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## **Simultaneous nitrate and oxygen respiration in coastal sediments: Evidence for discrete diagenesis**

by Jay A. Brandes<sup>1</sup> and Allan H. Devol<sup>1</sup>

### **ABSTRACT**

Oxygen and nitrate porewater profiles from sediments of Puget Sound, the Washington continental margin, and the Chukchi Sea were determined using a whole core squeezing apparatus. The two oxidants were observed to have equal sediment penetration depths and similar profile shapes in nearly all cores. Oxygen and nitrate, therefore, behaved in a similar manner in these shallow sediments: an observation that is not consistent with existing models of sediment diagenesis. A two-dimensional model was constructed in which nearly all oxidant ( $O_2$  and  $NO_3^-$ ) consumption took place in scattered, highly reactive discrete micro-sites. The model produced a sedimentary environment in which reactions at each micro-site were limited by oxidant concentrations with oxidant gradients extending well beyond the micro-sites into relatively nonreactive bulk sediments. Thus for a given depth surface within the sediment, oxygen concentrations were much lower at micro-sites than average concentrations on that surface. Furthermore, at most micro-sites oxygen concentrations were sufficiently low enough to permit simultaneous denitrification, which explained the apparent similarity between oxygen and nitrate concentration profiles within these sediments. The model suggests that a relatively few, short-lived reaction sites are responsible for most oxygen and nitrogen reduction within oxic sediments under shallow seas, and it is consistent with emerging concepts about the fate of organic carbon in coastal sediments.

### **1. Introduction**

Marine sedimentary respiration involves a series of oxidants that are commonly assumed to be consumed in order of free energy release, i.e. first oxygen, then nitrate and manganese, followed by iron and sulfate in that order (Froelich *et al.*, 1979). Also, it is assumed that the presence of a higher energy-releasing oxidant acts as an inhibitor of the use of lower energy releasing oxidants. Therefore oxidation in marine sediments is viewed as taking place in discrete depth zones. In deep-sea (> 3000) sediments where carbon fluxes are low, the zones where each oxidant is dominant are thick enough (> 1 cm) to be clearly delineated by conventional porewater collection techniques (Froelich *et al.*, 1979; Murray and Kuivilla, 1990; Reimers *et al.*, 1992). Shelf and slope sediments have higher reaction rates due to increased input of reducible carbon; here the distance between oxic surface sediments and the sulfate

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reduction zone may decrease to a few centimeters or less (Reimers *et al.*, 1992; Archer and Devol, 1992; Canfield *et al.*, 1993). At such small scales the measurement of oxidant concentrations using core sectioning techniques becomes problematic and can lead to errors when attempting to calculate fluxes or determine oxidant porewater profiles. For example, until recently nitrate fluxes into coastal sediments were seriously underestimated due to a lack of resolution in nitrate porewater profiles (Christensen *et al.*, 1987).

The relationship between oxygen and nitrate in shallow sediments has also been difficult to quantify due to the small vertical scale over which they are present in these locations. Previous studies of nitrate and oxygen respiration within shelf and slope sediments have usually relied upon measurements taken from different sub-cores for the two analytes (Jahnke *et al.*, 1989; Archer and Devol, 1992; Reimers *et al.*, 1992, Canfield *et al.*, 1993). In several published instances there appear to be examples of equal oxygen and nitrate penetration depths (e.g. Figs. 3 and 5 in Canfield *et al.*, 1993; Figs. 2 and 5 in Reimers *et al.*, 1992); however, the nitrate profile resolution is much coarser than that of the oxygen profile as a consequence of relying upon sectioned cores for the porewater nitrate profile as opposed to the finer scale oxygen profile determined by oxygen electrodes. Profiles obtained via the two methods are thus difficult to compare due to different integration scales both horizontally and vertically; nonetheless, the suggestion that oxygen and nitrate may exhibit equal penetration depths in shallow sediments is not consistent with classic models of sediment diagenesis in which different oxidizing agents are consumed sequentially with depth according to thermodynamic considerations (Berner, 1980). Additional evidence demonstrating sulfate reduction within "oxic" sediments has been observed (Canfield and Des Marais, 1991; Jørgenson and Bak, 1991; Canfield, 1993); this also suggests that sequential models may not be applicable in shallow sediments.

Whole core squeezing methods (Bender *et al.*, 1987; Martin *et al.*, 1991) allow for nitrate measurements on a much finer length scale, and more importantly allow for nitrate and oxygen measurements to be made on the same porewaters; as a consequence integration scales are the same for both solutes. This eliminates the possibility that measurements will be affected by different sample collection artifacts, but does not preclude sampling artifacts that affect both measurements. However, the relationships between solutes will be the least affected by artifacts.

In this paper we present oxygen and nitrate profiles collected from shallow continental margin sediments at three different oceanic environments. This study was undertaken to better understand how oxygen consumption and denitrification interact in sediments with sub-centimeter oxygen penetration depths. Specifically, we wanted to create a more realistic model describing the interaction of respiration of these two oxidants in shallow margin sediments.

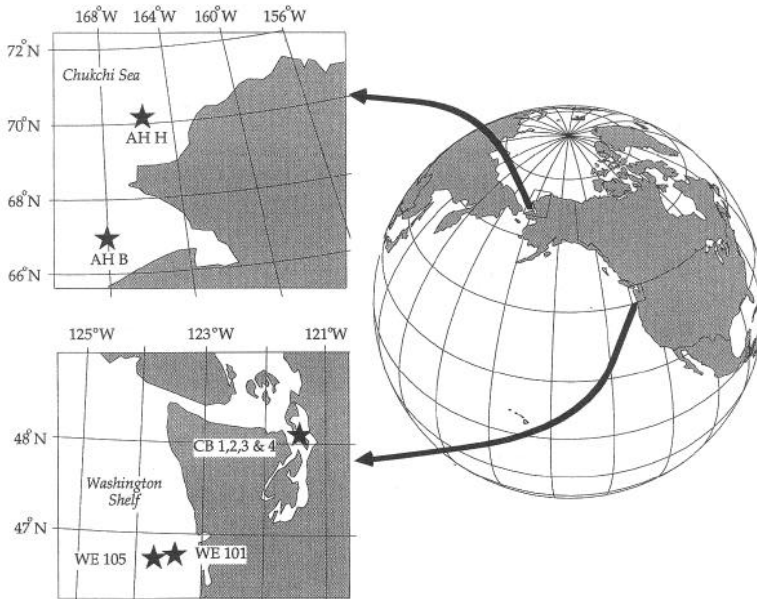


Figure 1. Sampling locations for stations discussed in text.

## 2. Methods

*Study area and sediment porewater profiling.* Measurements were made in sediments from the Washington State continental shelf, Puget Sound, and the Chukchi Sea (Fig. 1). Station locations and depths are given in Table 1.

Sediment cores and overlying waters were collected using a variety of sampling methods. Sediments from the Washington shelf were collected using a Mark 2 box corer and a HAPS corer was used in the Chukchi Sea. In 1992 a Soutar box corer was

Table 1. Names, locations, depths, core collection devices used, oxygen and nitrate penetration depths, interface tilt and subcore diameter for stations discussed in this paper.

| Station name | Location         | Depth (m) | Core collection device | $\text{O}_2$ Penetration depth (mm) | $\text{NO}_3^-$ Penetration depth (mm) | Interface tilt (mm) | Subcore diameter (mm) |
|--------------|------------------|-----------|------------------------|-------------------------------------|--|---------------------|-----------------------|
| AH B         | Chukchi Sea      | 45        | HAPS corer             | 8–10                                | 8–10                                   | <.7                 | 135                   |
| AH H         | Chukchi Sea      | 25        | HAPS corer             | 8.5–9.5                             | 12–14                                  | .7                  | 135                   |
| CB 1         | Puget Sound      | 45        | Soutar corer           | 4.5                                 | 4                                      | 3.5                 | 70                    |
| CB 2         | Puget Sound      | 45        | Soutar corer           | 6–7                                 | 7                                      | 2.8                 | 135                   |
| CB 3         | Puget Sound      | 60        | Soutar corer           | 4–6                                 | 4–6                                    | 2.8                 | 135                   |
| CB 4         | Puget Sound      | 60        | Soutar corer           | 5–8                                 | 4–5                                    | 7.7                 | 135                   |
| WE 101       | Washington Shelf | 145       | Mark III corer         | 5                                   | 5                                      | 3.5                 | 70                    |
| WE 105       | Washington Shelf | 330       | Mark III corer         | 7                                   | 4                                      | 3.5                 | 70                    |

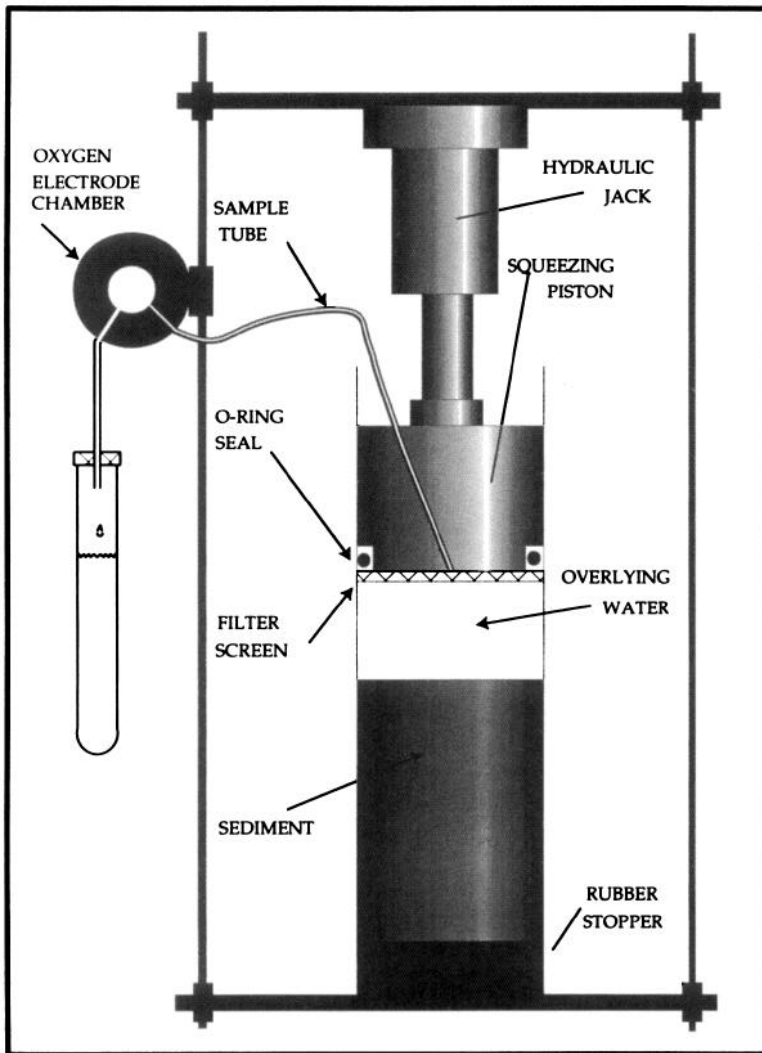


Figure 2. Whole Core Squeezing (WCS) apparatus.

used to collect Puget Sound sediments, while in 1993 an *in situ* benthic flux chamber (Devol, 1987) was employed in a core collection only mode. Subcores from each principal core were collected immediately after on-deck securing of the coring device, and the overlying waters and porewaters were sampled thereafter using a Bender *et al.* (1987) type whole core squeezing (WCS) apparatus (Fig. 2). The total time taken for whole core squeezing through the oxic zone was normally less than 25 minutes (from initial subcoring) or about 15 minutes (from emplacement of WCS piston into subcore). A calibrated jack mounted on the upper plate of the apparatus provided

the force to move the piston used to squeeze the core. Sample waters were expressed through an 8 micron mesh filter attached to the underside of the WCS piston, channeled into grooves milled into the underside of the piston, then through polyethylene tubing into a temperature controlled chamber where oxygen concentrations were measured with an inline polarographic electrode (Radiometer model E5046). Total system volume (filter + tubing + electrode) was less than 20% of the each subsample's volume. After passing through the oxygen electrode chamber, sample waters were collected in polyethylene test tubes for analysis of nitrate and nitrite.

Nitrate and nitrite concentrations were measured by the cadmium reduction method (Armstrong *et al.*, 1967), using a low volume, nonsegmented FIA system (Anderson, 1979; Lambourn *et al.*, 1991). Oxygen electrode readings were calibrated against independently determined overlying water oxygen concentration (Winkler titration or Orion oxygen electrode). Zero oxygen concentrations were assumed when the electrode current consumption reached an asymptotically low value over several samples. After each movement of the WCS piston, a one minute equilibration period was allowed prior to recording the electrode current consumption. Longer waiting periods were not found to affect the measured current.

### 3. Results

*a. Depth of oxygen and nitrate penetration.* In many nearshore and continental shelf sediments, the combination of high surface productivity and relatively shallow water column depth results in high organic carbon fluxes to the sediments, which, in turn, promotes high respiration rates. These high rates are typically evidenced by shallow dissolved oxygen penetration depths, usually on the order of < 1 cm (Archer and Devol, 1992; Canfield *et al.*, 1993). Directly calculating oxidant penetration depths from WCS data was not straightforward in our study because the sediment subcores were usually tilted with respect to the WCS sampling piston. Therefore some averaging between overlying waters and porewaters took place in samples from the region between first piston contact with sediments and last contact with overlying waters (Fig. 3). A simple method of calculating true oxidant penetration depths is to measure the distance between the last contact point of the WCS piston with the sediment surface and the zero concentration depth. This method assumes that the whole subsampled sediment column is tilted with respect to the WCS piston. Calculated in this way, dissolved oxygen penetration depths in Washington shelf sediments were estimated at 5 to 7 mm (Table 1). These values were similar to penetration depths measured in the same region by Archer and Devol (1992) using an *in situ*  $\text{O}_2$  electrode mounted on a benthic flux chamber. Oxygen and nitrate penetration depths in Puget sound sediments varied from 4 to 8 mm, averaging about 6 mm, while Chukchi Sea sediment penetration depths were significantly deeper and varied between 10 and 14 mm. Nitrate (and nitrate + nitrite) penetration depths

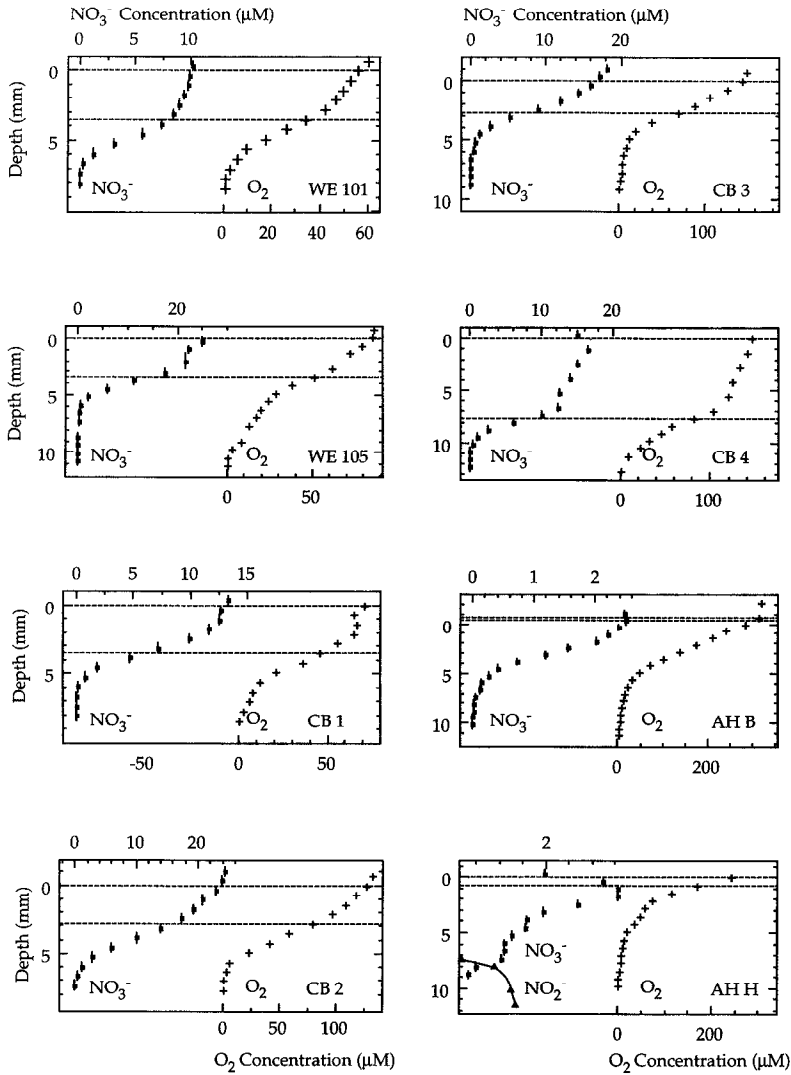


Figure 3. Oxygen and nitrate porewater concentrations vs. sediment depth (mm). Oxygen data are represented by crosses and are plotted against the lower axis, while nitrate data are represented by bars (plus squares at the midpoint of each bar) covering the interval over which the sample was collected, and are plotted against the upper axis. Nitrate data are represented by triangles connected by a solid line in profile AH H and are plotted against the upper axis. Horizontal dotted lines indicate the depth at which the WCS piston made initial contact with the sediments (upper) and the depth at which the last visible presence of overlying water between the WCS piston and the sediment surface was observed (lower).

were similar to oxygen, and were not observed to be greater than oxygen penetration depths in most cases. The similarity of penetration depth between the two oxidants was a robust feature and appeared in sediments with overlying oxygen and nitrate concentrations ranging from 60 to  $>300 \mu\text{M/L}$  and 25 to  $3 \mu\text{M/L}$ , respectively (Fig. 3).

*b. Porewater profiles.* All of the oxygen and nitrate profiles except those from Chukchi Sea sediments (which had little surface tilt) exhibited similar “reverse S” shapes which, as we will later show, were due to distortion of porewater profiles by the process of sampling an irregular surface with the WCS. Despite this distortion, nitrate and oxygen concentrations also exhibited similar profile shapes and curvature (Fig. 3). The similarity of curvature was most easily seen in the plot of the first derivative of concentration vs. depth (Fig. 4). Again, in most cases, the derivatives of the oxygen and nitrate profiles were very similar. The most notable feature in each derivative plot is a minimum in value that coincides with the final observed entrance of the WCS piston into the sediments. Therefore, in both penetration depth and porewater profile, oxygen and nitrate appear to behave in a similar fashion within the study sediments. This observation leads to the hypothesis that both oxidants are utilized similarly throughout most of the oxic layer of these sediments and implies that the removal rates of oxygen and nitrate in coastal sediments are closely tied, a finding that is at odds with previous models of nitrate and oxygen respiration that assumed a clear separation of the two processes (Goloway and Bender, 1982; Jahnke *et al.*, 1982; Bender and Heggie, 1984); however, it is in accordance with measurements by Canfield *et al.* (1993), who found that the oxygen consumption and denitrification zones could not be clearly separated in some of their sediment samples.

*c. Correlations with independent measurements.* Although most profiles show identical oxygen and nitrate penetration depths, there are individual variations that indicate the overall character and features of each core profile are preserved. Profiles taken from the Chukchi Sea have subsurface maxima in  $\text{NO}_3^-$  that are not observed in the Puget Sound or Washington Shelf profiles (Fig. 3). Also, a clear nitrite maximum occurred at the base of the oxic zone at station AH H that was not observed in any of the other cores. The presence of subsurface nitrate maxima at AH B and AH H indicates a nitrate flux out of the sediments to the overlying waters, as was observed in benthic flux chamber measurements collected at the same site (Devol, unpublished data). Sedimentary nitrate profiles collected from Puget Sound and the Washington shelf decrease sharply with depth, indicating a flux of nitrate into the sediments from overlying waters; again this is confirmed by benthic flux chamber measurements made in these areas (Devol and Christensen, 1993; Devol, unpublished data).



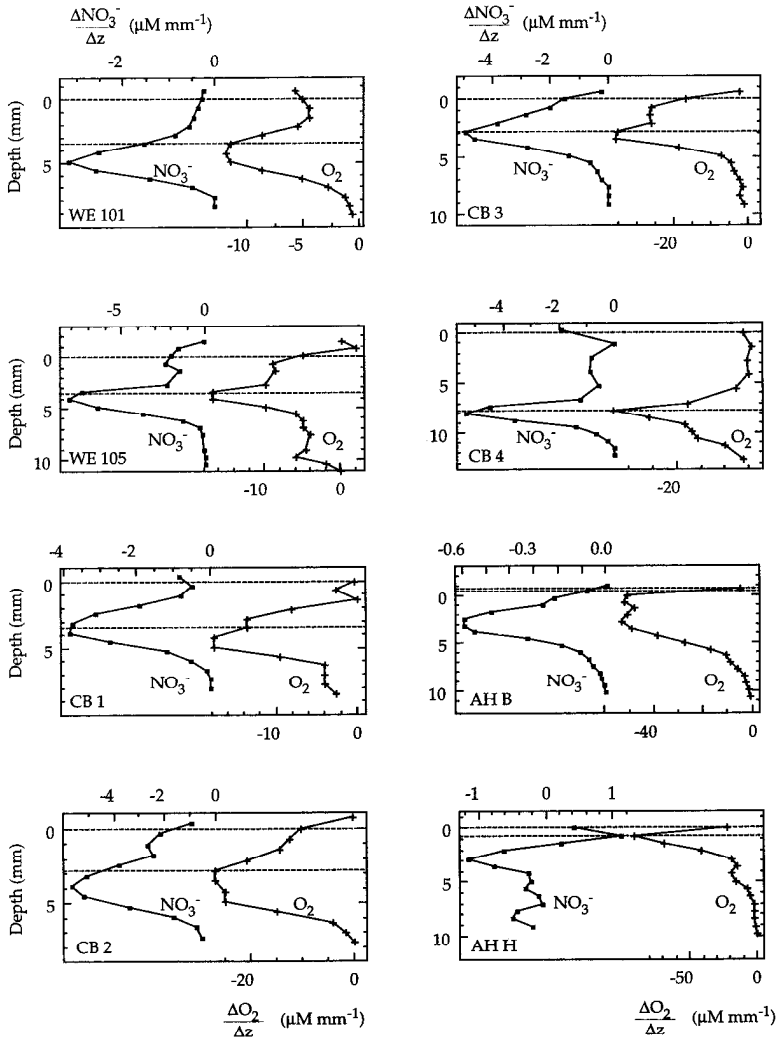


Figure 4. First order derivatives of concentration ( $\Delta[c]/\Delta z$ ) vs. depth (mm) for oxygen and nitrate. Symbols and axis designations are the same as Figure 3.

#### 4. Profile deconvolution

**Sampling artifacts.** Prior to analyzing the relationship between porewater oxygen and nitrate, sampling distortions introduced by WCS need to be addressed. The primary questions to be answered are; (1) how does the WCS sampling technique affect the true sediment porewater profiles and, (2) is the relationship between the oxygen and nitrate altered by this method? The WCS method integrates porewaters over a significant horizontal area, which may include porewater signals from several micro-environments with differing oxygen and nitrate concentrations, so care must be taken

in interpreting the results and in modeling the data. The primary limitation of the method is that its accuracy in sampling porewaters across the sediment water interface depends upon the degree of tilt of the sediment surface in relation to the core tube walls, and the subsequent integration of overlying waters and porewaters. Sediments are often skewed in reference to the box core or may contain topographic features such as local basins and hills, and some surface unevenness is usually present due to small scale features. Therefore there is usually some interval where the WCS integrates both porewaters and overlying waters.

The interaction between the tilted sediment surface and the WCS piston produces the "reverse S" shape in the porewater profiles (Fig. 3). As is illustrated in Figure 5, when the piston moves through the subcore from position A through B to C, the ratio of overlying waters to porewaters decreases. By point C, the whole piston is in contact with the sediments and the sample is entirely porewater, albeit porewater from a variety of depths. This results in a series of porewater samples that consist of a moving average from different sediment layers and/or overlying waters. The overall effect of this process is to produce porewater profiles that exhibit a reverse "S" shape (Fig. 5).

This sampling artifact is perhaps more clearly observed in the plots of  $\Delta[\text{O}_2]/\Delta z$  and  $\Delta[\text{NO}_3^-]/\Delta z$  vs. depth (Fig. 4). Both profiles at all stations exhibit subsurface minima in the derivative values. The true, undistorted derivative profile of  $\text{O}_2$  with depth within the sediments should reach its most negative value very near the surface of the sediment, because there is a sharp decrease in concentration at that point between overlying waters and porewaters. Our measured profiles (Fig. 4) do not show the most negative derivative value to exist at the point of first contact (depth = 0 in Fig. 5) between the sediments and the piston, but instead show a minimum that coincides with the point of last contact (depth  $Z_1$  in Fig. 5) between the sediments and the piston in each core. To explain this we return to our conceptual model (Fig. 5). Before the piston first contacts the sediment (point A, Fig. 5), the sample consists of overlying waters that are identical, and the derivative ( $\Delta[\text{O}_2]/\Delta z$  or  $\Delta[\text{NO}_3^-]/\Delta z$ ) is zero. As the WCS piston enters the sediments and begins to integrate overlying waters with porewaters (B in Fig. 5) the sample concentrations begin to drop with respect to the previous sample, and the derivative becomes more negative. Only when there is no contribution of the overlying waters (sample C, Fig. 5) can the derivative begin to rise toward zero as porewaters with smaller concentration changes are integrated into the sample.

The sampling distortions introduced by the WCS method have a significant effect on the overall shape of the individual porewater profiles, and must be taken into account when porewater respiration is modeled. However, because oxygen and nitrate concentrations at each depth were determined from the same porewater sample, both profiles are affected to the same degree and their relationship is unaffected. In spite of the distortion introduced by the process of sampling by WCS

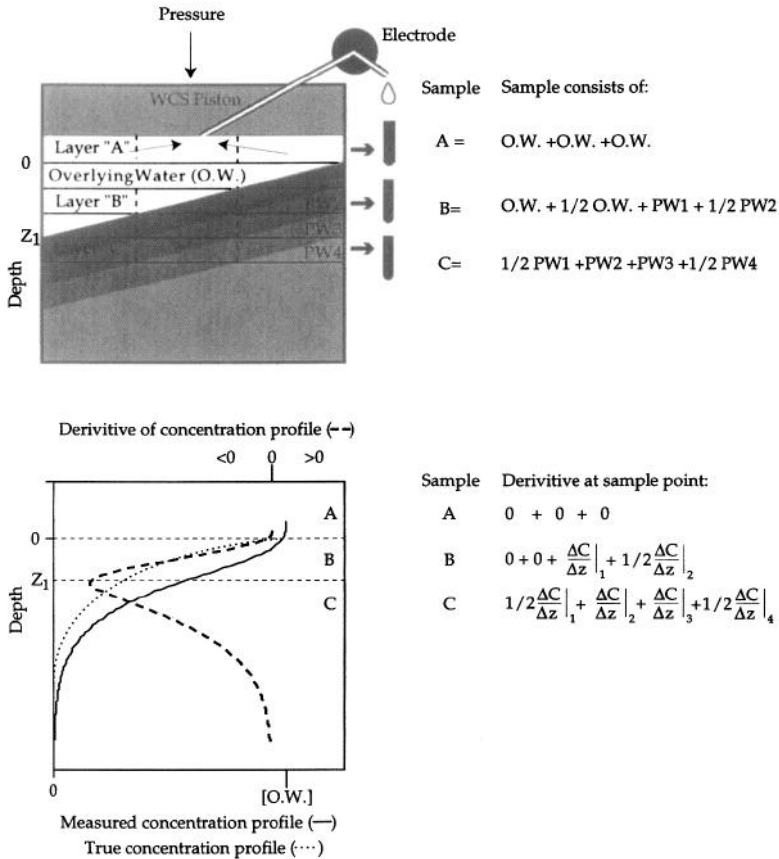


Figure 5. Process of sampling across a tilted interface by WCS. Upper figure illustrates a tilted core and the composition of samples collected as WCS piston moves through positions A, B and C into core. Depth 0 is defined as the point of first contact of the WCS piston with the sediment surface, while depth Z<sub>1</sub> is defined as the point of last contact by the WCS piston with overlying waters. Lower figure illustrates the resulting concentration (plotted against lower axis) and concentration derivative ( $\Delta[c]/\Delta z$ , plotted against upper axis) profiles vs. sediment depth generated by WCS sampling, the approximate positions in profile occupied by samples collected at A, B and C, as well as the true, undistorted oxidant profile (plotted against lower axis) within the sediment.

over a tilted interface, the observation is preserved that nitrate and oxygen behave in a similar fashion, with similar penetration depths and similar profile curvatures within the sediments studied.

**5. Pore water models**

a. *One dimensional models.* To examine the relationship between oxygen and nitrate in these sediments one dimensional models were investigated. One dimensional

models have been employed to model porewater concentration profiles collected by electrode and core sectioning techniques (Wilson *et al.*, 1985; Revsbech and Jørgensen, 1986; Reimers, 1987; Reimers *et al.*, 1992; Archer and Devol, 1992; Canfield *et al.*, 1993). Although the appropriateness of such models relies upon the degree of heterogeneity of the sediments, one dimensional models have been successfully employed in modeling the larger scale features contained in porewater profiles, and can be used as an "Occam's razor" to discard unlikely hypotheses. For simplicity's sake, the model results for one typical Puget Sound station are presented.

The general equation employed for oxygen was the steady-state form of the diffusion-reaction equation (Berner, 1980) with a concentration-dependent reaction rate term:

$$0 = \frac{\partial}{\partial z} D_{\text{O}_2} \frac{\partial \text{O}_2}{\partial z} - R_{\text{O}_2} \cdot [\text{O}_2] \quad (1)$$

where  $D_{\text{O}_2}$  is the sediment diffusion coefficient for oxygen, and  $R_{\text{O}_2}$  is the first order oxygen respiration coefficient. In this form the general solution to Eq. (1) will be exponential.

In the same fashion as oxygen, nitrate profiles were modeled using a reaction-production-diffusion model:

$$0 = \frac{\partial}{\partial z} D_{\text{NO}_3^-} \frac{\partial \text{NO}_3^-}{\partial z} - R_{\text{NO}_3^-} [\text{NO}_3^-] + \frac{16}{138} R_{\text{O}_2} \cdot [\text{O}_2] \quad (2)$$

where  $D_{\text{NO}_3^-}$  is the sediment diffusion coefficient for nitrate,  $R_{\text{NO}_3^-}$  is the first order denitrification rate constant,  $R_{\text{O}_2}$  is the first order oxygen respiration rate constant obtained from Eq. (1), and 16/138 is the amount of nitrate produced during oxygen respiration given Redfield stoichiometry. Diffusion coefficients,  $D_{\text{O}_2}$  and  $D_{\text{NO}_3^-}$ , were corrected from the free water values (Li and Gregory, 1974; Lehrman, 1979) for tortuosity and porosity, using Archie's relation (Berner, 1980), and an assumed constant porosity of .85. If a significant porosity gradient existed in the upper sediment column the assumption of constant porosity would lead to an underestimate of the model respiration, but this error would affect both nitrate and oxygen profiles similarly. As we are using these models to compare sedimentary respiration rates of oxygen and nitrate in sediments to each other, the effects of this error will be minimized. Similarly, irrigation terms were not included.

We cannot with certainty define a nitrification rate expression, as we do not have detailed  $\text{NH}_4^+$  profiles from the upper 1 cm of these sediments. However, for consistency we chose to model the nitrification term as a Redfield ratio dependent rate (Eq. 2), which, for the Puget Sound station results in a total nitrification value roughly equal to the nitrate flux into the sediments. Nitrogen gas flux data (Devol, 1987; Devol and Christensen, 1993; A. Devol, unpublished data, J. Brandes, unpublished data) also suggest that the sedimentary nitrification term is of the same order

as the nitrate flux into the sediments in both the Washington shelf and Puget Sound, and therefore a significant internal sedimentary nitrate source exists in these areas.

The model sediment column was divided into "oxic" and "suboxic" zones, with denitrification only allowed in the "suboxic" zone and set to zero in the "oxic" zone. Models were solved numerically using a tridiagonal matrix solution (Press *et al.*, 1992) given the upper boundary condition that the surface concentration equal the overlying water concentration, and that there is no flux out of the model at the lower boundary.

Finally, because the porewater chemical profiles were distorted by sampling over a tilted interface, the model results were filtered to mimic this effect. The actual profile cannot be accurately deconvoluted to remove the distorting effects of WCS sampling because doing so would require accurate knowledge of the exact surface topography. While we know the approximate shape and tilt of the sampled sediments, completely accurate surface maps of each sediment's surface were not collected. Distorting the model solution is therefore the simplest method to allow comparison of solutions to observed data. If the WCS subcore were rectangular and the sediment surface consisted of a tilted plane, then each sample collected would be a simple moving average of the chemical concentrations in each section impinged upon by the piston (Fig. 5). However, because the core is round, more waters are obtained from the middle of the cylinder than from the edges (from the perspective of Fig. 5) thus, in the integrated sample, the waters from the middle of the core are weighted more than those from the edges. This effect was mimicked by filtering the model result through a sine-weighted moving average:

$$[\text{conc}]_{\text{ave.}} = \frac{\sum_{n=1}^{m+1} \sin\left(\frac{n\pi}{m+1}\right) [\text{conc}]_i}{(m+1)^* \sum_{n=1}^{m+1} \sin\left(\frac{n\pi}{m+1}\right)} \quad (3)$$

where  $m$  is the number of model layers over which the solution is filtered. The value of  $m$  was set equal to the surface tilt divided by the model resolution.

The primary objective of this study was to investigate the relationship between denitrification and oxygen consumption. Previous denitrification models (Goloway and Bender, 1982; Jahnke *et al.*, 1982; Bender and Heggie, 1984) have been based upon the assumption that denitrification is completely inhibited by the presence of  $\text{O}_2$  (Knowles, 1982). This assumption is more or less corroborated by laboratory and field studies, although denitrification or denitrification enzyme activity in the presence of oxygen (Sacks and Barker, 1949; Justin and Kelly, 1978; Robertson and Kuening, 1984; Robertson *et al.*, 1989) has been observed. Ample evidence from the water column (Broecker, 1974) and deep sea sediments where oxygen does not decrease to zero (Froelich *et al.*, 1979; Jahnke *et al.*, 1989; Martin *et al.*, 1991;

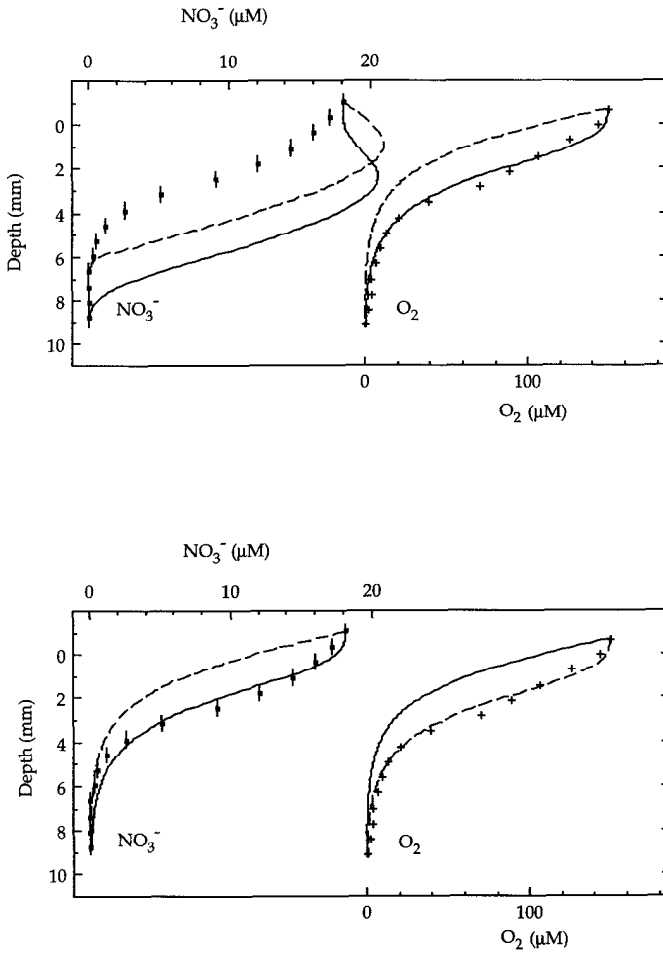


Figure 6. One-dimensional model results for station CB 3. Dotted lines represent one-dimensional model results, while solid lines represent model results after the WCS simulation filter is applied. Upper figure gives model results for constant reaction, no oxic denitrification case. Lower figure illustrates model result for constant reaction rate case with denitrification allowed throughout the entire model sediment column. Axes and symbols are identical to those in Figure 3. Model porosity was .85.

Reimers *et al.*, 1992) indicates that denitrification does not occur in the ocean where oxygen is present, however. The model was first solved for the null case where denitrification was not allowed in the presence of oxygen (Fig. 6). For this case the model reproduced the oxygen concentration profile reasonably well, however, it did not reproduce the observed nitrate concentration profile. Indeed, any model with separate depth zones of oxygen and nitrate removal cannot describe both solute profiles when they are so closely correlated in shape and penetration depth. A model

in which both oxygen and nitrate are removed at an apparently equal depth within the sediment (e.g. Wilson *et al.*, 1985), although capable of matching the equal penetration depth aspect of our data, is also insufficient to model both profiles because this type of model required that most of the bulk porewater concentration gradient be diffusive in nature and that the nitrate and oxygen profiles be different due to nitrification. Our profiles clearly indicate that both oxidants exhibit curvature throughout the oxic sediment layer, and hence imply that nitrate and oxygen respiration is taking place throughout much of the oxic layer.

To illustrate this point, the model was also solved for the case where denitrification was allowed at all oxygen concentrations; i.e. both oxygen and nitrate removal rates were first order throughout. With these assumptions nitrate and oxygen profiles were fit reasonably well (Fig. 6). It is interesting to note that the nitrate model fit was dependent on the oxygen model through the nitrification term (this term provided half of the total nitrate available in the sediments for denitrification). A dependence on the oxygen consumption produced a bias in the nitrification term toward the sediment surface that required denitrification to take place in very oxic conditions, because no subsurface nitrate peak was observed in the Puget Sound profile. A shift of nitrification to the lower, less oxic reaches of the sediment column would reduce the model requirement for "oxic" denitrification, but would not eliminate it. This is due to the close relationship observed between oxygen and nitrate profiles.

Although the one-dimensional model presented above will reasonably reproduce the observed profiles, it is unsatisfying because it requires denitrification at high average oxygen concentrations, which is inconsistent with most laboratory and field studies. It is more likely that the sediments investigated were not homogenous, but instead had suboxic zones within their upper reaches that allowed denitrification. To model this type of system we investigated two multidimensional models.

*b. Multidimensional models.* There are two types of published multidimensional models that theoretically allow suboxic zones to coexist horizontally adjacent to oxic zones; burrow irrigation models (Aller, 1980; 1982) and a spherical microzone model (Jørgensen 1977; Jahnke, 1985). Benthic irrigation is an important contributor to the overall flux of chemicals between the sediments and overlying waters on the Washington Shelf (Devol and Christensen, 1993). However, for the Washington shelf, porewater oxygen profiles collected by WCS had penetration depths (5–8 mm, Table 1) very similar to those estimated from *in situ* O<sub>2</sub> microelectrode profiling (4–8 mm, Archer and Devol, 1992). Archer and Devol (1992) argued that their oxygen profiles were largely unaffected by irrigation. As the profiles obtained by WCS give substantially the same results, it appears that, on the scale sampled by this method oxygen profiles and presumably nitrate profiles do not appear to be significantly affected by irrigation. At the other sites investigated in this report *in situ* oxygen profile data do not exist, but given the similarity between the penetration

depths in the Washington shelf and Puget sound (Table 1) and apparent low importance of benthic irrigation in Arctic waters (Hulth *et al.*, 1994), we feel justified in not investigating this model further.

The microzone model (Jahnke, 1985) was also investigated. This model relies upon porous reaction sites or microzones distributed within the sediment. In order for this model to produce significant net denitrification in the middle and upper oxic sediment column, significant suboxic volumes within mid and upper sediment microzones need to be generated. This requires high respiration rates and creates a sharp discontinuity in the gradient between the porewaters within and outside of each microzone, because the model uses the bulk porewater concentration at a given depth to set the microzone's outer boundary condition.

This sharp change in concentration gradient across the porewater-microzone boundary is the primary shortcoming of the microzone model. Although a sharp change in the  $\text{O}_2$  gradient between the overlying waters and the sediment porewaters is found at the sediment's surface (Archer and Devol, 1992; Canfield *et al.*, 1993), this break is supported by the very large change in the diffusion coefficient at this point, from  $\sim 1 \text{ cm}^2/\text{sec}$  in overlying waters outside the diffusive boundary layer to  $\sim 1 \times 10^{-5} \text{ cm}^2/\text{sec}$  in porewaters (Boudreau and Guinasso, 1982). There is, however, no reasonable expectation of a similar 5 orders of magnitude change in diffusion coefficient across the porewater-microzone boundary. Measured diffusion coefficients in biological structures and other organic materials found in sediments are within an order of magnitude of typical porewater coefficients (Aller, 1983). Therefore, without a physical barrier to diffusion, any gradients generated within these microzones should propagate outward into the surrounding porewaters. Indeed, Alldredge and Cohen (1987) studied suboxic and anoxic microzones in fecal pellets and found that the diffusive gradient extended well away from the physical boundaries of the pellets. That these gradients were established in a turbulent environment is even more convincing evidence that, in a sediment environment where diffusion coefficients are orders of magnitude lower, any highly reactive microzones would have diffusive paths extending far beyond the microzone's actual boundaries.

*c. A discrete diagenesis model.* To better understand the processes governing oxygen and nitrate respiration in coastal sediments, it is worthwhile to examine what is known about the primary source of reductant, carbon. Most of the carbon reaches these sediments in the form of discrete pellets of fecal material that rain down from the euphotic layer. One can hypothesize that the initial diagenesis of this carbon would be concentrated at discrete sites consisting of these fecal materials, starting with their arrival at the sediment surface. This suggests a model featuring discrete, rather than homogeneously distributed, diagenesis of carbon within shallow sediments. Rapid diagenesis of discrete particles would create highly respiring sites,



which would influence the general porewater chemistry of the surrounding sediments through generation of diffusive gradients extending away from the sites. Gradient extension would produce oxidant concentrations at the surface of each reaction site that would be at a level much below that of the bulk porewaters. The steepness of the diffusive gradient extending away from each reaction site would depend upon the interactions between the reaction site and surrounding porewaters, and would be steeper in the direction of the sediment surface but less steep in the direction of a nearby reaction site, or below the site. In order to model these processes numerical models based upon the two dimensional form of the steady-state reaction-diffusion equation were used:

$$0 = D_{O_2} \left( \frac{\partial^2 O_2}{\partial z^2} + \frac{\partial^2 O_2}{\partial x^2} \right) - Ro_a[O_2] - Ro_b \quad (4)$$

for oxygen and

$$0 = D_{NO_3^-} \left( \frac{\partial^2 NO_3^-}{\partial z^2} + \frac{\partial^2 NO_3^-}{\partial x^2} \right) - Rn[NO_3^-] + Ro_b \quad (5)$$

for nitrate. In contrast to the model of Jahnke (1985), this model examines the interactions between highly respiring micro-sites and surrounding porewaters.  $D_{O_2}$  and  $D_{NO_3^-}$  have been defined previously. The bulk of the oxygen respiration term,  $Ro_a$ , was confined to a few ( $< 20$ ) discrete sites consisting of one model grid point each ( $100 \times 100$  microns in size), while the rest of the sediment was assumed to have a low bulk oxygen uptake,  $Ro_b$ , sufficient to oxidize ammonium to nitrate assuming Redfield stoichiometry for oxygen respiration (this was about 10% of the total oxygen consumption). This differs from the nitrification assumptions given for the one dimensional model discussed previously in that the bulk of the oxygen respiration term is decoupled from the nitrification term, but the assumption is reasonable because ammonium is soluble and is distributed throughout the sediment. Denitrification,  $R_m$ , was confined to the same discrete sites as oxygen respiration, and only allowed to take place where oxygen concentrations had dropped below  $10 \mu\text{M}$  (Knowles, 1982). For simplicity the diffusion coefficients for both  $O_2$  and  $NO_3^-$  were taken as equal in both  $x$  (horizontal) and  $z$  (vertical) directions, and a constant porosity throughout the sediment column was again assumed.

The equations were solved over a  $100 \times 100$  grid using a point successive over relaxation technique (Press *et al.*, 1992). Reactive site distribution and site respiration rate were adjusted until a best fit by eye was obtained. The model surface concentration was set equal to the observed surface concentration, while zero flux conditions were set at the other three model boundaries. Respiration was confined to one model grid point per reactive site. Strictly speaking, the model cannot examine each reaction site in detail due to its limited resolution; much larger model reactive

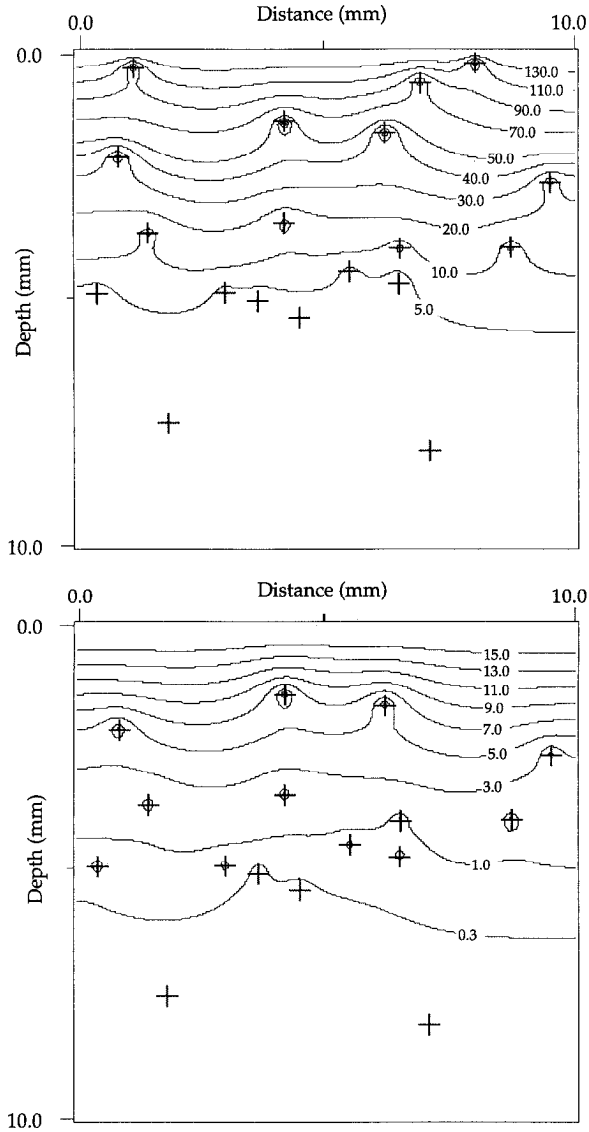


Figure 7. Contour graph of results for two-dimensional model for station CB 3 for oxygen (upper) and nitrate (lower). Model dimensions are  $1 \times 1$  cm. Crosses represent discrete microzone sites. Contour lines are in  $\mu\text{M}$ . Model porosity is .95.

sites or higher model resolutions would be required to do so. However, the influence of each microzone on the surrounding sediment chemistry and the cumulative effect of microzone respiration on the total sediment oxidant profile could be observed.

The two-dimensional model was applied to two data sets, station CB 3, from Puget Sound (Fig. 7) and station AH B, from the Chukchi Sea (Fig. 8). To reproduce the

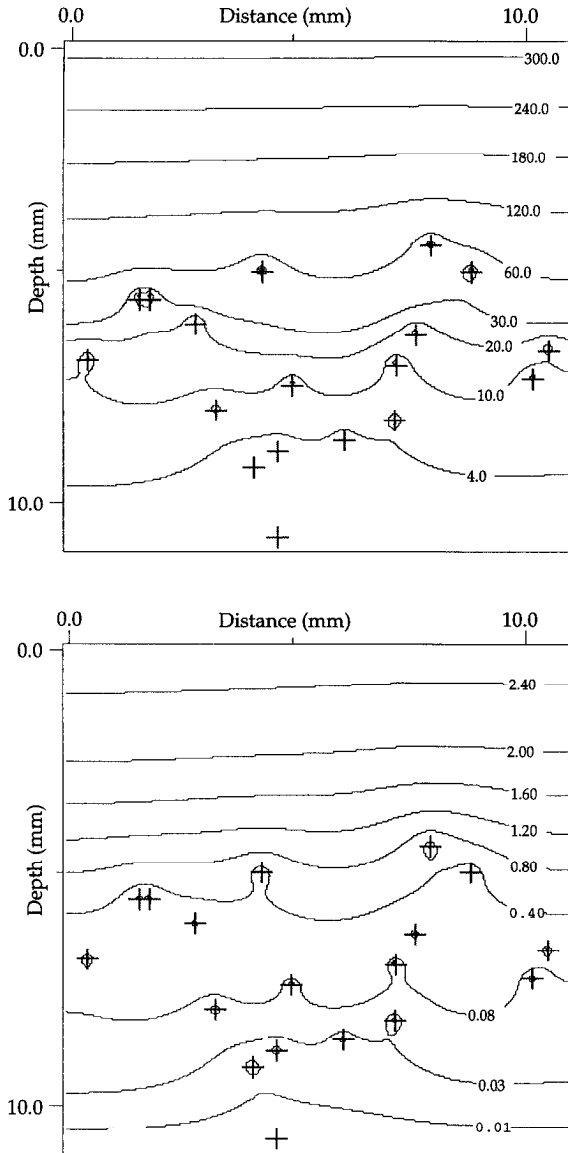


Figure 8. Contour graph of results for two-dimensional model for station AH B for oxygen (upper) and nitrate (lower). Model dimensions are  $1 \times 1$  cm. Crosses represent discrete microzone sites. Contour lines are in  $\mu\text{M}$ . Model porosity is .80.

profiles from CB 3 required nineteen highly respiring reactive sites distributed over the model grid. The location of these sites within the model matrix was not arbitrary, but was adjusted to give the approximate best fit to the WCS data as determined visually (Fig. 9). For the three discrete micro-sites in the station CB 3 model that

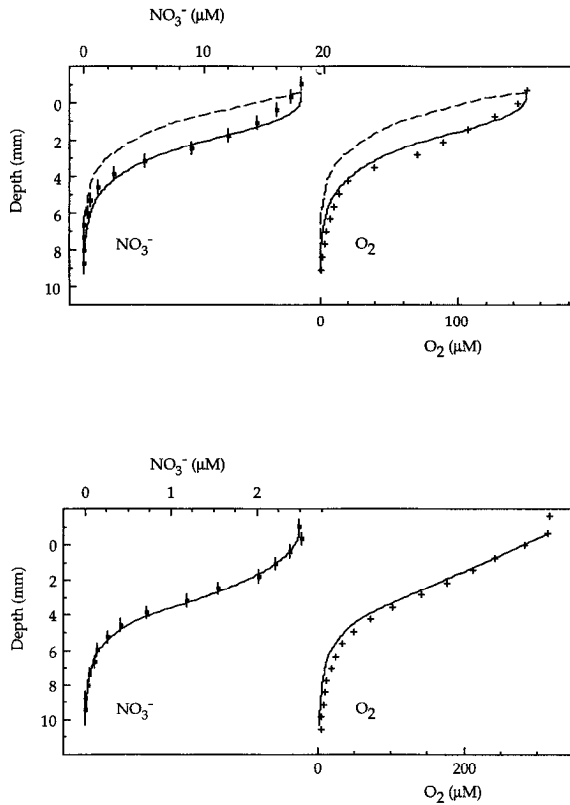


Figure 9. Data and spatially averaged two-dimensional model results from stations CB 3 (upper) and AH B (lower). Axes designations and model result designations are identical to Figure 7. No filtered model is shown for AH B due to the almost level interface at this location.

were located above 1.5 mm depth, oxygen at the reaction site did not drop below  $10 \mu\text{M}$ , and these sites did not allow denitrification. The nitrate model result for station CB 3 (Fig. 7) was, therefore, similar in appearance to the oxygen result, with the exception that the top three oxic reaction sites were absent. To compare the model results with the data shown in Figure 3, the two-dimensional results were reduced to one dimension by averaging the model sediment concentration over each horizontal interval ( $z = \text{constant}$ ), then filtering these results (Eq. 3) to mimic the WCS sampling distortion. The results for station CB 3 (Fig. 9) show that the model does replicate the bulk porewater  $\text{O}_2$  and  $\text{NO}_3^-$  profiles. As with the one-dimensional model results, there is some difficulty in tracking the near surface data that is probably due to the filter not completely duplicating the effects of WCS sampling through a tilted surface, but overall the results are as satisfying as those obtained using the one dimensional models with denitrification allowed at all  $\text{O}_2$  concentrations (Fig. 6).

The other profile modeled was from a subcore with very little tilt taken at AH B (Table 1). To model the nitrate and oxygen profiles at AH B required a distribution of eighteen discrete sites, with no sites closer to the surface than 3 mm (Fig. 8). This distribution was required because of the nearly linear oxygen profile over the upper 3 mm of sediment, which implied that little oxygen consumption occurred in this region, given the model assumption of a constant porosity. However, a porosity change in the upper 3 mm of the sediment column would require a significant oxygen respiration rate in this area simply to achieve a linear oxygen profile, and therefore require the existence of respiring sites in this area. All model reaction sites became suboxic ( $O_2 < 10 \mu\text{M}$ ) and had active denitrification (Fig. 8). Reducing the two dimensional model results to one dimension showed that the model accurately reproduced the nitrate profile but slightly underestimated the oxygen profile (Fig. 9). This deviation was a result of requiring a  $Ro_a$  value high enough to reduce oxygen concentrations at each site to below  $10 \mu\text{M}$  and allow denitrification at all sites. If denitrification were allowed at slightly higher oxygen concentrations within each site, or the model reactive sites were larger, the overall oxygen respiration rate could be reduced while still allowing a large enough denitrification rate in oxic sediments to match the observed nitrate concentration profile.

It should be noted that the profile from station AH B is similar in overall structure, if not in scale, to profiles obtained by Wilson *et al.* (1985) and Jahnke *et al.* (1989) from the Madeira abyssal plain, where oxygen and nitrate consumption took place solely at depth in an organic-rich turbidite layer. However, a one dimensional model such as they employed is clearly inappropriate here, as both oxygen and nitrate oxidation clearly begin in sediments averaging  $\sim 100 \mu\text{M l}^{-1}$  oxygen content. It may be that sediment respiration was occurring along an uneven oxidation front; however if this were true it would also be expected that oxygen respiration would be greater along the upper reaches of this front and nitrate respiration greater along its lower reaches, which is not implied by our 2-D model. The predominance of respiration at depth at this site may indicate that oxidation here is driven in part by remineralization of reduced material from beneath the oxic zone (Canfield *et al.*, 1993; Aller, 1994), rather than fresh organic material from the water column.

Given the assumptions about site size and inhibition of denitrification rate by  $O_2$ , the location and respiration rates of each particle within the model are limited to a relatively narrow range of values. Placing more reactive particles in the upper 5 mm of sediment in the either model would require lower oxygen respiration rates for each particle, reducing the number of denitrifying sites in the upper reaches of the model and resulting in a poorer fit of nitrate model results to the data. Without concentrating sediment respiration into a few discrete sites, oxygen concentrations at the sites cannot be drawn down to levels that allow denitrification within the upper oxic sediment column, which is a prerequisite for modeling the nitrate data.

However, it must be emphasized that this is a conceptual model and will remain so until actual data on discrete site reaction rates, sizes and distributions are available.

## 6. Discussion

*a. On the nature of microzones.* Sediment respiration has typically been treated as a bulk quantity applied to the entire oxic sediment zone (Froelich *et al.*, 1979). When variations in reductant reactivity have been considered, as in the "multi-G" model, that variation has also been treated as a bulk property (Berner, 1980; Boudreau and Ruddick, 1991). Recent work on carbon oxidation in coastal sediments (Mayer, 1994; Keil *et al.*, 1994a, b), suggests that the majority of the carbon residing in coastal sediments is relatively nonreactive on timescales of a few decades, due to sorption to mineral grain surfaces. Most carbon reaching coastal sediments is not associated with sediment grains and is therefore rapidly respired (Hedges *et al.*, 1988; Hedges and Keil, 1995). Although it is possible that the carbon reaching the sediment surface as fecal pellets could be rapidly redistributed over the upper sediment column, the model results presented here imply that remineralization of the carbon input is not distributed homogeneously throughout the bulk sediment, but is instead concentrated in a relatively few discrete sites.

The discrete diagenesis model approach to sediment respiration implies a relatively short lifespan for the sites, which is consistent with the ephemeral nature of the majority of the carbon input to coastal sediments. For example, in the model solution for CB 3 (Fig. 7), there were a total of 19 micro-sites distributed throughout a 1 by 1 cm slice of sediment, which resulted in an average site density of about 80 sites/cm<sup>3</sup>. Dividing the model respiration by 80 respiring particles per cm<sup>2</sup> (integrating over the thickness of the oxic zone) results in a respiration rate of about 7 nM O<sub>2</sub> day<sup>-1</sup> particle<sup>-1</sup>, or using Redfield stoichiometry, 5 nM C day<sup>-1</sup> particle<sup>-1</sup>. If the 100 × 100 micron model reactive sites are carbon-rich particles, i.e. %50 C by weight, then each site initially would have a total carbon content of 75 nM C, which would be exhausted in 15 days given our calculated respiration rate. It should be emphasized that the respiration rates of particles near the surface of the model are higher than rates for particles near the bottom, leading to shorter lifetimes for near-surface particles than our calculation suggests. Larger particles (or those with additional oxidizable material) could last longer and could extend the particle lifetime further. The assumption of larger discrete respiration sites would be reasonable given that the model site size is on the lower end of the fecal matter size spectrum. A caveat to these model results is that they are based on a two-dimensional model, not a three-dimensional one as would be required to more accurately model the interactions between reactive sites and porewaters. The chief difference between two- and three-dimensional models is that, in a three-dimensional model, oxidant gradient influences on the bulk porewater profile are increased due to diffusion from the y direction of the model; this results in fewer but

more highly respiring reactive sites required to match an integrated porewater profile, as compared to a two-dimensional model. Nevertheless, the basic conclusions about the nature of sediment respiration and interactions between reaction sites and surrounding porewaters would be unchanged by inclusion of a third model dimension.

Another factor influencing the particle lifetime could be the formation of a diffusive barrier around micro-sites. As discussed earlier, low diffusivity coatings will not prevent the formation of diffusive gradients around discrete reaction sites, but they will have an effect upon the overall rates of reaction necessary to achieve suboxic conditions within the sites. In shallow sediments, bacteria have been observed to form mucus-clay aggregate layers around larger particles (DeFlan and Mayer, 1983). Alldredge and Cohen (1987) also noted the importance of low diffusivity coatings around fecal pellets in maintaining anoxia within pellets. If the diffusion coefficient in a layer surrounding each site is reduced by an order of magnitude (Aller, 1983) from the bulk sediment value, then the respiration rate necessary to maintain suboxic conditions would be reduced, and accordingly the particle lifetime would be extended by an order of magnitude. This would produce a commensurate requirement for more reactive sites in order to duplicate the same overall respiration rate. It would not, however, change the relationship between oxygen respiration and denitrification, as both processes would still be confined to microzones. The magnitude of this effect would depend upon the thickness of the low diffusion coefficient layer surrounding the particle, but it could only extend particle lifetimes by, at most, an order of magnitude to several months. Over longer periods of time gradients would shift as new particles are brought into the oxic zone, and older particles exhaust their supply of reductant. Therefore as a first approximation the two-dimensional steady state model is reasonable for describing sediment respiration over short periods of time, i.e. days to weeks, but over longer periods the picture may change, in response to changes in supply and distribution of reactive sites.

*b. Discrete site sources.* The picture presented by our discrete diagenesis model is that of a sediment column with a relatively few highly reactive sites providing most of the total respiration. Continual replenishment of these sites would be required to maintain co-removal of oxygen and nitrate. There are two main sources of highly reactive matter to the oxic layer of coastal sediments. The most obvious of these is the particle rain to the sediments themselves. The organic rain rate reaching a particular sediment surface is determined by two factors: the surface productivity and the water column depth (Betzer *et al.*, 1984; Martin *et al.*, 1987). Because 30% to 50% of marine primary productivity takes place in waters overlying continental margin sediments (Romankevich, 1984; Walsh, 1988, 1991), there is a considerable supply of organic carbon to these sediments and at typical fecal pellet settling

velocities of 50–100 m day<sup>-1</sup> (Shanks and Trent, 1980), this supply will have had only a few days at most to oxidize while in the water column. Therefore these sediments have a ready supply of relatively “fresh” organic carbon. This reactive carbon supply may also be rapidly re-distributed throughout the mixed layer by benthic organisms (Graf, 1989).

The second, less obvious source of oxidizable material to the oxic sediment layer is from mixing of reduced inorganic material into the oxic zone. This process can be important in coastal sediments because of two factors: 1) the thinness of the oxic zone, and 2) the presence of bioturbation in these sediments, which can transport reduced material up into the oxic layer. Conveyor belt feeding benthic macrofauna that rework sediments on a vertical scale longer than the oxic layer thickness may bring reduced material to the surface sediments, or may remove oxic layer material from the surface to their burrows (Plante and Jumars, 1992; Aller, 1994). In either case reduced material can be exposed to  $\text{O}_2$  and  $\text{NO}_3^-$ , either by direct transposition or by removal of overlying material. Episodic mixing by storms (Vanderborgh *et al.*, 1977), may also mix sediments vertically. Vertical mixing may be less important than horizontal mixing, however. Wheatcroft *et al.* (1990) have shown that horizontal mixing occurs on a 100 times faster time scale than vertical mixing. Given an oxygen penetration depth of 4–8 millimeters (Archer and Devol, 1992; Canfield *et al.*, 1993), and surface relief changes of more than a few millimeters, sub- or anoxic sediments at the base of the oxic zone could be exposed by horizontal bioturbation. We commonly observe surface features of >2–3 millimeters height in our collected cores, so that this process is undoubtedly important. No distinction is made between sources of reduced material in the discrete diagenesis model; exposure and subsequent oxidation of sediments containing reduced metals and sulfides (Canfield *et al.*, 1993; Canfield, 1994) may provide much of the total sink for oxygen and nitrate in some sediments.

## 7. Conclusion

The similarity of shape and penetration depth of porewater oxygen and nitrate profiles in the shallow water sediment samples examined here requires a reexamination of assumptions about the vertical separation and homogeneity of oxidative processes in these sediments. We view the porewater profile similarity of the two primary oxidants (in order of usage and energy release per mole, Stumm and Morgan, 1981) as a sign that oxidation in these shallow sediments is not spatially homogenous, but instead has a dynamic micro-structure created by discrete sites where the majority of sediment diagenesis occurs. This structure depends upon a balance between oxidant diffusion and the input of reducible material, with oxidation rates being limited by the oxidant supply. Because the lifespans of the individual sites may be quite short, the carbon input to the sediments may be respired/ altered much more rapidly than previously thought. As different oxidant sources become more



important (i.e. a seasonal carbon input spike to the surface layer vs. storm movement of surface sediment layers that exposes suboxic sediments) the porewater oxidant profiles could adjust between high-surface oxidation rate profiles (Archer and Devol, 1992) to more linear profiles (Canfield *et al.*, 1993). Further testing of the discrete diagenesis model could be accomplished by measuring multiple vertical and horizontal oxygen profiles with micro-electrode arrays or by searching for increased areas of microbial activity or denitrification using assays and thin sectioning of sediment cores.

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