Research papers

Benthic flux of oxygen and nutrients across Oregon/California shelf sediments

W.M. Berelson a,*, J. McManus b, S. Severmann c, C.E. Reimers b

a Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089, United States
b College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, United States
c Institute Marine and Coastal Science and Earth and Planetary Sciences, Rutgers, The State University of New Jersey, NJ 08901, United States

1. Introduction

Recent studies suggest a trend toward an increase in the frequency of hypoxic ([O2] < 63 μM) waters throughout much of the Eastern Pacific (Bograd et al., 2008; Chan et al., 2008; Stramma et al., 2008). When low oxygen waters impinge on shelf sediments, the economic consequences of these incursions can be significant in terms of disruption to benthic ecosystems (Grantham et al., 2004; Chan et al., 2008; Gewin, 2010). Although the ultimate driving mechanism for this trend is debated, some relationship to changes in wind patterns has been inferred (Bakun and Weeks, 2004; Keeling et al., 2010). There is a growing concern that the Oregon-N. California continental shelf region is experiencing an increase in the frequency of hypoxic water incursions, and that this increase in hypoxia is having deleterious effects on benthic fauna (e.g., Grantham et al., 2004; Chan et al., 2008; Gewin, 2010). This region is also sensitive to the influx of water and sediments delivered by the numerous small rivers (e.g., Wetz et al., 2006; Hastings et al., 2012), which deliver large pulses of sediment in a seasonally modulated pattern. The two rivers close to our particular study regions include the Eel River (N. California), which maintains an exceptionally high annual suspended sediment load of ~15 x 106 kg, and the Umpqua River (S. Oregon), ~1.4 x 106 kg (Wheatcroft and Sommerfield, 2005). Regional scale changes in sediment and nutrient delivery via rivers, upwelling intensity, and coastal ocean circulation all exert a dynamic impact on oceanic and benthic food webs.

Changes in productivity can have an immediate impact on benthic chemistry, especially in shelf regions where organic carbon (Corg) delivery to the seabed and benthic community
respiration and nutrient remineralization rates are closely linked (Graf et al., 1983; Dale and Prego, 2002, Berelson et al., 2003). However, the linkage between benthic diagenetic processes and C–N–P remineralization rates is complex (Ingall and Van Cappellen, 1990; Wang and Van Cappellen, 1996; Prokopenko et al., 2006). This coupling is potentially important in our study region where fresh delivery of continentally-derived sediment occurs just prior to the onset of upwelling and spring productivity (e.g., Colbert, 2004; Wetz et al., 2006). In order to examine this potential variability, our study incorporates two time points (May and September, 2007) and shelf regions 350 km apart to provide some measure of variability in benthic processes (Fig. 1).

Another key parameter in controlling benthic fluxes from continental shelf sediments is the intensity and style of bioturbation and bioirrigation (Aller, 1982, 1994; Hammond et al., 1985). The muddy sediments that accumulate on the Oregon–California shelf have clear evidence of macrofaunal activity, burrow holes are evident in bottom photographs (Fig. 2). The most abundant macrofauna are polychaetes (Wheatcroft, 2006). These, and other benthic macrofauna are requisite aerobes, yet they penetrate centimeters into anoxic sediments.

High levels of macrofaunal activity make determining the benthic flux of a dissolved species difficult. Pore water gradients and diffusive flux calculations often do not reflect the true transport mechanism (Archer and Devol, 1992, Elrod et al., 2004, Pakhomova et al., 2007). Benthic chambers deployed in situ are considered one way to capture the net exchange rate of dissolved species across the sediment–water interface (e.g., Tengberg et al., 1995, Berelson and Hammond, 1986). Although benthic chambers are by no means free from artifacts, they present an adequate tool for examining both in situ flux values and fluxes under varying conditions. One way in which artifacts can be generated is by changing chemistry within a benthic chamber over the course of a deployment. A change in net chemical transport during chamber water incubation can be indicative of the various feedbacks and sensitivities of different reactions to short-term redox change (e.g. Sundby et al., 1986). Such an experiment is short-term, the changes in flux that develop can be tracked over hours rather than days-weeks, but these changes are nonetheless important suggesting the first response in flux (intensity, direction) to changes in overlying water chemistry.

Reimers et al. (2012) compared benthic oxygen fluxes determined using three approaches; pore water profile modeling, eddy correlation approach and benthic chambers. Our study sites overlap with their study sites, we measured benthic fluxes from...
Table 1
Station location and environmental parameters.

<table>
<thead>
<tr>
<th>Location ID#</th>
<th>Depth (m)</th>
<th>Lat.</th>
<th>Long. (W)</th>
<th>Chambers</th>
<th>BW O$_2$ ($\mu$M)</th>
<th>BW NO$_3$ ($\mu$M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIF-I (April-May 2007)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Umpqua R. Sta. 1</td>
<td>105</td>
<td>43'56.0'</td>
<td>124'19.2'</td>
<td>2</td>
<td>60</td>
<td>31.4</td>
</tr>
<tr>
<td>Umpqua R. Sta. 2</td>
<td>190</td>
<td>43'55.2'</td>
<td>124'41.4'</td>
<td>2</td>
<td>64</td>
<td>35.0</td>
</tr>
<tr>
<td>Eel R. Sta. 3</td>
<td>90</td>
<td>40'57.0'</td>
<td>124'18.1'</td>
<td>2</td>
<td>93</td>
<td>32.4</td>
</tr>
<tr>
<td>Eel R. Sta. 6</td>
<td>125</td>
<td>41'00.0'</td>
<td>124'20.3'</td>
<td>2</td>
<td>94</td>
<td>31.5</td>
</tr>
<tr>
<td>BIF-II (September 2007)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Umpqua R. Sta. 1</td>
<td>105</td>
<td>43'56.0'</td>
<td>124'19.2'</td>
<td>2</td>
<td>78</td>
<td>34.0</td>
</tr>
<tr>
<td>Umpqua R. Sta. 2</td>
<td>190</td>
<td>43'55.2'</td>
<td>124'41.4'</td>
<td>3</td>
<td>60</td>
<td>35.5</td>
</tr>
<tr>
<td>Eel R. Sta. 3</td>
<td>90</td>
<td>40'57.0'</td>
<td>124'18.1'</td>
<td>3</td>
<td>142</td>
<td>26.1</td>
</tr>
<tr>
<td>Eel R. Sta. 6</td>
<td>125</td>
<td>41'00.0'</td>
<td>124'20.3'</td>
<td>2</td>
<td>125</td>
<td>28.0</td>
</tr>
</tbody>
</table>

Silty-muddy continental shelf (90–200 m) sediments offshore from the outflow of the Umpqua River (Stations 1, and 2—comparable to Reimers et al., 2012) and offshore from the Eel River (Stations 3 and 6) (Table 1, Fig. 1). Fieldwork took place in May 2007 (BIF-I) and sites were revisited again in September 2007 (BIF-II). The focus of our study was to examine benthic iron fluxes (BIF, the name of our field campaign, Severmann et al., 2010), Mn fluxes (McManus et al., 2012), and summarize nutrient benthic flux data derived from in situ chamber incubations. We also provide a comparison of oxygen flux estimates from these sites to other data from along the western US shelf.

2. Methods

We deployed free-vehicle benthic chambers (Berelson and Hammond, 1986) for ~24–48 h at various stations to incubate the sea floor in situ and to assess changes in chamber water chemistry. An hour or two after free-vehicle landing, chamber lids close and the chambers (three per lander) isolate bottom water in contact with sediment. Chamber heights ranged from 8.2–12.6 cm; these are typical chamber heights for the lander used in this study and represent chamber volumes of 5.8 to 8.0 liters (Berelson and Hammond, 1986). The overlying water was stirred with a paddle to simulate bottom water turbulence, the paddle stir rate was 7 RPM. With each sample draw, ~120 ml of chamber water is sucked through a filter frit (0.2 μm) and a line of Teflon tubing into a reservoir. Along route, this water flushes and fills two 10 ml sample tubes (one plastic and one glass). This repre-
sents an extraction of 1.5–3% of the chamber volume, per draw. Over the course of incubation, six samples were drawn from each chamber. Trace metal-free CsCl was injected into each chamber one hour after lid closure, and its initial dilution was used to quantify chamber volume. The loss rate of cesium was deter-
moved to assess chamber-water exchange with pore waters and the possibility of chamber leakage (Townsend, 1998; Berelson et al., 1999).

Nutrients were analyzed using a continuous flow segmented analysis system at Oregon State University, the procedures are detailed in Gordon et al. (1995). We assessed precision for the chamber nutrient values by reproducing a mixed coastal seawater solution. The nutrient concentrations (μM) and 1σ uncertainties for this sample were 1.241 ± 0.006, 19.9 ± 0.11, 81.3 ± 0.19, 0.131 ± 0.163 for phosphate, nitrate plus nitrite, silicate acid, and ammonium, respectively (n = 10). The standard ammonium concentration is low relative to many of our lander samples, hence we used replicate analyses of lander samples to define a precision of ±5%. Cesium was measured via quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, an Agilent 7500ce), at UC Riverside, this analysis was reproducible to ± 3%.

Oxygen analyses were made on shipboard using chamber samples that were collected in glass tubes. Before each use, an optode (Presens) was standardized between seawater equilibrated with air and seawater treated with sodium sulfite (0 μM). Measurements (precision of ± 4 μM on replicates) were made within an hour of recovery. Carbonate Alkalinity was calculated from TCO$_2$ measurements made on a UIC Coulometer (± 0.1 μM) and pH measurements, which were analyzed using a glass combination electrode calibrated to NBS standards (± 0.01 pH units). Ambient bottom water nutrient and oxygen concentrations were determined from measurements of Niskin samples recovered from hydrocasts. These data were used to correct chamber sample values because with each draw, ambient water enters the cham-
ber to replace sample water. This correction is made assuming the entering water mixes with the chamber water after a draw is complete (Hammond et al., 1996).

Fluxes were established as a linear change of concentration versus time for 0–20 h, multiplied by effective chamber height (volume/area). The loss of Cs with time was fit with an exponen-
tial function and the fitting exponent, α (1/d), is considered a proxy for the bioirrigation rate of exchange between pore waters (Cs-free) and chamber water (Townsend, 1998; Berelson et al., 1999).

In September and October 2004 and July 2005, locations near Sta. 1 and 2 were also studied using a free vehicle micro-electrode profiler (Reimers et al. 2001, 2012) and a frame-mounted hydraulically-damped gravity corer with a digital still-camera (Insite Pacific Inc. Scorpio). The camera was triggered to take oblique photos of the seafloor as the corer landed. The micro-
profiler has channels for four oxygen microelectrodes and a four-
wire resistivity sensor (Reimers and Glud, 2000). Oxygen mea-
surements were made in vertical steps of 0.125 mm, and the micro-
electrodes (Unisense Ox-25) were calibrated assuming a linear slope and two calibration points: an average bottom water reading 5–10 mm above the sediment–water interface, and an average background reading in anoxic subsurface sections of the sediment. Fluxes were determined by applying Ficks First Law calculations to microelectrode profiles (Reimers et al., 2012).

3. Results

A linear trend in analyte concentration vs. incubation time within a benthic chamber is indicative of a constant flux for the duration of the deployment (Bender et al., 1989; Jahne and Christiansen, 1989). In general, chamber results show linear trends in concentrations of nitrate, silicate, and phosphate as a function of deployment time (Fig. 3). Oxygen uptake was also generally constant with incubation time, although in some chambers, there was a change in oxygen uptake rate as oxygen concentrations declined, as will be discussed later. With the exception of some BIF-II ammonium flux data, we report fluxes from the first 20 h of an incubation. The trends in alkalinity and TCO$_2$ vs. time showed a large scatter but were also fit with a linear trend-line for the first 20 h. The trend in ammonium chamber data showed a linear increase with time during the spring cruise (BIF-I; Fig. 3a), however, some chambers deployed in the Fall 2007 cruise (BIF-II) exhibit deviation from the linear trend (Fig. 3b). The uncertainty in the reported flux value is derived by the product of the uncertainty in the linear fit to the chamber data and the uncertainty in the estimate of chamber volume as extracted from the Cs data (Hammond et al., 1996).

Fluxes from individual chambers from each lander deployment are reported and these data were averaged to provide the mean
station flux (Table 2). Considering all the chamber flux determinations over both field seasons, oxygen uptake rates varied from \(-2.3\) to \(-9.9\ mmol\ m^{-2}\ d^{-1}\) (a negative flux indicates transport into the sediments) and TCO\(_2\) flux varied from \(4–31\ mmol\ m^{-2}\ d^{-1}\), however, the uncertainty in each TCO\(_2\) flux was quite large. One phosphate flux during BIF-I was into the sediment (Sta. 3), whereas all the others were into the overlying water; the range was \(-0.05\) to \(0.20\ mmol\ m^{-2}\ d^{-1}\). Phosphate fluxes had the greatest intra-site variability, as much as a factor of five between chambers. The ammonium flux was either out of the sediments or negligible and the range in fluxes was \(0–1.9\ mmol\ m^{-2}\ d^{-1}\). We report ammonium flux for the early incubation period (first 10 h) in cases where the flux changed significantly with time (BIF-II). Silicate fluxes ranged from \(5.8\) to \(15\ mmol\ m^{-2}\ d^{-1}\) and were consistent to \(\pm 40\%\) within a site. Nitrate fluxes were always into the sediments and varied from \(0.6\) to \(2.2\ mmol\ m^{-2}\ d^{-1}\). Alkalinity fluxes ranged from \(2–28\ meq\ m^{-2}\ d^{-1}\) and were generally close to but less than the TCO\(_2\) flux values. The Cs fitting exponent, \(\alpha\), ranged from 0.42 to 2.4 day\(^{-1}\).

In cores we examined, worm burrows were common to depths to 8 cm and present to depths \(>15\ cm\). Photographs of the sea floor at the Umpqua River stations (July 2005) further demonstrate the bioturbated and bio-irrigated nature of this environment (Fig. 2). Microelectrode profiles (discussed in detail in Reimers et al., 2012) show steep gradients near the sediment–water interface and the absence of oxygen below 3–4 mm (Fig. 4). However, some profiles do capture sediment horizons in which oxygen rises again and the interpretation is that a burrow tube has been intersected by the electrode.

4. Discussion

4.1. Temporal and spatial variability

Continental shelf benthic environments may be highly variable with respect to conditions that generate a benthic flux (e.g., Berelson et al., 2003). Our study area (Fig. 1) encompasses two regions adjacent to river mouths, where sediment discharge is highly variable and seasonal (Wheatcroft, 2006). Additionally, the upwelling season was beginning at the time of the spring cruise (BIF-I) and ending by the time of the fall cruise (BIF-II). We do not believe that we have sufficient temporal or spatial coverage to quantitatively compare fluxes, hence the discussion below offers a qualitative assessment of flux variability.

During BIF-I, it appears that only nitrate fluxes were significantly different between the northern and southern stations, higher in the north, lower in the south. This appears to be true for BIF-II for both nitrate and oxygen fluxes; higher in the north, lower in the south. There is also a suggestion that irrigation rates (\(\alpha\)) were higher in the north.

Temporal differences in fluxes do not vary by more than a factor of two, often the differences are \(<30\%\). The data suggests somewhat larger fluxes in general during BIF-I time. However, the inter-relation between benthic fluxes and environmental factors...
is not necessarily straightforward. For example, during the BIF-II cruise, bottom water oxygen values were higher than during BIF-I by 30–50%. Higher bottom water oxygen concentration will provide a greater driving force for diffusive transport of O₂ (Cai and Reimers, 1995; Cai and Sayles, 1996) and may also play a role in nutrient flux partitioning and possibly in bioirrigation rates.
In summary, seasonal and spatial differences in fluxes are not large and hence we focus on flux ratios throughout this region and the behavior of nutrient fluxes as oxygen declines in a chamber.

4.2. Stoichiometry

Flux ratios can lend insight into reaction stoichiometry and diagenetic processes occurring in a sediment column. Measured O$_2$:TCO$_2$ flux ratios suggests that oxygen consumption is not solely responsible for the TCO$_2$ flux via organic carbon oxidation because the values measured (~0.2 to 0.7) are generally much lower than the ratio expected (1.3–1.4) if oxygen were the major oxidant for organic C and N. These results, with the caveat regarding alkalinity fluxes discussed below, suggest that denitrification and other suboxic and anoxic diagenetic processes are likely responsible for much of the TCO$_2$ flux observed.

Alkalinity fluxes were equivalent to or less than TCO$_2$ fluxes (Table 2). As an upper limit, if all the alkalinity flux were attributable to carbonate dissolution, the range of carbonate dissolution would be 1–14 mmol C m$^{-2}$ d$^{-1}$. More important to this discussion, if the alkalinity were entirely accounted for by carbonate dissolution, the TCO$_2$ fluxes attributable to C$_{org}$ oxidation would be reduced by 12–50%. We proceed with the assumption that there is no carbonate dissolution and the TCO$_2$ flux is a suitable representation of C$_{org}$ oxidation, but acknowledge that this assumption makes our estimates of C$_{org}$ oxidation an upper limit.

The flux ratio of TCO$_2$ to phosphate should provide an indication of either excess phosphate liberated from sources other than C$_{org}$ (such as dissolution of iron oxide carrier phases), or phosphate sequestration into authigenic phosphate-bearing mineral phases (Ruttenberg and Berner, 1993; McManus et al., 1997). The summary of all station flux values (Table 2) shows variability in the TCO$_2$:PO$_4$ flux ratio, ranging from 60 to 500 (average = 200 ± 140, 1 s.d.). Only two stations, Eel River at 125 m (Sta. 6) during BIF-I and Umpqua River at 190 m (Sta. 2) during BIF-II, show a ratio significantly lower than the Redfield ratio of ~110 (Fig. 5), suggestive of phosphate liberation from sources other than C$_{org}$. Given the very high rates of Fe flux from these sediments (Severmann et al., 2010), one might have expected TCO$_2$:PO$_4$ flux ratios consistently lower than the Redfield ratio. However, the highest iron flux site, BIF-I-1, has a TCO$_2$:PO$_4$ flux ratio = 128 ± 50, which is indistinguishable from the Redfield ratio. Our interpretation of these flux ratios is that the efflux of phosphate is not mechanistically linked to the processes generating Fe flux in these particular settings.

Studies with benthic chambers at a muddy shelf site in Monterey Bay (100 m), Central California showed positive correlations between TCO$_2$ and fluxes of ammonium, nitrate (uptake) and silicate (Berelson et al., 2003). Similar associations are found for the sediments off S. Oregon/N. California (Fig. 5). Correlations between ammonium, nitrate, oxygen (uptake) and silicate with TCO$_2$ fluxes show linear correlation coefficients of $r$ = 0.66, 0.59, 0.31, and 0.88, respectively. One reason for these correlations could be that all nutrient fluxes are controlled by an external factor, such as bioirrigation rate. Previous chamber work has shown that dissolved silicate flux and bioirrigation rate were very closely coupled (Berelson et al., 2002), however plots of $\alpha$ vs. TCO$_2$, ammonium, silicate and nitrate fluxes show weak or no correlation ($r$-values, 0.38, 0.13, 0.04 and 0.01 respectively). This implies that irrigation rate may not be a major controlling parameter with respect to these nutrient fluxes. Oxygen fluxes and $\alpha$ values do show a negative correlation with an $r$-value of 0.64 (Fig. 5) whereby higher irrigation rates corresponded with higher oxygen uptake rates. Organic matter delivery to these sediments may be the major driver of nutrient fluxes and silicate efflux may be closely coupled to C$_{org}$ remineralization if diatom debris is a major component of the particulate organic rain. However, it appears that only oxygen consumption is closely coupled to bioirrigation intensity.

Fig. 5. Flux vs. flux plots for average station fluxes of ammonium, nitrate, silicate, phosphate vs. TCO$_2$. Also shown are fluxes vs. $\alpha$, the bioirrigation rate constant. Error bars represent the s.d. of the mean station flux value (Table 2).
At most sites and during both seasons, nitrate uptake exceeds ammonium effluxes such that these sediments are net sinks for fixed nitrogen. However, at two Eel River stations, BIF-I-6 and BIF-II-3, ammonium fluxes exceeded nitrate uptake fluxes. In contrast to observations in Monterey Bay (Berelson et al., 2003), this excess of ammonium flux over nitrate uptake is not associated with low TCO2 fluxes. Although both nitrate uptake and ammonium fluxes are correlated with TCO2 fluxes, their sum shows no covariance with TCO2 flux (r=0.01).

4.3. Fluxes of oxygen

In situ microelectrode profiling shows rapid consumption of oxygen within a few millimeters of the sediment–water interface (Fig. 4) indicating the high reactivity of these surficial muds, but also the occasional invasion of oxygenated waters into the sediment column via irrigation tubes. The derived diffusive fluxes (from 2004–2005) average 40% less than the chamber fluxes of BIF-I and II (Table 3). Similar differences between diffusive and chamber fluxes were observed on the Washington Shelf (Christensen et al., 1984; Archer and Devol, 1992) and in a recent study off the Oregon shelf (Reimers et al., 2012). In Reimers et al. (2012) study, benthic chambers and the eddy correlation technique yielded total oxygen uptake rate estimates from −3 to −10 mmol m⁻² d⁻¹ at three Oregon shelf stations (80 m). These measurements were made in June and August 2009, yet are consistent with the rates reported in this study.

The convergence of flux values determined with chambers and eddy correlation techniques and the difference between diffusive flux estimates from the modeling of profiles and total O₂ fluxes determined with chambers is likely described as a consequence of a bioirrigation enhancement of the total flux. As demonstrated in Fig. 5, bioirrigation rates (z) are well correlated with oxygen uptake rates and that rates are higher during BIF-II than BIF-I (Table 2). We conclude that this region of the Oregon/N. California shelf is one in which bio-irrigation plays an important role in oxygen uptake, but a lesser role in the overall efflux of dissolved Si, ammonium or phosphate.

4.4. Benthic oxygen uptake along the western US continental shelf

The fluxes measured in this study can be compared to fluxes measured with the same in situ chambers from the shelf of Monterey/Pt. Sur and off Southern California (San Pedro Shelf). Additionally, Devol and Christensen (1993) report fluxes measured with benthic landers from sites off the coast of central Washington and Reimers et al. (2012) report oxygen fluxes determined with Devol-chambers as well as using eddy correlation techniques from several Oregon Shelf sites. This compilation (Table 4) includes measurements made in muddy shelf sediments from depths ranging from 62–190 m. Oxygen uptake rates measured from the Washington, Oregon, Northern and Central California margins are all quite similar, both in range and mean uptake rate. Given how many factors may impact oxygen consumption, including, seasonality, bio-irrigation, and biogenic matter input, it is notable that the range of oxygen consumption rates at these sites, 2.3–18.3 mmol m⁻² d⁻¹ differs only by a factor of 9, and that the mean values agree to within a factor of 2. There appears to be a general consistency to the magnitude of oxygen consumption in shelf sediments over a broad time period, across many seasons, and over >1000 km spatial separation. Oxygen uptake at the Southern California shelf site (San Pedro Shelf) may be different due to influences from sewage outfall located up-current from the study area (Berelson et al., 2002).

Most benthic chamber oxygen data show some curvature in concentration vs. time indicating a decline in uptake rate as the incubation proceeds; this is apparent in data published (Devol and Christensen, 1993, figure 2; Reimers et al., 2012, figure 11) and from our work (Fig. 3). The curvature in the BIFs chambers is subtle, some show very linear trends in oxygen vs. time, yet other chambers, e.g. those from Sta. NH02 (Devol and Christensen, 1993), show very large changes in oxygen uptake rate occurring over incubation periods of 14 h. All fluxes reported account for oxygen uptake during the initial phase of chamber incubation when oxygen decline vs. time is occurring most rapidly.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Comparison between oxygen uptake rates derived from pore water profiles and chambers (BIFs).</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>Station, Umpqua River</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Oxygen uptake fluxes (into the sediments) determined using benthic chambers from continental shelf sites along the west coast of the US.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location Shelf</td>
<td>Depth range (m)</td>
</tr>
<tr>
<td>Washington</td>
<td>98–161</td>
</tr>
<tr>
<td>Oregon</td>
<td>81–82</td>
</tr>
<tr>
<td>Oregon/N. Calif.</td>
<td>90–190</td>
</tr>
<tr>
<td>Central California</td>
<td>95–101</td>
</tr>
<tr>
<td>Southern California</td>
<td>62–68</td>
</tr>
</tbody>
</table>

* Reimers et al. (2012).
* This study, BIFs.
* Berelson et al. (2002) Station 3.
One interpretation of the decline in oxygen flux vs. time is the negative feedback between oxygen concentration and uptake.

The role of benthic oxygen uptake in light of hypoxia along the Oregon coast has been discussed by Reimers et al. (2012). This work included a calculation of how long it would take to deplete oxygen from a portion of the water column considering only uptake by the sediments. Our measurements are consistent with those reported by Reimers et al. (2012), oxygen consumption on the sea floor at a rate of 6 mmol m⁻² d⁻¹ will deplete a 100 m water column at a rate of 0.06 μM/day. This will require a long residence time of water on the shelf in contact with the sea floor in order to deplete oxygen by several μM. The negative feedback between oxygen concentration and uptake rate observed in benthic chambers may provide a negative feedback to exacerbated hypoxia. It is clear that oxygen flux has a very short response time with respect to oxygen concentration compared to other nutrient species, as discussed below.

4.5. Do fluxes change as oxygen concentration declines?

As incubation time proceeds and oxygen concentration declines within a benthic chamber, the response of redox-sensitive species will be predicated on their reaction kinetics in the sediments and in the bottom water, changes in transport mechanism, and changes in the distance scale over which pore water solutes enter chamber water. A number of authors have demonstrated changes in reactive metal fluxes (e.g., Mn and Fe) as chamber oxygen values approached 0 μM (Sundby et al., 1986; Pakhomova et al., 2007). As discussed in Severmann et al. (2010) and Homoky et al. (2012), there appears to be a non-linear response of iron flux in the Oregon and N. California sediments related to chamber oxygen concentration. One possible explanation discussed by these authors is that this pattern is driven by oxidation artifacts, either within sample storage tubes or the chamber. Although also redox sensitive, Mn flux at BIF sites is invariant with chamber oxygen concentration (McManus et al., 2012).

Changes in the flux of other nutrient species with incubation time reflect the processes responsible for changes in oxygen uptake. Data shown in figure 2 of Devol and Christensen (1993) for a site off the Washington coast indicates negligible change (< 10%) in the flux of nitrate, silicate, phosphate or ammonium whereas the oxygen flux clearly is changing by more than a factor of 10. At BIF sites there are also small or undetectable changes in flux vs. incubation time for nitrate, silicate, phosphate and manganese (McManus et al., 2012). The ammonium fluxes detected in chambers deployed during BIF-I also show little change in flux over time. However, chambers deployed during BIF-II do show some significant changes in concentration vs. time (Fig. 3). The fluxes during the first 5–15 h of incubation are 3–14 times less than the fluxes occurring after this time.

An examination of chamber data from Monterey/Central California and from that published by Devol and Christensen (1993) show no other instances where there was a large change in ammonium flux with incubation time. The ammonium fluxes from shelf sediments along the Washington, Oregon, North and Central California margins are of similar magnitude (Fig. 6). While there may be something peculiar about BIF-II sediments during the Fall season, there is no factor that we can clearly identify. One potential concern is that an enhanced ammonium flux from shelf sediments during periods of overlying water hypoxia could serve to stimulate productivity and provide positive feedback to hypoxic conditions, yet its absence at many other similar sites suggests that this is not a regular or predictable outcome.

5. Summary and conclusions

Free vehicle benthic chambers have been used to define benthic nutrient fluxes in the region of the S. Oregon/N. California shelf (90–200 m). Two sites off the Umpqua River and two off the Eel River were studied in the spring and fall, 2007 to establish flux values, compare them to other flux estimates from the US west coast continental shelf and to evaluate the impacts of changing oxygen concentration on benthic flux.

1. Nitrate and oxygen fluxes and bioirrigation rate (α) values showed some differences between northern stations off the Umpqua River and southern stations off the Eel River. Nitrate uptake rates and bioirrigation rates were greater in the north, oxygen uptake rates greater in the south. Differences in fluxes between the two cruise periods indicate only nitrate and bioirrigation rate shows variability. The fluxes of silicate, phosphate, ammonium, TCO 2 and alkalinity are generally consistent between these sites and over different seasons.

2. Oxygen uptake, if driven by aerobic respiration, is likely responsible for < 50% of the C org oxidized in these sediments as denitrification and other electron transport processes generate the TCO 2 flux observed. Even though these sediments generate very large Fe fluxes (Severmann et al., 2010), there is little phosphate flux that can be considered in excess of the amount predicted by Redfield stoichiometry, the average TCO 2:PO 4 3⁻ flux ratio=200 ± 140. Correlations between the fluxes of ammonium, nitrate and silicate with TCO 2 are positive with linear correlation coefficients, r=0.66, 0.59, and 0.88, respectively. Bioirrigation rate coefficients correlate well with oxygen fluxes (r=0.64) but poorly with nutrient fluxes. These shelf sediments are a net sink of water column fixed nitrogen as nitrate uptake rates generally exceed ammonium effluxes.

3. In situ microelectrode profiling at Stations 1 and 2 in the northern study region show steep gradients and complete oxygen consumption within 2–4 mm of the sediment–water interface. Fluxes predicted by modeling these profiles with a diffusion/reaction equation are 40% less than the fluxes measured by benthic chambers. Results of oxygen flux determinations in 2007 (this study) with other measurements made using another benthic lander and with eddy correlation techniques (Reimers et al., 2012) are in agreement indicating
oxygen uptake rates of 3–10 mmol m$^{-2}$ d$^{-1}$. Oxygen uptake rates between the Washington Shelf and Central California margin are of comparable magnitude, between 6 and 12 mmol m$^{-2}$ d$^{-1}$. If these rates are representative of the broader region, it appears that benthic oxygen uptake is not likely to impact water column hypoxia by more than a few µM for a water column several 10's of meters thick.

4. As chamber oxygen concentrations decline during an incubation, the concentration trends of phosphate, nitrate, silicate and manganese remain linear. There is no short-term response in flux of these species to changing oxygen concentration. During the spring field season, the ammonium fluxes were also constant over the incubation period, but in the fall, ammonium fluxes showed a 3–14 fold increase, 5–15 h into the incubation. Such a response to chamber conditions had not been previously observed in over 50 chamber fluxes analyzed along the US west coast margin.

The incursion of low oxygen waters onto the shelf off S. Oregon and N. California subjects the benthic community to new conditions that can negatively impact macrofauna. This incursion may last for hours (tidal cycles) or weeks to months. Fluxes of oxygen, nitrogen, phosphorus, and manganese are of comparable magnitude, between 6 and 1681–1699 (Papers). Cai, W.-J., Sayles, F.L., 1996. Oxygen penetration depths and fluxes in marine sediments. In: Marine Chemistry 13, 131–134.

Acknowledgments

This work was supported by NSF Grants to JM (OCE-0624777), SS (OCE-0624704), CR (OCE-1061218) and WB (OCE-0624443). We acknowledge the support of the crew of the R/V WECOMA. T. Riedel, W. Beaumont, B. Johnson, M. Davies, L. Collins, J. Muratli, W. Homoky, J. Owens, D. Hubbard, R. Sanders are acknowledged for their help with shipboard operations and analyses. Joe Jennings at Oregon State University handled the nutrient analyses. L. Chong and W. Homoky, J. Owens, D. Hubbard, R. Sanders are acknowledged for their help with statistical analyses. We acknowledge the helpful comments provided by CSR reviewers.

References


