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Measuring benthic respiration rates and nutrient inventories using sediment core samples from the Oregon Continental Shelf

Peter J. Chace*[2a], Clare E. Reimers[1], and Rhea D. Sanders[1]

[1]College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, United States
[2]School of Science, Monmouth University, NJ 07764, United States
[a]Hatfield Marine Science Center 2013 REU Program

Abstract

Oregon Continental Shelf sediments were characterized for fluxes of oxygen and major nutrients. Such characterizations utilized *ex situ* incubations of sediment cores taken from the Oregon Continental Shelf in Fall and Summer ocean seasons. Sediments were found to have considerably lower rates of respiration during the hypoxic summer months when compared with rates in the more oxygen rich autumn, which saw fluxes 3-4 times higher. Sediments were also assessed for nutrient fluxes, utilizing the same sediment incubations. Stoichiometric analysis of these fluxes indicates exchange rates affected by anaerobic processes such as denitrification and sulfur oxidation. Such processes may represent a biogeochemical response to the seasonal hypoxia that's grown in frequency in the last decade on the Oregon Continental Shelf.

Introduction

In recent years, upwelling-driven hypoxia has become a recurrent environmental condition in the northeast Pacific (Grantham et al. 2004). These hypoxic ($[O_2]$ below 2.0ppm) events drive mobile fish and invertebrate populations closer to shore, and have resulted in several large die-offs that come with

the potential to effect fisheries. Many studies have already examined the physical oceanographic processes potentially driving such hypoxic events, but less is known about the effects on the benthic chemical processes across the continental shelf, or feedbacks of benthic fluxes to other ecosystem processes.

Knowledge of these processes is impeded by a lack of long-term data sets on the biogeochemical make-up of the sediments on the Oregon Continental Shelf. Such data involves long-term acquisition of sediment cores from Shelf habitats and an assessment of these sediments on a chemical basis. The most common methods utilized for such characterization involve oxygen and nutrient analysis. The latter of these entails the extraction of porewater from sediments (Jahnke at al. 2005), which allows for the determination of remineralized carbon, nitrogen, and phosphorus present in the sediment (Tribble et al. 1990)and subsequent development of stoichiometric ratios that can be indicative of particular sediment processes. The standard aerobic ratios for chemical processes are generally referred to as "Redfield" regeneration ratios and are predictable for the majority of open marine systems (Redfield 1934). These ratios differ greatly from the normal Redfield numbers when sediments undergo anaerobic processes such as denitrification (Burdige 254-291).

Oxygen fluxes, also understood as a measure of aerobic respiration rates of the sediment, are important for understanding the reaction of sediments to hypoxic or anoxic conditions. Knowing at what rate the sediment consumes oxygen is vital to understanding how much the sediment contributes to the already hypoxic water column. Techniques employed to make such determinations are numerous and each come with their associated levels of error and complexity. One of the most straightforward techniques is the incubation of sediment cores taken directly from study sites. Cores are sealed completely and a time-series of oxygen concentration is measured in the overlying water; the resulting drop in $[O_2]$ is then used to determine an overall flux. The same method can be utilized to test for fluxes in nutrients. Traditional oxygen analytical methods would require an extraction of a water sample from

the sealed vessel or the consumption of a certain amount of oxygen within a sample, altering the sample itself. These two approaches create the potential for contamination and can hence be unreliable when working with small volumes such as in this study (Marsh and Manahan 1999).

Materials and Methods

Sediment cores were obtained over a seven-day period at-sea from July 9th to July 16th, 2013. Collections were made utilizing a Multi-corer as part of a ten-day NSF cruise, designated OC1307A, on the *R/V Oceanus* (NSF OCE-1061218). Three separate sites were sampled for the purposes of determining benthic fluxes of oxygen and nutrients by means of core incubations. Each site had three replicate incubations performed with no one experiment being longer than 74 hours or shorter than 41 hours. Each core incubated also had overlying water sampled at the start and conclusion for assessing nutrient fluxes. Replicate cores were also obtained at each site and utilized for porewater extraction to determine nutrient inventories of sediments.

Incubation Methods

Cores were initially obtained in 1m-long tubes and then extruded into smaller 26cm-long, 9.4cm diameter tubes for incubation. Approximately 6cm of overlying water was left in each incubation tube (this varyied from core to core). Once the core was extruded into the 26cm tube it was closed on the bottom using a plastic cap that was then wrapped in 33+ electrical tape. The chamber was then submerged into a bucket of at-depth water collected with a rosette of Niskin bottles at the same site. Once submerged, the top of the core was capped and wrapped in tape to seal it. This top cap contained a magnet on a slow-moving motor which served to rotate a 5cm stirring bar in the incubation chamber to simulate mixing of the overlying water without disturbing the surface of the sediment.

Oxygen concentrations were monitored over time in the overlying water of each incubation core utilizing a PreSens Precision Sensing® Optical Oxygen Sensor. The system allowed for the measurement of oxygen concentrations without the need to open the sealed incubation chamber, by optically measuring a reactive "spot" fixed on the inside of the clear tube, 1-2cm above the sediment-water interface. The optic sensor excites the spot with light energy and then measures a fluorescence response that can be related to an oxygen concentration. Measurements were made initially on a 4-6 hour interval, however, once a general rate of oxygen consumption was established some reading intervals were increased to 8-10 hour increments. Each incubation was followed until it showed near-anoxic (less than 5.0μM) levels, or had at least 11 intervals of measurement over a 2-3 day period.

Porewater Nutrients

Replicate cores for extracting pore waters were obtained during the same coring events undertaken to obtain the incubation cores. The 1m-long tubes used for these cores had been pre-drilled with small holes running down opposing sides of the core tube, the holes were covered in electrical tape prior to the deployment of the multi-corer. Once at the surface the electrical tape was cut and Rhizons® were inserted to extract porewater from the core at downcore intervals (ideally including increments at 1, 2, 3, 4, 5, 6, 7, 8, 10, 14, 20, and 26cm, as well as the overlying water). This porewater was allocated into 4ml PTFE bottles for analysis of nutrients. These samples were frozen shortly after being obtained for later analysis. A 2mL amber glass bottle was also filled with remaining porewater and fixed with 5μL of $HgCl_2$ for the determination of Dissolved Inorganic Carbon. Any remaining sample was acidified for trace metal analyses.

Nutrients were analyzed using a continuous flow segmented analysis system at Oregon State University, as explained in Gordon et al. (1995). Overlying water from each core, as well as ambient

water collected from Niskin bottle deployments, was also analyzed using the same system. Dissolved inorganic carbon was determined as detailed in Hall and Aller, 1992.

Results

Oxygen time-series measurements from the incubated cores were utilized to calculate benthic oxygen fluxes (*mmol/(m^2*day)*) for sites HH80, DU100, and SU80, and determined as -1.4 ±0.7, -0.8 ±0.2, and -0.7 ±0.2, respectively. These estimates take into account the overlying water volume in each core incubation and the overall consumption of oxygen over the incubation period. These fluxes were intended to be compared to those obtained by concurrent analysis utilizing both microelectrode profiling and eddy correlation techniques, detailed in Reimers et al. (2012). However, such analysis was hindered by limitations in current interpretation of data obtained from these techniques and thus will not be featured here.

Table 1 Finalized oxygen flux values determined by sediment core incubations, eddy correlation, and microelectrode profiling.

*All Fluxes in mmol/m^2*day*

	OC1210A		OC1307A	
Station	Core Incubation	stdev	Core Incubation	stdev
YH80	-4.8045883	1.9368678		
HH80			-1.5	0.7
DU100	-3.704437	0.2716403	-0.92	0.01
SU80	-2.5775513	0.1324941	-0.8	0.2

Figure 3 shows a comparison of the oxygen fluxes determined here to similar measurements made in October 2012 using cores from sites DU100 and SU80. There is a 3-4 fold difference between the two sampling periods. Figure 4 lays out the same fluxes seen in Figure 3, but includes two more sites that were also measured by core incubations, each on a different cruise. The fluxes show spatial patterns from North to South. The southernmost sites, DU100 and SU80, are in close proximity to the mouth of the Umpqua river, as seen in figure 5, a site of high sediment deposition resulting in siltier, finer-grained sediments.

$$Slope\left(\frac{\mu mol}{L * hr}\right) * \frac{L}{1000mL} * \frac{mL}{cm^3} * \frac{Volume\ (cm^3)}{Area\ (cm^2)} * \frac{(100^2)cm^2}{m^2} * \frac{24hr}{day} * \frac{mmol}{1000\mu mol}$$

Equation 1 Used to determine flux of both oxygen and nutrients within incubated sediment cores; 'Volume' is that of the overlying water in the incubation core, while 'Area' is the surface of the idealized sediment-water interface (consistent for each core).

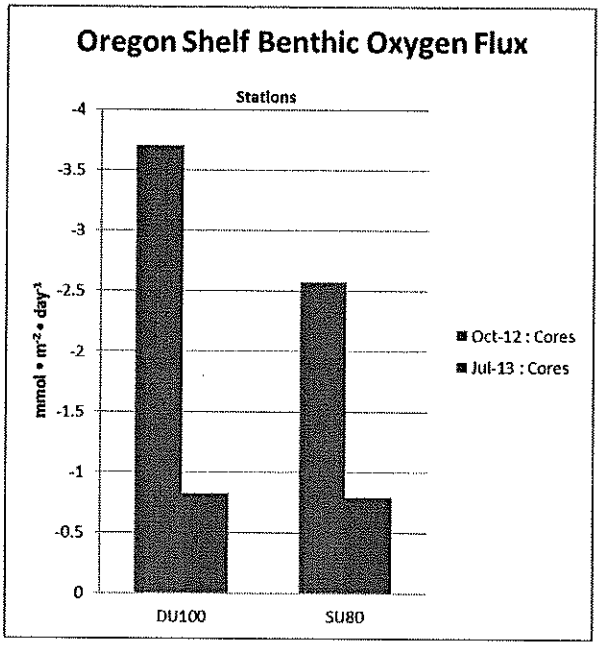

Figure 3 Seasonal comparisons of two overlapping sites' oxygen fluxes.

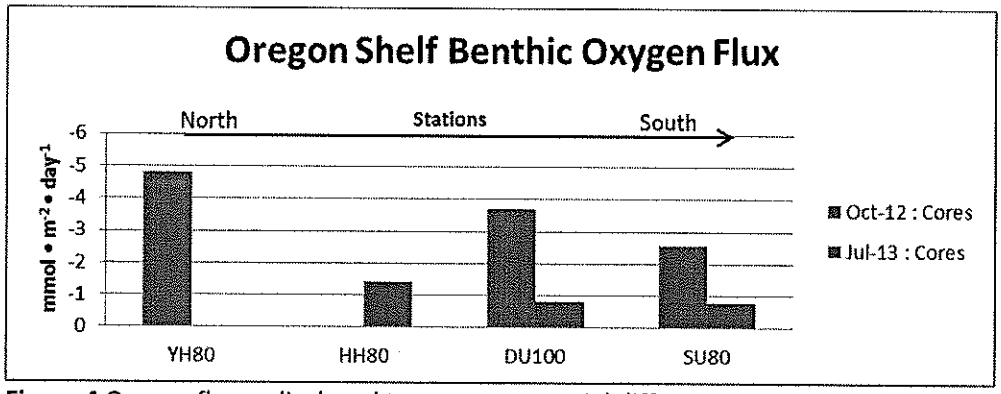

Figure 4 Oxygen fluxes displayed to represent spatial differences.

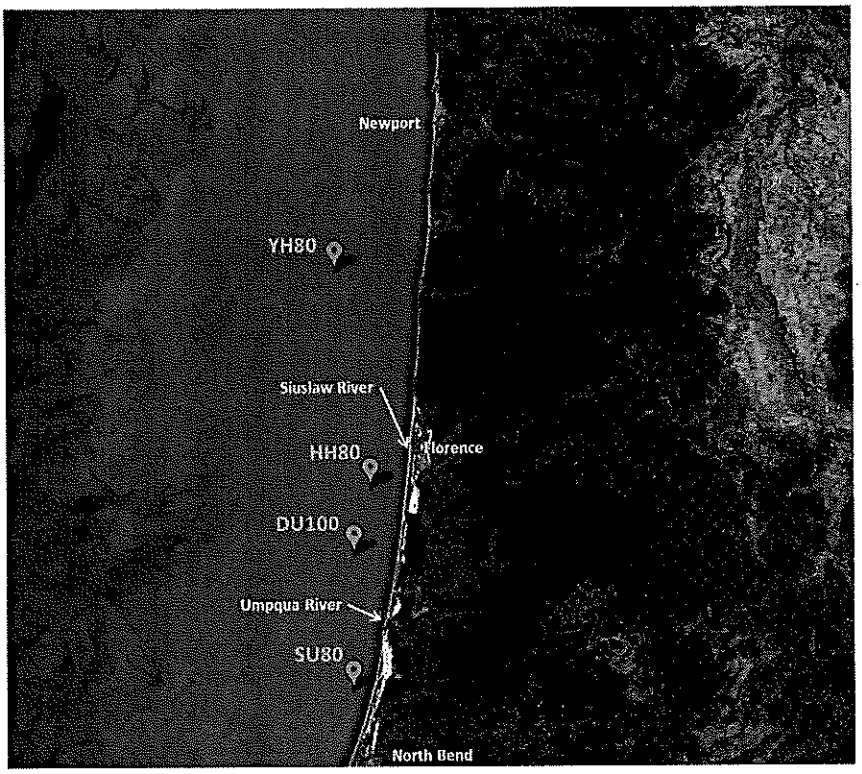

Figure 5 Map with site locations.

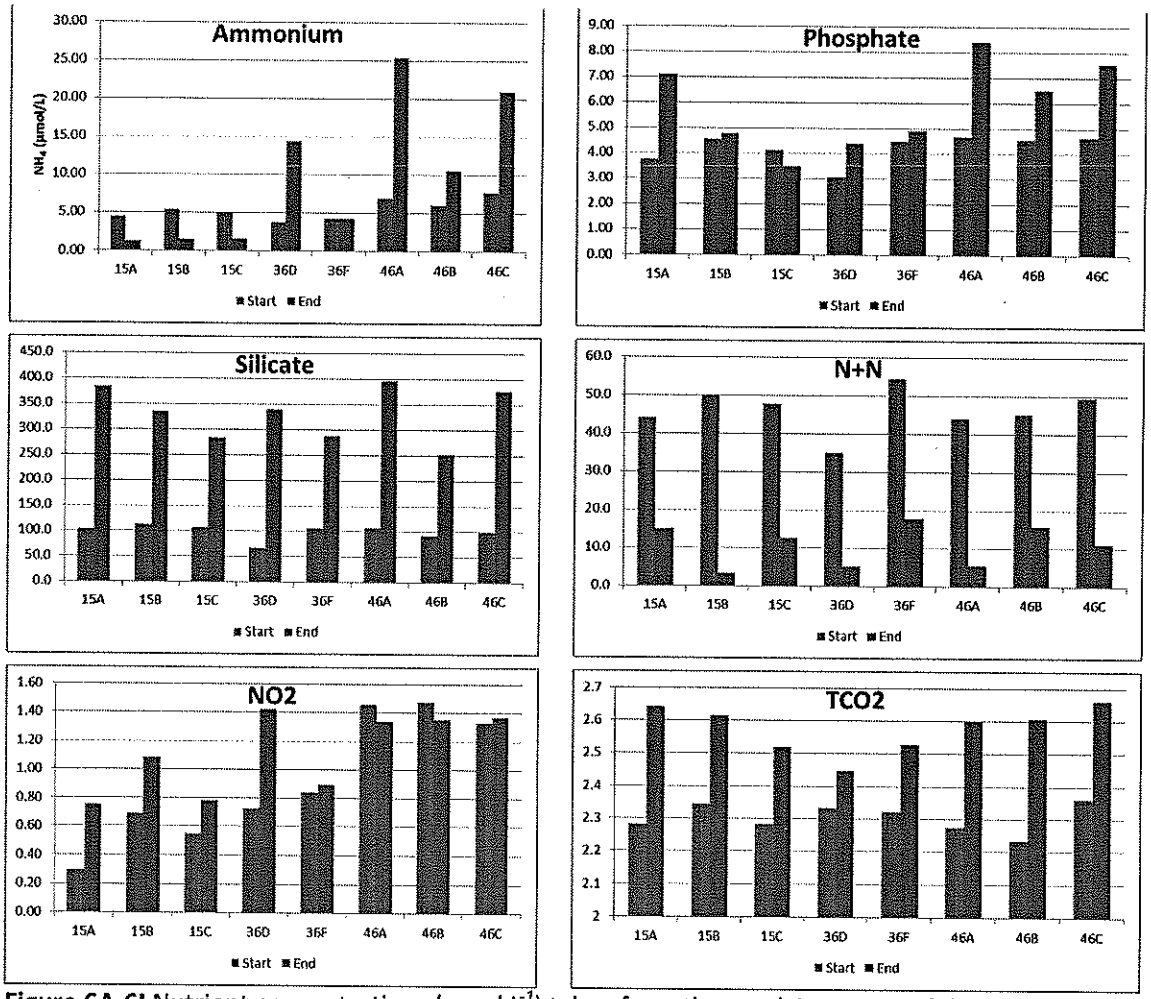

Figure 6A-6I Nutrient concentrations ($\mu mol\ L^{-1}$) taken from the overlying water of the sediment incubations performed at the three sites HH80, DU100, and SU80 on the July 2013 cruise; each displaying samples taken at the beginning and end of the incubations. **won't include NO2+PO4**

Figure 6 shows nutrient concentration changes in the overlying waters of the incubation cores from the start to end of each incubation period. Relevant fluxes are displayed for ammonium, phosphate, silicate, Nitrate plus Nitrite, and TCO2. The fluxes for sites SU80 and DU100 have a notable similarity, which is understandable given their close geographic proximity. This same proximity means the two sites also share similar sediment characteristics in terms of grain size and sedimentation rates (Hastings et al. 2012).

Table 2 Ratios of fluxes measured in sediment incubation cores (*mmol/(m²*day)*)

Sites	Core ID	ΣCO2:O2	ΣCO2 : ΣNitrogen	ΣCO2:N+N	ΣCO2:PO4	ΣN:PO4
HH80	15A	-4.8	-11	-12	110	-9.8
HH80	15B	-6.4	-5.3	-5.8	1100	-210
HH80	15C	-2.3	-6.1	-6.7	-390	64
DU100	36D	-3.4	-6	-3.9	85	-14
DU100	36F	-5.3	-5.6	-5.6	490	-87
SU80	46A	-8.2	-16	-8.5	87	-5.4
SU80	46B	-7.3	-15	-13	190	-13
SU80	46C	-7.8	-12	-7.8	100	-8.7

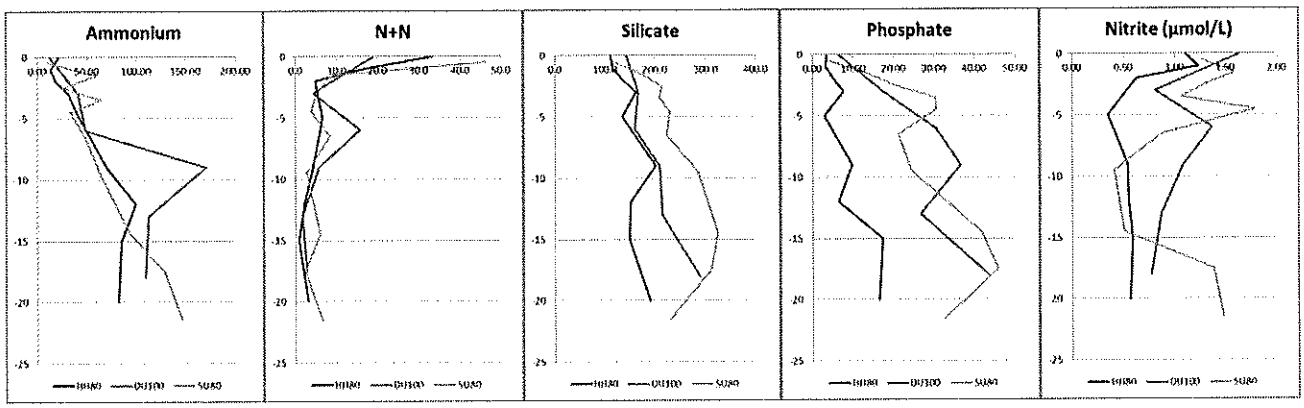

Figure 7 Porewater Profiles of nutrients from July 2013 cruise.

Replicate porewater cores were analyzed for nutrient inventories and are plotted in figure 7 to show the changing concentration of nutrients with the depth in sediment. Such measurements were integrated to a common depth of 18cm and coupled with porosity data to determine the total load of nutrients within the sediment. Seasonal comparisons for total Ammonium, Phosphate, Nitrate plus Nitrite, and Silicate can be seen in figure 8.

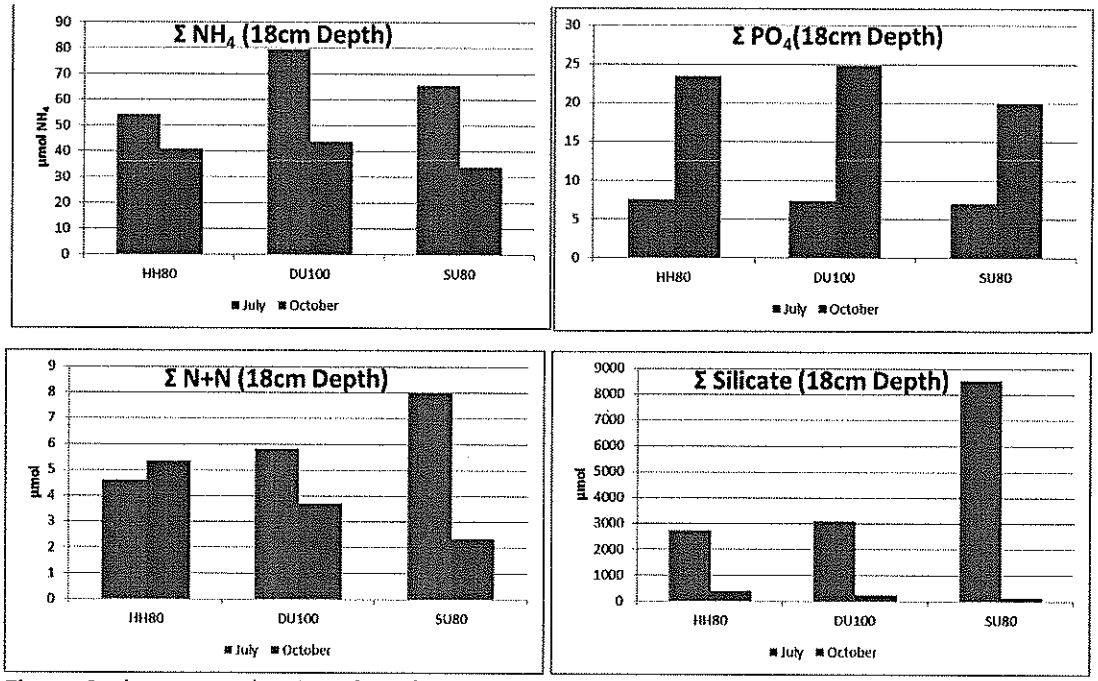

Figure 8- the seasonal ratios of total nutrients present in the sediment down to a depth of 18cm

Discussion

Temporal and Spatial Variance

The three sites examined HH80, DU100 and SU80 are compared for the purposes of indicating spatial and temporal variation in terms of oxygen and nutrient fluxes. Both DU100 and SU80 experience similar rates of deposition and a commonality in sediment characteristics as a result of their proximity to the Umpqua River deposit plume. Site HH80, however, is located north of the Umpqua plume, and away from any major rivers. The sediment found at HH80 has a lower porosity (0.42) and is affected differently by ocean currents due to its location, lending a good comparison to the more southerly sites.

Only sites DU100 and SU80 were sampled on both the October 2012 cruise and the July 2013 cruise. The two remaining sites tested by core incubation, YH80 and HH80, were only tested on one cruise, so their analysis is limited. Because both these sites are located north and away from the Umpqua plume, and share similar sediment characteristics, they make ideal comparison locations to the DU100 and SU80 sites.

Figure 1 indicates the full sets of three sites where cores were incubated and measured during the July 2013 cruise. This figure specifically excludes an incubation core 36E, taken from the DU100 site, and its oxygen flux. This core is also excluded from any of the subsequent final flux calculation. The core was excluded on the basis that a ctenophore was trapped in the overlying water in the incubation tube and caused a steep increase in respiration within the core, giving a false reading of the oxygen flux at the sediment-water interface.

Seasonal variation on the Oregon Continental Shelf brings with it considerable variations in oxygen concentration. With this varying concentration, one would also expect variation in the flux of oxygen at the sediment-water interface. Traditionally, Summer upwelling causes lower oxygen, which was seen during the July 2013 cruise, and oppositely the Fall/Winter months see overall higher levels of oxygen. When comparing the relative fluxes over the two seasons sampled for this study, we see a 69-75% increase with flux into the sediment going from Summer to Fall/Winter. This would suggest that those interstitial communities within the sediment are switching to other sources of electron acceptors under the more anaerobic conditions. It also indicates that under hypoxic conditions, such sediments, while they're still respiring, aren't respiring under normal rates, compounding the already problematic low oxygen levels.

These fluxes can also be examined on a spatial basis. There's a clear variation in the sites when looked at from a longitudinal perspective. The more north a site the higher its oxygen flux relative to the other sites sampled at that time. This can be attributed to the higher load of organic matter deposited by the Umpqua Plume onto the more southerly sites.

Replicate cores taken at each site were also utilized for porewater analysis (Figure 7). Integrating these profiles to a common depth of 18cm, a comparison can be made across seasons for the total nutrient loads in the sediments for sites HH80, DU100, and SU80. This showed shifts in the nutrient load of the porewater, with each site losing 85-99% of the silicate when comparing the upwelling season to

the fall season. Similar results were also found for Ammonium, which saw a 19-37% loss. Both of these indicate elevated levels of anaerobic respiration in the fall months or enhanced exchange in the summer perhaps due to bioirrigation. Phosphates seen in the Winter were also 3-4 times more than summer, supporting the same argument.

Stoichiometric Analysis.

Nutrient fluxes are indicative of processes occurring within the sediment, or at the sediment-water interface. Figure 6 shows the before and after nutrient analysis of the incubated sediment cores. Expected diffusion of silicate and phosphate out of the sediment is seen in every core sampled, along with the expected increase in dissolved inorganic carbon (DIC) resulting from aerobic and anaerobic oxidation. Both sites DU100 and SU80 showed expected releases of ammonium, resulting from the decomposition of organic matter, there was a slight increase in nitrites in some cores, likely linked to the spike in ammonium. The overall Nitrate plus Nitrite however, was very different, as there was a clear negative flux, losing 65-93% of starting overlying reserves of nitrate + nitrite.

These fluxes were examined for stoichiometric ratios, Table 2, which can be indicative of the respiration processes dominating in the sediment. TCO2:N for sites HH80 and DU100 (with the exception of core 15A) hold close to the standard Redfield ratio for more aerobic systems of 6.625:1 (Redfield 1934). Core 15A saw no difference in the total nitrogen flux when compared to the other HH80 and DU100 cores. Its overlying water, however, was almost 2cm higher than the other cores in the HH80 incubations.This core was also noted as having several mysid shrimp disturbing the sediment during its incubation.Both of these factors could havecontributed to the higher TCO2, which was double that of the other HH80 incubation fluxes. SU80 cores had almost 3 times higher TCO2:N than TCO2:N for both HH80 and DU100 , indicative of anaerobic processes likely driven by the high deposition of organic matter.

Examination of the TCO2:O2 stoichiometry for HH80 and DU100 also reveal similar findings to that of the previously noted TCO2:N ratios. The lower ratio, while not the 1.3-1.4 ratio of pure aerobic respiration, is indicative of aerobic processes being prevalent. The same deviations seen again with the SU80 site, lending continued evidence to that site experiencing elevated levels of denitrification and other anaerobic processes. Table 2 also includes TCO2:PO4 and N:PO4 ratios, however, none of the ratios appear to be consistent among the sites sampled. The cause is likely a combination of inconsistent diffusion of phosphates out of the sediment and their involvement in other chemical processes such as adsorption to iron oxides not immediately obvious from this analysis.

Conclusion

Summer upwelling along the Oregon Continental Shelf brings with it lower levels of oxygen. It's clear that this lower oxygen is driving the sediment to rely more on anaerobic processes during such events. The sediment community appears to be able to adapt to the seasonal shift in markedly different habitat conditions, but the effect of an increased frequency of hypoxia on these communities is still unknown. Only long-term data sets are able to shed light on such questions, and with a lack of extensive sediment flux data for the last century there is a need to continue generating usable data in this area. Future efforts could benefit from utilizing more than three incubation replicates per site, with 5-6 cores per incubation-period generating clearer results. A case could also be made to sample a wider range of sediment types. While SU80 and DU100 are both different from the compared HH80 site, there are still much sandier sediments prevalent on the Shelf, as well as other areas which would likely result in different community responses that may be more or less sensitive to such hypoxic events.

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