and silicate fluxes (see below), macrobenthic irrigation is an important and, frequently, the dominant mode of solute exchange in Washington shelf sediments.

Archer and Devol (1992) have shown that macrobenthic irrigation of Washington shelf sediments greatly enhanced oxygen exchange over that which would be supported by molecular diffusion alone. Furthermore, the degree of enhancement decreased with decreasing oxygen concentration. This was done by comparison of the purely diffusive flux of oxygen across the sediment water interface, as estimated from the microelectrode profiles, with the actual flux determined from the tripod time series. For shelf sediments the average tripod flux was consistently between 2 and 3 times larger than the average diffusive flux, indicating the importance of macrobenthic irrigation (Table 4). However, for the slope sediments where oxygen concentrations were low, about 40 μM , diffusive fluxes and tripod fluxes were about the same. Whether this was due to restriction of macrobenthic organisms by low oxygen concentration or some other cause could not be determined from the available data. Nevertheless, the importance of irrigation of shelf sediments was clearly evident.

The silicate and nitrate fluxes can be used to extend that analysis (Fig. 8). A simple comparison of the ratio of the tripod flux to the molecular flux for O_2 , NO_3^- , and $\text{Si}(\text{OH})_4$ confirms the importance of irrigation. For all three solutes tripod-determined fluxes are up to a factor of four greater than the corresponding molecular fluxes across the sediment water interface. Furthermore, the relationship of flux enhancement with oxygen concentration noted for the oxygen flux was observed for NO_3^- and $\text{Si}(\text{OH})_4$ as well. Although the flux ratio has been plotted vs.

Table 4. The ratio of the Tripod measured flux to the purely molecular flux calculated from the gradient across the sediment water interface (T/M) for the solutes oxygen, nitrate and silicate. Also tabulated for all three solutes are the coefficients of the various irrigation models discussed in the text: (1) the exchange velocity (α), (2) the irrigation coefficient (β) and (3) the "bio-diffusion" coefficient (D_b). Coefficients were estimate using the equations described in the text. Bulk sediment diffusion coefficients, D_s , were estimated as $D_s = D_m/(\phi F)$, where the formation factor F was estimated as $F = \phi^{-2}$ (Archie's Law; Berner, 1980). Molecular diffusion coefficients were taken from Li and Gregory (1974) for NO_3^- , Lehrman (1979) for O_2 and Wollast and Garrels (1971) for Si.

Station	T/M_{O_2}	T/M_{NO_3}	T/M_{Si}	α_{O_2}	α_{NO_3}	α_{Si}	β_{O_2}	β_{NO_3}	β_{Si}	$D_b\text{-O}_2$	$D_b\text{-NO}_3^-$	$D_b\text{-Si}$
1A	2.30	1.61	2.17	6.01	1.65	1.15	0.320	0.106	0.142	28.4	17.5	11.6
2B		1.54	2.44		1.35	0.50		0.087	0.062		16.8	13.1
3A	1.67	1.90	2.39	4.25	1.96	0.59	0.226	0.126	0.072	20.6	20.7	12.8
6A									0.000			
7A		1.84	1.42		0.94	0.23		0.061	0.028		20.0	7.6
10A	1.04	0.81	1.57	0.19	-0.40	0.57	0.010	-0.026	0.071	12.8	8.9	8.4
12A	1.17	0.60	0.89	0.83	-1.20	-0.10	0.044	-0.077	-0.012	14.4	6.5	4.8
14A	2.88	2.85	3.78	9.42	3.64	1.97	0.500	0.234	0.244	35.4	31.1	20.2
16A									0.216			
17A		2.11	3.64		2.67	1.95		0.171	0.241		22.9	19.5
18B	2.94	2.37		9.08	2.72		0.482	0.175	0.146	36.2	25.7	
19B	1.15	1.50		1.30	1.02		0.069	0.066	0.085	14.2	16.3	
101A		1.99			1.88			0.121			21.6	
103A		1.40	1.23		1.24	0.42		0.080	0.052		15.3	6.6
104A		2.06	1.65		3.37	1.08		0.217	0.134		22.4	8.8
105A		0.93	1.02		-0.21	0.02		-0.013	0.003		10.2	5.5
107A		2.06	2.11		2.70	1.45		0.173	0.180		22.5	11.3

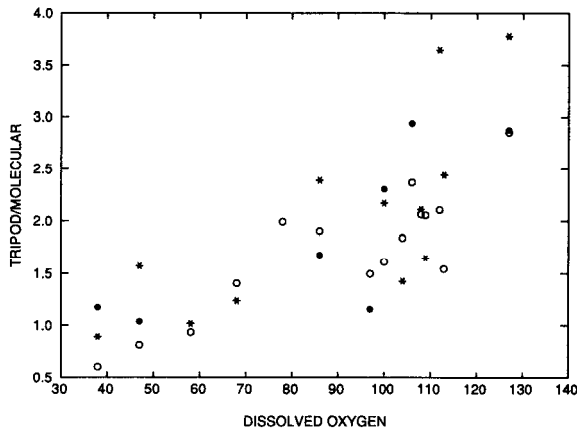


Figure 8. The ratio of the average tripod determined flux to the calculated molecular diffusive flux versus dissolved oxygen (μM) for oxygen (filled circles), nitrate (open circles) and Silica (asterisks). See Table 4 legend for diffusion coefficient references.

oxygen here, the apparent relationship may only be fortuitous because oxygen concentration, water depth and distance from shore are all correlated in the sampling area. Thus, the close match between the observed and molecular fluxes at low oxygen concentrations could result from: 1) exclusion or change in species composition of the irrigating organisms due to low oxygen concentrations, 2) decreased carbon rain rate to the deepest station to the extent that there is not enough substrate to support a population of irrigators, or 3) decreased importance of some unknown continentally derived factor that helps support macrobenthic irrigators. Nevertheless, the decrease in irrigation intensity affects the flux enhancement factor similarly for all solutes.

The similar flux enhancement factor for all three solutes at each station could be explained simply by macrobenthic burrow walls acting as increased surface area for contact with the overlying water. Thus, if the length scales of the solute gradients across the burrow walls are related to each other in a similar proportion to those across the sediment surface, then the enhancement factors would also be similar. Of the various macrobenthic irrigation models that have been developed, perhaps the most elegant is Aller's radial diffusion model, e.g., Aller (1980). Although the concepts are consistent with the flux enhancement factors found for Washington coast sediments, application of the model requires data on specific abundance and distribution of organisms, data which were not collected as part of this study. At least two other simple irrigation models have been proposed. The first is the parameterization of irrigation as an "eddy" or "bio-diffusion" coefficient (Vanderborgt *et al.*, 1977; McCaffrey *et al.*, 1980), viz:

$$\text{Tripod Flux} = \phi D_b \frac{dC}{dz}$$

where ϕ is the porosity, D_b is the bio-diffusion coefficient, and C is the concentration of the chemical species of interest. The second is the parameterization as a non-local source term:

$$\text{Tripod Flux} = \phi D_s \frac{\partial C}{\partial z} + \alpha \int_0^z (C_o - C_i) dz$$

where D_s is the sediment diffusion coefficient (the molecular diffusion coefficient corrected for tortuosity, e.g. Berner, 1980), $\partial C/\partial z$ is the gradient across the sediment water interface, C_o is the bulk concentration in the overlying water, C_i is the pore water concentration and α is the average (integrated) irrigation exchange coefficient (Emerson *et al.*, 1984; Archer and Devol, 1992; Martin and Banta, 1992). The irrigation coefficient, β , of Christensen *et al.* (1987b) is similar to the treatment above but with $\alpha = \phi\beta \cdot D_s$. Essentially, the non-local exchange model divides the total flux into two parts, the purely diffusive flux across the sediment surface and the biologically enhanced exchange component.

If an irrigation model is sufficient, then at any given station the irrigation parameter, either D_b , α or β , should be the same for all solutes. We calculated the irrigation parameters, D_b , α and β , for the three models discussed above using the observed tripod fluxes and pore water concentration profiles [for $\text{Si}(\text{OH})_4$ the expression used for irrigation was $\alpha(C_o - C_\infty)$, where C_∞ was the steady state pore water value reached at depth]. None of the models were very satisfactory (Table 4). When the irrigation coefficient was formulated as α , significantly different α 's were obtained for each solute, with the α value being about twice as great for oxygen as for nitrate and that for nitrate about twice as great as silicate; consequently, the relationships with oxygen were also different. Expression of irrigation in terms of β reduced the difference between NO_3^- and $\text{Si}(\text{OH})_4$ to about 25% but the β value for oxygen remained significantly higher. The biodiffusion model gave results similar to β model except that it was O_2 and NO_3^- that were in general agreement with $\text{Si}(\text{OH})_4$ as the outlier. Discrepancies of similar magnitude were obtained by Martin and Banta (1992) when they compared α values determined from Br^- addition and pore water ^{222}Rn deficits in cores from Buzzards Bay, with the ^{222}Rn deficit typically resulting in the higher estimate.

It appears, then, that none of the simple irrigation models work entirely satisfactorily when more than one solute is considered. This may be because the mechanism is not purely diffusive and that other processes such as mixing and advection should be included. It is interesting to note, however, that specific inclusion of D_s in the irrigation expression seems to reduce the variation between the three solutes and probably implies a strong diffusive dependence. In fact, including the molecular diffusion in D_b by division by D_s essentially results in the enhancement factor plotted in Figure 8 and, although there is much scatter, this treatment of mixing better describes the data than the others.

d. Organic carbon oxidation rate. The carbon oxidation rate can be estimated as the sum of the stoichiometric values calculated from the individual oxygen respiration, denitrification and sulfate rates. For the entire data suite the average benthic carbon oxidation rate was 19 ± 2 (s.e.) $\mu\text{mole cm}^{-2} \text{s}^{-1}$ or $72 \text{ gC m}^{-2} \text{y}^{-1}$. When only the shelf stations were considered, the average was 24 ± 1.3 (s.c.) $\mu\text{mole cm}^{-2} \text{s}^{-1}$ or $90 \text{ gC m}^{-2} \text{y}^{-1}$. This value is similar to the value estimated by Christensen (1989), although that value was based on Pamatmat's (1973) lower values for oxygen consumption (Fig. 5) but was heavily weighted by a high rate at the mouth of the Columbia River.

The overall average of $90 \text{ gC m}^{-2} \text{y}^{-1}$ can be compared to a primary production value of $740 \text{ gC m}^{-2} \text{y}^{-1}$ (Perry *et al.*, 1989). Thus it appears that about only 10% of the primary production is oxidized in the sediments. This is in contrast to the value of 25% determined for shelf sediments of the New York bight (Rowe *et al.*, 1988). One major difference between the two areas is that most of the New York bight shelf is less than 100 m deep, while about 50% of the Washington shelf is greater than 100 m deep. Given the well documented decrease in carbon rain rate with depth (Betzer *et al.*, 1984; Martin *et al.*, 1987), it may be that the lower average percentage of primary production oxidized by the sediments off Washington State simply reflects a lower percentage reaching the sediments. It has also been suggested that a significant portion of the primary production on the Washington shelf is exported to the slope (Christensen, 1989) whereas this is apparently not the case off New York (Falkowski *et al.*, 1988). Off-shelf export could also reduce the carbon rain rate to the sediments.

It is instructive to look at the relationship of carbon oxidation rate with depth. The overall carbon oxidation rate is primarily determined by the rain rate of carbon to the sediments. This decrease is well documented and can be described empirically as a power function of depth (Betzer *et al.*, 1984; Martin *et al.*, 1987). Furthermore, Christensen (1989) fit sediment oxygen consumption rates from various areas to a power function of depth. A power function also best describes the relationship between overall sediment carbon oxidation and depth for Washington margin sediments, $R = R_{100} (z/100)^\gamma$, where R is the rate, R_{100} is the rate at 100 m and γ is a constant (Fig. 9). In a power function the exponent determines how rapidly the rate attenuates with depth. For the Washington margin the exponent is -0.91 ± 0.10 (s.e.), indicating a relatively rapid decrease. As discussed previously, our calculation of the overall carbon oxidation rate neglects any oxygen consumption due to sulfide oxidation. However, it is unlikely that this would significantly alter the attenuation coefficient because the individual depth attenuation coefficients for O_2 , NO_3^- and SO_4^{2-} are all strikingly similar to the attenuation coefficient calculated above. Our depth dependent attenuation coefficient of -0.91 is not statistically different from the value of -0.858 determined from sediment trap data by Martin *et al.* (1987). Thus, assuming a direct relationship between benthic carbon oxidation rate and organic carbon rain rate, given the benthic carbon oxidation rate at 100 m depth (the reference depth of Martin *et al.*) both relationships predict substantially the same

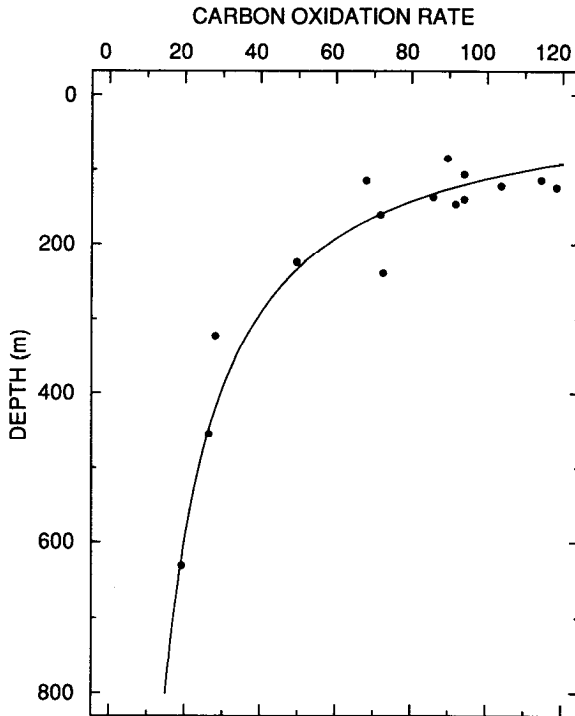


Figure 9. Carbon oxidation rate as calculated from the sum of the average oxygen flux, the average nitrate flux and the sulfate reduction rate versus depth. The fitted power curve is described in the text. It should be noted that the two shallow stations from the nearshore sand deposit are not included because cores could not be obtained for sulfate reduction rate measurement.

flux at the deep station. In contrast, Betzer *et al.* (1984) developed a relationship that predicts a carbon rain rate attenuation coefficient of -0.628 . This is a much lower attenuation rate and when scaled to the measured 100 m oxidation rate results in a benthic flux at the deepest station of about twice that observed, with extrapolation to deeper depths resulting in even greater discrepancies.

Although the above discussion is specific to the Washington margin and it assumes a constant relationship between benthic carbon oxidation and organic carbon rain rate, it does bring out an important point. Current sediment organic carbon mass balances and other analyses using benthic oxidation rates and carbon rain rates, as well as some paleoceanographic studies, frequently rely on such empirical relationships (e.g., Christensen, 1989; Jahnke *et al.*, 1990; Sarnthein and Winn, 1990; Suess, 1980). To continue to advance our understanding of the past and present carbon cycling in the oceans we need a better knowledge of how and why both organic carbon rain rate and benthic carbon oxidation rate vary with such variables as depth

and overlying water productivity and if these relationships differ between areas with and without oxygen minimum zones.

Acknowledgments. We thank R. Citterman and L. D. Lambourn for maintaining successful operation of the benthic tripod. L. Balistreri, B. Paul, E. Olsen, H. Hartnett and J. Brandes assisted in the analytical determinations. The manuscript has benefitted from suggestions provided by J. W. Murray. The tripod deployments could not have been done without the skillful seamanship of the captains and crews of the *R/V New Horizon* and *R/V Wecoma*. This work was supported by NSF Grants #OCE 86-01397 and #OCE88-17109.

REFERENCES

- Andersen, F. O. and W. Helder. 1987. Comparison of oxygen microgradients, oxygen flux rates and electron transport system activity in coastal marine sediments. *Mar. Ecol. Prog. Ser.*, *37*, 259–264.
- Aller, R. C. 1980. Diagenetic processes near the sediment-water interface of Long Island Sound. I. Decomposition and nutrient element geochemistry. *Adv. Geophys.*, *22*, 237–350.
- 1990. Bioturbation and manganese cycling in hemipelagic sediments. *Phil. Trans. R. Soc.*, *331(A)*, 51–68.
- Aller, R. C., J. E. Mackin, W. J. Ullman, C. Wang, S. Tsai, J. Jin, Y. Sui and J. Hong. 1985. Early chemical diagenesis, sediment-water solute exchange, and storage of reactive organic matter near the mouth of the Changjiang, East China Sea. *Cont. Shelf. Res.*, *4*, 227–251.
- Archer, D. E. and A. H. Devol. 1992. Benthic oxygen fluxes on the Washington shelf and slope: A comparison of *in situ* microelectrode and chamber flux measurements. *Limnol. Oceanogr.*, *37*, 614–629.
- Archer, D. E., S. E. Emerson and C. Reimers. 1989. Dissolution of calcite in deep-sea sediments: pH and O₂ microelectrode results. *Geochim. Cosmochim. Acta*, *53*, 2831–2846.
- Armstrong, F. A. J., C. R. Stearns and J. D. H. Strickland. 1967. The measurement of upwelling and subsequent biological processes by means of the Technicon Autoanalyzer and associated equipment. *Deep-Sea Res.*, *14*, 381–389.
- Bender, M. L., W. Martin, J. Hess, F. Sayles, L. Ball and C. Lambert. 1987. A whole core squeezer for interfacial pore water sampling. *Limnol. Oceanogr.*, *34*, 1214–1225.
- Bender, M. L., R. Jahnke, R. Weiss, W. Martin, D. T. Heggie, J. Orchardo and T. Sowers. 1989. Organic carbon oxidation and benthic nitrogen and silica dynamics in San Clemente Basin, a continental borderland site. *Geochim. Cosmochim. Acta*, *53*, 685–697.
- Berelson, W. M., D. E. Hammond and K. S. Johnson. 1987. Benthic fluxes and the cycling of biogenic silica and carbon in two southern California borderland basins. *Geochim. Cosmochim. Acta*, *51*, 1345–1363.
- Berner, R. A. 1980. *Early Diagenesis: a Theoretical Approach*. Princeton University Press, Princeton NJ, 241 pp.
- Betzer, P. R., W. J. Showers, E. A. Laws, C. D. Winn, G. R. Ditullio and P. M. Kroopnik. 1984. Primary productivity and particle fluxes on a transect of the equator at 153W in the Pacific Ocean. *Deep-Sea Res.*, *31*, 1–11.
- Billen, G. 1982. An idealized model of nitrogen cycling in marine sediments. *Am. J. Sci.*, *282*, 512–541.
- Blackburn, T. H. and K. Henrikson. 1983. Nitrogen cycling in different types of sediments from Danish waters. *Limnol. Oceanogr.*, *28*, 477–493.

- Carpenter, R., J. T. Bennet and M. L. Peterson. 1981. ^{210}Pb activities in and fluxes to sediments of the Washington continental slope and shelf. *Geochim. Cosmochim. Acta*, *45*, 1155–1172.
- Carpenter, R. and M. L. Peterson. 1989. Chemical cycling in Washington's coastal zone, in *Coastal Oceanography of Washington and Oregon*, M. L. Landry and B. Hickey, eds., Elsevier, NY, 367–509.
- Christensen, J. P. 1989. Sulfate reduction and carbon oxidation rates in continental shelf sediments, an examination of off shelf carbon transport. *Cont. Shelf. Res.*, *9*, 223–246.
- Christensen, J. P., J. W. Murray, A. H. Devol and L. A. Codispoti. 1987a. Denitrification in continental shelf sediments has major impact on Oceanic nitrogen budget. *Global Biogeochem. Cycles*, *1*, 97–116.
- Christensen, J. P. and G. T. Rowe. 1984. Nitrification and oxygen consumption in Northwest Atlantic deep sea sediments. *J. Mar. Res.*, *42*, 1099–1116.
- Christensen, J. P., W. M. Smethie and A. H. Devol. 1987b. Benthic nutrient regeneration and denitrification on the Washington continental shelf. *Deep-Sea Res.*, *34*, 1027–1047.
- Codispoti, L. A. 1989. Phosphorus vs nitrogen limitation of new and export production, in *Production of the Oceans: Present and Past*, W. H. Berger, W. H., V. S. Smetacek and G. Wefer, eds, Wiley and Sons, NY, 377–394.
- Codispoti, L. A. and J. P. Christensen. 1985. Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific. *Mar. Chem.*, *16*, 277–300.
- Devol, A. H. 1987. Verification of flux measurements made by *in situ* benthic chambers. *Deep-Sea Res.*, *34*, 1007–1026.
- 1991. Direct measurement of nitrogen gas fluxes from continental shelf sediments. *Nature*, *349*, 319–321.
- Devol, A. H., J. J. Anderson, K. Kuivila and J. W. Murray. 1984. A model for coupled sulfate reduction and methane oxidation in the sediments of Sannich Inlet. *Geochim. Cosmochim. Acta*, *48*, 993–1004.
- Emerson, S. R. and J. I. Hedges. 1988. Interpreting the organic carbon content of marine sediments. *Paleoceanogr.*, *3*, 621–634.
- Emerson, S. R., R. Jahnke and D. Heggie. 1984. Sediment water exchange in shallow water estuarine sediments. *J. Mar. Res.*, *42*, 709–730.
- Emerson, S. R., C. Stump, P. M. Grootes, M. Stuiver, G. W. Farwell and F. H. Schmidt. 1987. Estimates of degradable organic carbon in deep sea sediments from ^{14}C concentrations. *Nature*, *329*, 51–53.
- Falkowski, P., C. N. Flagg, G. T. Rowe, S. L. S. Smith, T. E. Whitley and C. D. Wirick. 1988. The fate of a spring bloom: export or oxidation? *Cont. Shelf. Res.*, *8*, 457–484.
- Florek, R. J. and G. T. Rowe. 1983. Oxygen consumption and dissolved inorganic nutrient production in marine coastal and shelf sediments of the Middle Atlantic Bight. *Int. Rev. ges. Hydrobiol.*, *68*, 73–112.
- Fossing, H. and B. B. Jørgensen. 1990. Oxidation and reduction of radiolabeled inorganic sulfur compounds in an estuarine sediment. *Kysing Fjord. Geochim. Cosmochim. Acta*, *54*, 2731–2742.
- Froelich, P. N., G. P. Klinkhammer, M. L. Bender, N. A. Luedtke, G. R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman and V. Maynard. 1979. Early oxidation of organic matter in pelagic sediments of the equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta*, *43*, 1075–1090.
- Grant, J., F. Volkaert and B. L. Roberts-Regan. 1987. Resuspendable organic matter in Nova Scotian shelf and slope sediments. *Cont. Shelf. Res.*, *9*, 1123–1128.

- Grebmeier, J. M. and C. P. McRoy. 1989. Pelagic-benthic coupling on the shelf of the northern Bering and Chukchi Seas. III. Benthic food supply and carbon cycling. *Mar. Ecol. Prog. Ser.*, 53, 79–91.
- Gross, M. G., A. G. Carey, G. A. Fowler and L. D. Klum. 1972. Distribution of organic carbon in surface sediment, Northeast Pacific Ocean, *in* The Columbia River Estuary and Adjacent Ocean and Bottom Waters: Bioenvironmental Studies, A. T. Pruter and D. C. Alverson, eds., University of Washington Press, Seattle, 254–264.
- Grundmanis, V. and J. W. Murray. 1977. Nitrification and denitrification in marine sediments from Puget Sound. *Limnol. Oceanogr.*, 22, 804–813.
- 1982. Aerobic respiration in pelagic marine sediments. *Geochim. Cosmochim. Acta*, 46, 1101–1120.
- Hammond, D. E., C. Fuller, D. Harmon, B. Hartman, M. Korosec, L. G. Miller, R. Rea, S. Warren, W. Berelson and S. W. Hager. 1985. Benthic fluxes in San Francisco Bay. *Hydrobiologia*, 129, 69–90.
- Hedges, J. I. and D. C. Mann. 1979. The lignin geochemistry of marine sediments from the southern Washington coast. *Geochim. Cosmochim. Acta*, 43, 1809–1818.
- Hedges, J. I. and J. H. Stern. 1984. Carbon and nitrogen determinations of carbonate-containing solids. *Limnol. Oceanogr.*, 29, 657–663.
- Hickey, B. M. 1989. Patterns and processes of circulation over the Washington continental shelf and slope, *in* Coastal Oceanography of Washington and Oregon, M. R. Landry and B. M. Hickey, eds., Elsevier, NY, 41–116.
- Jahnke, R. A. 1990. Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica Basin, California. *J. Mar. Res.*, 48, 413–436.
- Jahnke, R. A., C. E. Reimers and D. B. Craven. 1990. Organic matter recycling at the seafloor: intensification near ocean margins. *Nature*, 348, 50–54.
- Jørgensen, B. B. 1982. Mineralization of organic matter in the sea bed: The role of sulfate reduction. *Nature*, 296, 643–645.
- Jørgensen, B. B. and J. Sorensen. 1985. Seasonal cycles of O₂, NO₃⁻, and SO₄⁼ reduction in estuarine sediments: The significance of an NO₃⁻ reduction maximum in the spring. *Mar. Ecol. Prog. Ser.*, 24, 65–74.
- Kelley, J. R. and S. W. Nixon. 1984. Experimental studies of the effect of organic decomposition on the metabolism of a coastal marine bottom community. *Mar. Ecol. Prog. Ser.*, 17, 157–169.
- Kemp, W. M., P. Sampo, J. McCaffrey, M. Mayer, K. Henriksen and W. R. Bointon. 1990. Ammonia recycling versus denitrification in Chesapeake Bay sediments. *Limnol. Oceanogr.*, 35, 1545–1563.
- Koike, I. and J. Sorensen. 1988. Nitrate reduction and denitrification in marine sediments, *in* Nitrogen Cycling in Coastal Marine Environments, T. H. Blackburn and J. Sorensen, eds., Wiley, NY, 251–274.
- Lambourn, L. D., A. H. Devol and J. W. Murray. 1991. *R/V New Horizon 90-5* cruise report: water column and porewater data. University of Washington Special Report #110, University of Washington, Seattle, 34 pp.
- Lehrman, A. 1979. *Geochemical Processes: Water and Sediment Environments*. Wiley, NY, 481 pp.
- Li, Y. H. and S. Gregory. 1974. Diffusion of ions in seawater. *Geochim. Cosmochim. Acta*, 38, 703–714.
- Martin, J. H., G. A. Knauer, D. M. Karl and W. W. Broenkow. 1987. VERTEX: carbon cycling in the northeast Pacific. *Deep-Sea Res.*, 34, 267–285.

- Martin, W. R. and G. T. Banta. 1992. The measurement of sediment irrigation rates: A comparison of the Br⁻ tracer and ²²²Rn/²²⁶Ra disequilibrium techniques. *J. Mar. Res.*, 50, 125-154.
- Martin, W. R. and F. L. Sayles. 1987. Seasonal cycle of particle and solute transport processes in nearshore sediments: RN-222/Ra-226 and Th-234/U-238 disequilibrium at a site in Buzzards Bay, MA. *Geochim. Cosmochim. Acta*, 51, 927-943.
- McCaffrey, R. J., A. C. Meyers, E. Davey, G. Morrison, M. Bender, N. Ludtke, D. Cullen, P. Froelich and G. Klinkhammer. 1980. The relation between pore water chemistry and benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island. *Limnol. Oceanogr.*, 18, 31-44.
- McManus, D. 1972. Bottom topography and sediment texture near the Columbia river mouth, in *The Columbia River Estuary and Adjacent Waters: Bioenvironmental Studies*, A. T. Pruter and D. C. Alverson, eds., University of Washington Press, Seattle, 241-253.
- Nittrouer, C. A., R. W. Sternberg, R. Carpenter and J. T. Bennett. 1979. The use of ²¹⁰Pb geochronology as a sedimentological tool: application to the Washington continental shelf. *Mar. Geol.*, 31, 297-316.
- Pamatmat, M. M. 1973. Benthic community metabolism on the continental terrace and in the deep sea in the North Pacific. *Int. Rev. Ges. Hydrobiol.*, 58, 345-368.
- Perry, M. J., J. Boulger and D. C. English. 1989. Primary production in Washington coastal waters, in *Coastal Oceanography of Washington and Oregon*, M. R. Landry and B. M. Hickey eds., Elsevier, NY, 117-138.
- Praul, F. G. and R. Carpenter. 1984. Hydrocarbons in Washington coastal sediments. *Est. Coast. and Shelf. Sci.*, 18, 703-720.
- Premuzic, E. T., C. M. Benkovitz, J. S. Gaffney and J. J. Walsh. 1982. The nature and distribution of organic matter in the surface sediments of world oceans and seas. *Org. Geochem*, 4, 63-77.
- Reimers, C. E., R. A. Jahnke and D. C. McCorkle. 1992. Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle. *Biogeochem. Cycles*, 6, 119-224.
- Romankevich, E. A. 1984. *Geochemistry of Organic Matter in the Ocean*. Springer-Verlag, NY, 234 pp.
- Rowe, G. T., R. Theroux, W. Phoel, H. Quinby, R. Wilke, D. Koschoreck, T. E. Whittedge, P. G. Falkowski and C. Fray. 1988. Benthic carbon budgets for the continental shelf south of New England. *Cont. Shelf Res.*, 8, 511-528.
- Sarnthein, M. and K. Winn. 1990. Reconstruction of low and middle latitude export productivity, 30,000 years B. P. to present: Implications for global carbon reservoirs, in *Climate-Ocean Interaction*, M. E. Schlesinger, ed., Kulwer, Amsterdam, 319-342.
- Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnol. Oceanogr.*, 33, 702-724.
- Smith, K. L. Jr. 1987. Food energy supply and demand: A discrepancy between particulate organic carbon flux and sediment community oxygen consumption in the deep ocean. *Limnol. Oceanogr.*, 32, 201-220.
- Smith, K. L. Jr., R. J. Baldwin and J. L. Edelman. 1989. Supply of and demand for organic matter by sediment communities on two central North Pacific seamounts. *Deep-Sea Res.*, 36, 1917-1932.
- Smith, M. S. 1982. Dissimilatory reduction of NO₂ to NH₄⁺ and N₂O by a soil *Citrobacter sp.* *Appl. Environ. Micro.*, 43, 854-860.

- Stefansson, U. and F. A. Richards. 1964. Distribution of dissolved oxygen, density and nutrients off the Washington and Oregon coasts. *Deep-Sea Res.*, *11*, 355–380.
- Strickland, J. D. H. and T. R. Parsons. 1972. A practical handbook of seawater analysis. 2nd ed. *Bull. Fish. Res. Bd. Can.* 167, Ottawa. 311 pp.
- Suess, E. 1980. Particulate organic carbon flux in the oceans—surface productivity and oxygen utilization. *Nature*, *288*, 260–263.
- Vanderborght, J. P., R. Wollast and G. Billen. 1977. Kinetic models of diagenesis in disturbed sediments. Part 2. Nitrogen diagenesis. *Limnol. Oceanogr.*, *22*, 787–803.
- Walsh, J. J. 1988. *On the Nature of Continental Shelves*. Academic Press, San Diego, CA, 520 pp.
- 1991. Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. *Nature*, *350*, 53–55.
- Walsh, J. J., E. T. Premuzic, J. S. Gaffney, G. T. Rowe, G. Harbottle, R. W. Stoenner, W. L. Balsam, P. R. Betzer and S. A. Macko. 1985. Organic storage of CO₂ on the continental slope off the Mid-Atlantic Bight, the southwest Bering Sea, and the Peru coast. *Deep-Sea Res.*, *32*, 853–883.
- Whitledge, T. E., S. C. Malloy, C. J. Patton and C. D. Wirick. 1981. Automated nutrient analysis in seawater. Brookhaven National Laboratory Report No. 51398, Brookhaven, 216 pp.
- Willason, S. W. and K. S. Johnson. 1986. A rapid, highly sensitive technique for the determination of ammonia in seawater. *Mar. Biol.*, *91*, 285–290.
- Wollast, R. and R. M. Garrels. 1971. Diffusion coefficient of silica in seawater. *Nat. Phys. Sci.* *229*, 94–100.