A multiproxy approach
to understanding the 'enhanced' flux of organic matter
through the oxygen deficient waters of the Arabian Sea

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Abstract

Free-drifting sediment net traps were deployed 14 times at depths between 80 and 500m for 1-3 days each during the late monsoon-intermonsoon transition in the central Arabian Sea. Two locations (19.5° and 15.5°N) were within the permanently oxygen deficient zone, and a third (11°N) had a shallow and thin oxygen minimum. The secondary nitrite maximum, which serves as a tracer of the oxygen deficient zone (ODZ) zone, thinned from ~250 m thick at stations 19.5°N and 15.5°N to ~50 m thick at station 11°N. Overall, organic carbon fluxes ranged from 13.2 g m^2 y^{-1} at 80 m to a minimum of 1.1 g m^2 y^{-1} at 500 m. Fluxes at the more oxygenated 11°N station attenuate faster than within the permanent ODZ. Martin curve attenuation coefficients for 19.5°N and 15.5°N are 0.59 and 0.63 and for 11°N it is 0.98. At least six potential mechanisms might explain why sinking particles sinking through the ODZ are more effectively transferred to depth; (M1) oxygen effects, (M2) microbial loop efficiencies and chemoautotrophy, (M3) changes in zooplankton dynamics, (M4) additions of ballast that might sorb and protect organic matter from decay (M4a) or change sinking speeds (M4b), (M5) inputs of refractory organic matter and (M6) temperature effects. These mechanisms are intertwined, and were explored using a combination of mineral (XPS) and organic matter characterizations of the sinking material, ship-board incubation experiments, and evaluations of existing literature. Direct evidence was found

1 supporting an oxygen effect and/or changes in the efficiency of the microbial loop including the addition
2 of chemoautotrophic carbon to the sinking flux in the upper 500 m. Less direct evidence was found for
3 the other potential mechanisms. A simple conceptual model consistent with our and other recent data
4 suggests that the upper ODZ microbial community determines the initial flux attenuation, and that
5 deeper in the water column zooplankton and sinking speed become more important. The exact
6 interplay between the various mechanisms remains to be further evaluated.

7 Keywords
8 Arabian Sea, biological pump, sinking particles, organic carbon, proteomics, targeted peptidomics, lignin,
9 amino acids, XPS, Martin curve

10 1.0   Introduction
11 Sinking particles are an important component of the biological pump. Once below the euphotic zone,
12 organic matter and nutrients in sinking particles are removed from the biogeochemical processes of the
13 upper ocean; the time scale of this sequestration depending on the depth to which the material sinks or
14 is remineralized (Buesseler & Boyd 2009). For sediment trap data, this is typically quantitated using
15 either a power decay function (Martin et al. 1987) or by relating organic matter fluxes to ballast mineral
16 flux (Armstrong et al. 2002). Using either approach, the decay function within Oxygen Deficient Zones
17 (ODZ; waters with zero or unmeasurable oxygenJensen et al. 2011) is different - less decay - from that of
18 the oxic portions of the ocean (Hartnett & Devol 2003; Roullier et al. 2014; Van Mooy et al. 2002). That
19 is, the relative proportion of organic matter that passes through ODZs is proportionally higher than that
20 for oxic waters. There are many possible reasons for this, and currently they are poorly evaluated.

21 Potential mechanisms (M) that might cause organic carbon fluxes through ODZ waters to be less
22 attenuated include those that are directly related to ODZs themselves; (M1) the possibility that *anoxic*
23 *degradation* is sufficiently slower or less comprehensive relative to oxic carbon remineralization, (M2)
24 the possibility that the microbial consortia in ODZ regions have a higher *growth efficiency* and
25 incorporate *chemoautotrophy* thus adding carbon to the flux, and (M3) *zooplankton dynamics* in ODZ
26 regions might alter the flux attenuation in a variety of ways.

27 Mechanisms that are not necessarily specific to ODZ regions, but might simply be coincident, include
28 (M4a) *mineral protection* where differences in bio and lithogenic mineral inputs control the
29 remineralization profile of sinking organic matter in the ocean, (M4b) changes in the *sinking speed* of
30 particles due to differences in ballast, and (M5) *inputs of recalcitrant organic matter* could alter the flux
31 attenuation. An additional potential mechanism (M6) is temperature. Marsay et al (2015) suggest that
32 temperature plays a role in determining the length scale of sinking particle remineralization, which could
33 result in changes in apparent flux attenuation. Each of these potential mechanisms for enhanced flux
34 through ODZ regions has merit, and are briefly introduced below.

35 While the long-term (decade to millennia) importance of (M1) oxygen effects on organic matter
36 preservation are well established (Arnarson & Keil 2007; Hedges & Keil 1995), the importance of oxygen

1 over short time periods or during early diagenesis has been an extremely hard issue to address (Cowie &
2 Hedges 1992b). There seems to be an effect; Harnett et al (1998) suggested that the diminished oxygen
3 exposure of ODZ sinking particles increases the efficiency with which they are transferred to deeper
4 waters, and Van Mooy et al (2002) observed direct oxygen effects in incubations of ODZ water from the
5 Eastern Tropical North Pacific.

6 The microbial loop within an ODZ can influence the flux in a number of ways. If the community grows
7 with a higher growth efficiency than oxic communities (M2a), then ODZ communities could more
8 biomass per unit respiration. For example, if a dark aerobic community has a growth efficiency of 10%
9 and a suboxic ODZ community has a growth efficiency of 20%, then for every unit of respiration twice as
10 much new biomass will result, and this will manifest itself as a change in the attenuation coefficient.
11 This concept has been loosely explored by Naqvi (2014, pers comm). Additionally, the long held
12 assumption that heterotrophic respiration is the only significant biogeochemical process in the
13 mesopelagic has been overturned by the discovery of abundant chemoautotrophic microorganisms
14 (Dalsgaard et al. 2003; Kuypers et al. 2003). Thus, a subcomponent of M2 could be the (M2b)
15 chemoautotrophic production of new organic matter in ODZs, which if it sinks would add to the flux
16 (Close et al. 2014; Roland et al. 2008).

17 Zooplankton dynamics within the ODZ are complex and could alter the sinking flux in a variety of ways.
18 When they migrate into the ODZ, zooplankton (M3a) deliver dissolved nutrients (Wishner et al 2013)
19 that can support chemoautotrophy and (M3b) create pulses of defecated material that is not subject to
20 remineralization in shallower waters (Cavan et al. 2015). Both these thing would enhance the flux.
21 However, the ODZ is a harsh environment for a eukaryotic obligate aerobe, and if the ODZ hosts fewer
22 zooplankton than an aerobic water column (Levin et al. 2015; Wishner et al. 2013) then it is logical to
23 hypothesize that (M3c) the overall effect of zooplankton respiration will be less, which might in-and-of
24 itself be enough to result in enhanced fluxes through the upper watercolumn.

25 Minerals are a strong determinant on organic matter burial in sediments (Keil & Cowie 1999; Keil et al.
26 1997). How this impact is felt in the water column remains largely unconstrained. Inorganic material
27 acts as a catalyst for particle formation, altering the flux of organic carbon (Lee et al. 2009). A possible
28 mechanism linking mineral and enhanced flux would be that minerals can provide abundant points of
29 interaction with organic matter, promoting aggregation and sorption (e.g., Passow and De La Rocha,
30 2006). (M4) Organic-mineral interactions might then protect the organic matter from remineralization,
31 at least on the short time scale of sinking particles (Arnarson and Keil, 2005). Overall organic carbon
32 export might be enhanced both by increasing sinking rates and slowing degradation. Whether this
33 mechanism could explain ODZ enhanced fluxes has not been explored.

34 Another potential factor linking carbon fluxes and mineral material is (M4b) sinking speed (Le Moigne et
35 al 2012). In both the Martin equation and the ballast model, sinking speed and remineralization rate
36 combine to control the flux and attenuation. If for some reason, ODZ regions have particles with
37 enhanced sinking speeds, then lower attenuation per unit depth would result. Changes in sinking speed
38 could result from changes in species composition or from changes in dust inputs, or the efficiency with

1 which zooplankton and other community members package material into sinking particles (Cavan et al

2 2015).

3 Lithogenic minerals might also impact sinking carbon by (M5) bringing refractory terrestrial organic

4 matter with them (Burdige 2005; Keil et al. 2004). To date, analyses of terrestrial carbon in sinking

5 fluxes has largely been constrained to oxic water columns very close to land where the inputs are

6 significant (Hedges et al. 1988).

7 Finally, the effect of temperature (M6) is to lengthen the depth scale of remineralization for colder

8 (slower) situations (Matsumoto 2007, Marsay et al 2015). Since many ODZ regions are tropical or

9 subtropical, temperature effects on particle degradation should result in higher attenuation (more

10 degradation) in warm ODZ waters, but this appears not to be the case.

11 We evaluated these possible mechanisms using a combination of sediment trap and incubation studies,

12 by measuring a variety of mineral and organic markers, and by comparing our data to recent literature

13 for the Arabian Sea that uses complimentary analyses that help us address mechanisms where our data

14 are insufficient. Direct analyses of our sediment trap materials included mineral surface area and

15 surface-associated elemental compounds (using X-ray photoelectron spectroscopy); organic matter

16 quantity and bulk ^{13}C and ^{15}N isotopic compositions, and total amino acid and lignin compositions.

17 Finally, targeted peptidomics was used to quantify key enzymes in the heterotrophic denitrification and

18 the chemoautotrophic anammox pathways.

19 ## 2.0   Methods

20 ### 2.1 Sample Collection

21 Surface tethered, free-drifting sediment net traps (Peterson et al. 2005) were deployed from the R/V

22 Roger Revelle for periods of 12-48 h. Sampling took place during the late monsoon/intermonsoon

23 transition between Sep 23 – Oct 6, 2007 in the central Arabian Sea (Figure 1). Three stations were

24 occupied; stations 1 and 2 were located within the region previously documented as the permanent

25 oxygen deficient zone (ODZ)(Naqvi 1991). Station 3 was located at the edge of the permanent ODZ and

26 had a much shallower and thinner ODZ (Figure 1). Water column characteristics were evaluated at each

27 station and at intermediate sites between stations based on water samples collected using 10 L Niskin

28 bottles on a conductivity–temperature–depth (CTD) rosette system. A Seabird O_2 sensor was calibrated

29 to shipboard Winkler assays and a blank value equal to the steady-state value observed in the heart of

30 the ODZ was subtracted from each measurement. This was done because oceanic ODZ regions including

31 the Arabian Sea are now known to be functionally anoxic (Jensen et al. 2011; Thamdrup et al. 2012;

32 Tiano et al. 2014; Ulloa et al. 2012). Nutrient concentrations have been reported previously (Bulow et

33 al. 2010; Newell et al. 2011).

34 Three stations were occupied and a total of 14 sinking particle samples collected at depths from the

35 thermocline to 500 m (Table 1). Two sizes of nets were used, a 2 m diameter net as originally described

36 by Peterson et al (2005), and a smaller 1.25 m diameter net (all dimensions scaled to the new diameter).

1 The smaller nets were used for shallower sampling (<200m) and the larger ones used at depths greater
2 than 200 m. Both nets used 53 μm mesh on the cone and were closed using a brass messenger system.
3 Nets were set either singly or in pairs (at two different depths) and tethered to the surface using polydac
4 line, a string of surface floats, and a surface spar with radio transmitter and light beacon. The net traps
5 were deployed open, and then closed using the messenger immediately prior to recovery. No poisons
6 were used. Each trap sample was analysed in duplicate.

7 Four additional samples were collected at depths >1000 m by deploying the net traps as vertical nets
8 and raising them through 100 m of the water column at 2m/min before closing the nets using
9 messengers (see Table 1). These samples were not used to evaluate fluxes but were analysed for their
10 organic components.

11 The 500 ml – 2 L samples from sediment trap collection cups were transferred to polypropylene bottles,
12 swimmers (which were very minimal in these oxygen-poor waters) were picked out, and the sample was
13 frozen and transported to the lab at the University of Washington. In the lab samples were thawed and
14 spun at 15,000 x g in ~200 ml aliquots. Resultant pellets of sinking material were separated from the
15 liquid, combined, weighed wet, freeze dried, and weighed again. After a small salt correction the dry
16 weight was used to calculate the mass flux.

17 ## 2.2 Elemental, XPS, Amino Acid and Lignin Analyses
18 Elemental analyses for particulate carbon, nitrogen quantities and ^{13}C and ^{15}N isotopic compositions
19 were carried out at the U.C. Davis Stable Isotope Facility (http://stableisotopefacility.ucdavis.edu) on
20 both raw and acidified samples. Acidification was achieved via direct application of 1 M HCl using the
21 technique described in Kennedy et al (2005).

22 XPS surface characterizations were done at the University of Washington's Surface Analysis Recharge
23 Center (http://www.nb.engr.washington.edu/content/surface-analysis-recharge-center-sarc) with
24 Surface Science Instruments (SSI) S- and M-probes as described in Arnarson and Keil (2001). Analyses
25 were made in duplicate with an average spot size of ~200 μm and a theoretical average scanning depth
26 into the sample matrix of ~20 nm. The measured atom percent of each detected element was
27 multiplied by its molecular weight and then weight percentages were calculated. We assume that
28 hydrogen has a negligible contribution on a weight basis (hydrogen is the only element that the XPS
29 cannot see; the detection limits for most other elements are ~1 atom percent; Arnarson and Keil, 2001).

30 Amino acids were liberated via acid digestion (Cowie & Hedges 1992a) and quantified by liquid
31 chromatography – triple quadruple mass spectrometry using an isotope pairing technique similar to that
32 of Piraud et al (2005). Briefly, samples were hydrolysed in 6 M HCl via programmed microwave
33 assistance in a MARS 5 microwave system (CEM Corp), brought to dryness in a CentriVap system
34 (LabConCo), resuspended in MilliQ water and filtered through a 13 mm 0.2 μm nylon membrane
35 (Acrodisc, PALL Life Sciences). Isotopically-labeled amino acids (Cambridge Isotopes) were then added.
36 Samples were run on an Agilent Poroshell 120 SB-C18 column (100mm) with solvents of a) Milli-Q
37 containing 0.05% Heptafluorobutyric acid (v/v) and b) acetonitrile containing 0.05% Heptafluorobutyric
38 acid (v/v). A six-point standard curve plus blanks was run each day, and the NIST Amino Acid standard

1   mixture with added isotopically labelled amino acids was run with every set of samples (e.g. every day)

2   as a test the accuracy of the LCMS. The multiple reaction monitoring parameters used for identification

3   are shown in appendix Table A1.

4   Lignin phenols were analyzed by microwave-assisted cupric oxide oxidation (Goni & Montgomery 2000)

5   followed by trimethylsilyl derivatization and capillary gas chromatography – mass spectrometry (Keil et

6   al. 2011). Yields of cinnamyl "C", syringyl "S" and vanillyl "V" phenols were used to evaluate vascular

7   plant sources of the sedimentary organic bulk mixture. These phenol yields are conventionally

8   represented as lambda (Λ8; mg per 100 mg of organic carbon) and Σ8 (the sum of the eight major

9   phenols normalized to 10 g of bulk sample).

10   ## 2.3 Targeted Peptidomics

11   Peptides specifically diagnostic to proteins of interest were identified using a targeted peptidomics

12   approach (Bertrand et al. 2013). Briefly, peptides were extracted as per Bridoux et al (2015) where

13   samples were suspended in a lysis buffer (7M urea, 2M thiourea, carrier ampholytes (2% v/v, pH 3-10),

14   dithiothreitol (DTT, 1% w/v), and protease inhibitor cocktail (1% v/v)) and lysed while ice cold using

15   sonication, precipitated with ice-cold 20% trichloroacetic acid in acetone (TCA/acetone, 1:5 v/v) for ~12

16   h at -20°C and enzymatically digested with trypsin following a protocol adapted from Nunn et al. (2010).

17   The resulting tryptic peptides were desalted using a macro-spin C_{18} column (NestGroup), resuspended in

18   20 µL of 5% Acetonitrile (ACN) /0.1% formic acid and introduced into a Waters Xevo TQ-S triple

19   quadru-pole mass spectrometer via a Waters Acquity nanoUPLC. Peptides of interest were separated on

20   a Waters HSS T3 150mm column with solvents of water with 0.1% formic acid (a) and acetonitrile with

21   0.1% formic acid (b). Spectra were evaluated using Skyline software https://skyline.gs.washington.edu.

22   Target peptides and their associated proteins are identified in appendix table A2.

23   ## 2.4 Incubation Studies

24   Toward the end of the cruise, sinking particles collected from 80 m depth at station 3 were incubated in

25   large trilaminate bags (Ward et al. 2009; Ward et al. 2008). The bags were vacuum emptied and then

26   filled with water from a Nisken bottle as per Ward et al (2008), during which time a small syringe

27   containing a slurry of sinking particles collected from the net traps was injected into the bags through a

28   3-way valve (see also Chang et al 2014). Injection volumes were kept constant but the quantities of

29   added organic matter were not measured. Oxygen was added to each bag using a syringe filled with O_2-

30   saturated seawater from 80m depth. The exact oxygen addition was not known until it was measured

31   using a flow-through optode system (Ocean Optics). Bags were sampled periodically for nutrients, pH

32   and alkalinity and oxygen content. The pH, alkalinity and nutrient data were used to calculate total DIC

33   assuming that all other sources of variability in alkalinity were negligible (Van Mooy et al 2002).

34   Changes in total DIC compared to the initial time point were used to evaluate respiration. In one

35   experiment, dust collected from the Sahara Desert (collected by R G Keil in Tunisia) was added to the

36   bags at quantities of ~100 µg L^{-1}. The dust had previously been screened to remove particles larger than

37   100 µm and had been slowly combusted to 400 °C in an effort to clean any existing organic matter off

38   the mineral surfaces (Arnarson and Keil 2001). The dust was suspended in seawater from the same

1 depth as the net trap for 24 hours before being added to the incubation bags, and was vigorously

2 vortexed immediately prior to being injected into the bag.

3 ## 3.0   Results

4 Based on the CTD casts and nutrient analyses for the 3 main stations and the 7 additional CTD-only

5 stations, the water column conditions changed along the transect. The area around station 2 (15°N) had

6 the highest standing stock of chlorophyll, and the region around station 3 (11°N) had the thinnest ODZ

7 (Figure 1). The secondary nitrite maximum, which can be used as a tracer of the functionally anoxic

8 zone, thinned from ~250 m thick at stations 1 and 2 to ~50 m thick at station 3 (Figure 1).

9 Sediment net traps have the advantage of large collection area relative to other sediment trap types,

10 allowing for rapid collection of large amounts of settling material in short periods of time (Peterson et al

11 2005). Total mass fluxes trapped by the drifting nets ranged from 63.2 g m^2 y^{-1} at station 2, 80 m depth

12 to a minimum of 11.1 g m^2 y^{-1} at station 3 500 m depth (Table 1). Organic carbon and total nitrogen

13 fluxes attenuated similarly to each other with depth (Figure 2), and the fluxes at station 3 attenuate

14 faster than at the other two stations, an observation enhanced after normalizing the fluxes to that at 80

15 m depth (the base of the euphotic zone)(Figure 2c). Martin curve attenuation coefficients for 19.5°N

16 and 15.5°N are 0.59 and 0.63 and for 11°N it is 0.98. The differences in attenuation coefficients equate

17 to degradation rate differences of ~35-50% assuming a constant sinking flux.

18 Organic carbon contents range from 8.9 – 24.6 wt% organic carbon, with the minimal values generally

19 associated with the deeper samples (Table 1, Figure 2). Organic Carbon is lost from the sinking particles

20 faster (shallower) at station 3 than the other two stations (Figure 2). Similar trends are observed for the

21 total nitrogen content of the samples (Table 1). The C_{org}:N ratio of the sinking particles is close to

22 Redfield at the surface and increases to ~9 with depth (Figure 3). The exception to this is station 1,

23 where the C:N ratios are ~9 at the two surface depths. Stable carbon isotopic compositions of the

24 sinking particle range from -20.8 to -23.4‰ with those from station 2 being enriched relative to station

25 3 (Figure 2).

26 Total carbon on the surfaces of the particles, as measured by XPS, is highest (60-72 atom percent) in the

27 80m samples and decreases to ~50% in the particles collected deeper (Figure 4a). The only other

28 elements detected by XPS were oxygen, silicon, calcium and nitrogen. As opposed to carbon, the

29 proportions of oxygen, silicon and calcium are enriched with depth (Figure 4b-d). Combining the bulk

30 elemental data with that collected by XPS allows for evaluation of the organic carbon `placement` within

31 the sinking particles via the $OC_{on\ the\ surface}$:OC_{bulk} ratio (Arnarson & Keil 2001). Values of this ratio are

32 between 2-3 in the surface waters and rise to 4-6 with depth (Figure 4e). The ratio is higher for the

33 deeper samples at station 3 than at the other two stations (Figure 4).

34 Using the Redfield ratio for organic matter, as modified by Hedges et al (2002), the amount of inorganic

35 mass was calculated as the difference between the mass flux and the total organic matter flux (Table 1).

36 Settling particles range from 55-84% inorganic matter. The inorganic matter flux ranges from 9-39 g m^2

1   y^{-1} and decreases with depth (Figure 2a). Station 2 has the largest inorganic mass flux, coincident with

2   the highest chlorophyll levels.

3   Amino acid abundances and compositions change as a function of depth, but show little variation with

4   station (Figure 5). The mole percent non-protein amino acids, which is an indicator of the diagenetic

5   state of the amino acid pool (Cowie & Hedges 1994), are less than 1 at the surface and less than 3 in the

6   deeper samples (Figure 5a). The amino acid degradation index (DI), as calculated using the formulation

7   of Dauwe and Middelburg (1999), ranges from 0.25 -1.0 and represents relatively 'fresh' organic matter

8   (Table A4). At stations 2 and 3 the DI decreases with depth (Figure 5b).

9   For the sediment trap samples, the CuOxide yield of lignin phenols is <2 mg gdw^{-1} (Table A5) and is less

10 at the deeper samples relative to the 80m samples (Figure 5c). When normalized to the total amount of

11 organic carbon present, there is an enhancement of lignin at station 1 relative to the other two stations

12 (Figure 5d). There was not enough sample material in the deep net tows for lignin analyses.

13 Target peptide quantities were typically below 400 fg mgdw^{-1} except for histone, which peaked at 17000

14 fg mgdw^{-1} (Figure 6). In general, target peptide quantifications decreased with depth and with oxygen

15 concentration, again except for histone and ABC transporter proteins, which showed no negative

16 relationship against oxygen (Figure 6).

17 Incubation experiments conducted using sinking particles from station 3, 80 m depth, showed inhibition

18 of DIC production when either oxygen concentrations were low (Figure 7a) or when dust was added to

19 the collapsible incubation bags (Figure 7b).

4.0   Discussion

21 Understanding carbon fluxes through ODZs is critical for ascertaining and predicting how oceanic

22 systems have and will respond to climate change. The size of ODZs are exceptionally sensitive to climate

23 change and variability; it only takes a 1% reduction of the ocean's O$_2$ content to double the size of the

24 ODZs (Deutsch et al. 2011), and some climate model simulations predict substantially larger

25 perturbations to the oceanic O$_2$ reservoir (~5%) within this century (Bopp et al. 2013). While ODZs

26 occupy a small percentage of the ocean (<1% by volume)(Paulmier & Ruiz-Pino 2009; Stramma et al.

27 2012), they account for 30-50% of the oceanic loss of N as N$_2$ (DeVries et al. 2012), driving N limitation of

28 ecosystem productivity over large swaths of the photic zone, and far from the ODZs themselves.

29 There are three major permanent ODZ regions; the Eastern Tropical North and South Pacific (ETNP,

30 ETSP) and the Arabian Sea. Unfortunately, to date there have been few systematic evaluations of

31 sinking particles within and outside these ODZ regions. The simplest way to evaluate different regions is

32 to take the available data and fit it to the Martin curve (Martin et al. 1987). While this power fit to data

33 does not have a direct ecological relevance for the 'attenuation' term, it does serve the purpose of

34 providing a convenient single number that can be compared between regions. In the original 'Martin

35 curve' paper, three sets of drifting sediment traps were deployed within ODZ region while the other six

36 locations were all well oxygenated (Martin et al. 1987). The attenuation coefficients for the ODZ regions

1   averaged 0.59 ± 0.24 whereas the oxygenated values averaged 0.89 ± 0.06. The authors did not focus
2   on the causes of this regional variability.

3   In the ETNP, Van Mooy et al (2002) observed low particle attenuation in ODZ at a station north of
4   Martin's and calculated an attenuation coefficient of 0.40. Using benthic lander data, flux attenuation
5   along the Washington and Mexican margins are thought to differ, with the ODZ waters off Mexico
6   having an average attenuation coefficient of 0.36 while the oxic Washington margin has an attenuation
7   coefficient of 0.93 (Devol et al. 1995; Devol & Hartnett 2001; Hartnett & Devol 2003). In these studies,
8   differences in attenuation were interpreted as oxygen effects on microbial degradation of the sinking
9   material.

10   In the ETSP, systematic evaluations beyond the single Martin evaluation (1987) are few. Levin et al
11   (2002) evaluated benthic system ecology and energy flow at 30°S over a two-year period and suggested
12   that oxygenation events were strongly associated with more carbon remineralization of the sinking flux
13   (which they did not directly evaluate). That is, they found indirect evidence that the attenuation
14   parameter was higher under the more oxic conditions. Using benthic data in a manner similar to that of
15   Devol and Hartnett (2002), Dale et al (2015) suggested that the attenuation in the ETSP was only slightly
16   attenuated (Martin coefficient of 0.54) and that the impact on the sediment was greater than that in the
17   water column. Deep sediment traps show variation suggestive of changes in fluxes of lithogenic material
18   (Hebbeln et al. 2000; Marchant et al. 2004) but the data are not complete enough to evaluate
19   attenuation.

20   In the Arabian Sea there is much flux data. Along the western margin, (Lee et al. 1998) combined
21   sediment trap, primary production and [234]Th data to evaluate particle fluxes. They did not fit their data
22   to a Martin curve, but all the information needed is available. Their attenuation values range from 0.10
23   to 0.49 within in the ODZ and was 0.96 at their oxygenated 10°N site. Roullier et al (2014) used a visual
24   profiler to evaluate sinking particles and calculated an attenuation coefficient of 0.22, suggesting little
25   attenuation within the ODZ. Similar results have been observed in many other studies and for a variety
26   of specific organic compounds (e.g. Haake et al. 1992). Our data are in accord; the attenuation of the
27   organic matter flux (e.g. Figure 2) is different between the three stations, with the one that is most oxic
28   and furthest south (station 3) having the most attenuated flux.

29   Thus it appears to be a truism that ODZ regions 'allow' proportionally more organic material to transit to
30   the deep sea relative to oxygenated systems. The mechanisms that might cause this remain poorly
31   evaluated and potentially include many different components, such as (M1) the possibility that anoxic
32   degradation is sufficiently slower or less comprehensive relative to oxic carbon remineralization (Van
33   Mooy et al. 2002), (M2) chemoautotrophy and a highly efficient microbial loop within the ODZ might
34   add carbon to the flux (Close et al. 2014; Roullier et al. 2014), (M3) zooplankton migration into ODZ
35   regions might enhance chemoautotrophy by providing dissolved nutrients, might result in defecation
36   and 'enhanced' fluxes within the upper ODZ (Wishner et al. 2013) or might reduce remineralization if
37   populations sizes are small, (M4) mineral protection where differences in bio and lithogenic mineral
38   inputs control the remineralization profile of sinking organic matter in the ocean (Arnarson & Keil 2005;
39   Howard et al. 2006), (M5) terrestrial inputs of recalcitrant organic carbon (Goni et al. 2009), and (M6)

1   changes in the sinking speed of sinking particles, where sinking speed and remineralization rate both

2   control the apparent attenuation through the water column adnd where changes in sinking speed can

3   be driven by a variety of processes (Berelson 2002; Roullier et al. 2014).

4   Although our data set cannot *directly* evaluate each of these potential mechanisms, the multiple proxy

5   approach we employed, combined with our ship-board incubation experiments and recent literature by

6   Rouillier et al (2014), can be used to develop a heuristic model of the particle flux in the Arabian Sea

7   ODZ.

8   *M1*: **carbon remineralization in ODZ regions is relatively ineffectual**

9   In sediments there is a well-established 'oxygen effect' where organic carbon remineralization is more

10   extensive under oxic rather than reducing conditions, especially over time scales of months to millennia

11   (Arnarson & Keil 2007; Cowie et al. 1995; Hedges et al. 1999). Little is known, however, about how

12   effective this mechanism is over short time periods or for organic material in the water column.

13   Hartnett et al. (1998) invoked an oxygen effect to explain consistencies between sediments and sinking

14   particles, but others including Lee (1992) have found little or no direct evidence of such an effect over

15   time periods of days. A particle with a sinking speed between 10-300 m d^{-1} (Riley et al. 2012) will spend

16   1-50 days in a typical ODZ (~500m thick; Deutsch et al 2011), suggesting that for this mechanism to be

17   important, it must operate over relatively short time periods. Our data allow evaluation of this

18   hypothesis via incubation experiments conducted at different oxygen concentrations, and by evaluating

19   proxies that might suggest an oxygen effect in samples collected by the net traps.

20   The deck-board incubation studies (Figure 7) strongly suggest an oxygen effect, with a threshold of

21   about 20 μM under our conditions. In fact, when the oxygen concentration was below 1 μmolar, there

22   was no observable increase in DIC production for the first 48 hours of incubation. This is consistent with

23   previous work of Ploug et al. (2001; 2008) who suggested that microbial communities on sinking

24   particles would begin switching from aerobic to anaerobic respiratory pathways at approximately these

25   same concentrations. The detection of an 'oxygen effect' in the incubations is suggestive, but given that

26   particles and associated microbial communities were concentrated and subjected to abrupt changes in

27   oxygen tension prior to beginning the experiments, these types of incubation studies need to be taken

28   with a grain of salt. If the results are to be generalized to the sinking particles under more native

29   conditions, either experiments need to be conducted under more realistic conditions, or geochemical

30   measurements that allow evaluation of an oxygen effect need to be evaluated on the sinking particles

31   themselves.

32   Two amino acid indicators are commonly used in sediments to evaluate degradation; the mole

33   percentage of non-protein amino acids (higher = more degraded) and the Dauwe-Middelburg index

34   (Dauwe et al. 1999)(lower = more degraded). When measured on the sinking particles, both these

35   indicators suggest a difference between the ODZ stations and the more oxygenated station 3 where the

36   sinking particles at station 3 have undergone more extensive degradation (Figure 5).

37   Another possible hint to an oxygen effect is the attenuation of the histone protein marker in the

38   samples. Histones are insoluble alkaline proteins that package DNA into structural units

1 (nucleosomes)(Kornberg 1974). Histones are found only in eukaryote nuclei, not in bacteria or archaea
2 (Kornberg 1974). We targeted the general diatom histone H4 because it is a good tracer for the transfer
3 of diatom protein to the ocean interior (Bridoux et al 2015). If there is an oxygen effect, we'd expect
4 histones traveling through the ODZ be less effectively degraded relative to the oxic station 3, but we do
5 not observe this. Instead, our histone values show no discerning trends with depth or oxygen content,
6 suggesting that for these proteins there is no clear oxygen effect. Thus the targeted peptidomics data
7 are inconsistent with the overall total amino acid data, suggesting that histones do not degrade in the
8 same way the bulk amino acid pool does. How these different measures relate and whether one is a
9 better marker for a degradative effect remains unknown.

10 Finally, measuring the amount of carbon on mineral surfaces relative to the total organic carbon content
11 of a sample can be a useful tool for evaluating the relative 'degradative state' of organic matter in
12 sediments (Arnarson & Keil 2001; Arnarson & Keil 2007). Fresh particles are typically rich in organic
13 matter (low $C_{surf}:C_{bulk}$) whereas particles that have undergone degradation usually have their remaining
14 carbon associated with mineral surfaces (high $C_{surf}:C_{bulk}$). Extending this concept to the sinking particles,
15 if an oxygen effect is the dominant reason for enhance fluxes, we might expect the ODZ particles to have
16 lower $C_{surf}:C_{bulk}$ ratios relative to the more oxic samples (Figure 4e). Indeed, we observe that $C_{surf}:C_{bulk}$
17 values at station 3 are higher than for the two ODZ stations.

18 Thus, the majority of indicators we measured are at least partially consistent with an oxygen effect, but
19 the evidence to date is somewhat circumstantial and certainly not definitive. It is known that addition of
20 fresh organic matter to incubations stimulates denitrification (Babbin et al. 2014; Chang et al. 2014),
21 suggesting that denitrification is responsive to additions of carbon, but what is not known is whether *in*
22 *situ* denitrification rates would match those of aerobic respiration under similar conditions.

23 *M2*: **Community Growth Efficiency & Chemoautotrophy**

24 Because ODZ regions host a wide range of chemoautotrophic organisms, there is the possibility that
25 chemoautotrophy adds carbon to the sinking flux (Close et al. 2014). This has been termed 'substrate
26 injection', and if this is common in the Arabian Sea ODZ there should be bulk isotopic and biomarker
27 measurements supporting this added material. Of the things we measured, the bulk stable ^{13}C isotopic
28 composition of the sinking material might be the best indicator of chemoautotrophy. Lipids from ODZ
29 chemoautoptrophic organisms can be isotopically enriched (Close et al. 2014) suggesting that the bulk
30 material, if it contains significant chemoautotrophic-derived carbon, might be similarly enriched. Our
31 data (Figure 3) show enrichment of the ^{13}C of the bulk sinking material at station 2 relative to station 3.
32 This indicates that the sinking particles may contain a significant chemoautotrophic input. Because the
33 endmember isotopic values are not know, a mixing model of euphotic zone and ODZ sources cannot be
34 made. None-the-less, the observation that the ODZ compositions are all enriched relative to the
35 samples from Station 3 suggest measureable inputs of material produced within the ODZ.

36 What material might this be? Quantifications of peptides associated with the chemoautotrophic
37 process anammox suggest that anammox proteins are present but do not contribute substantially to the
38 sinking flux (Figure 6). The two anammox peptide biomarkers were rarely detected (<50% of the

1 samples contained measureable amounts of the markers) and their abundance per unit mass was only
2 1-20% of that N$_2$O reductase, the peptide marker for the heterotrophic denitrification. We interpret this
3 as evidence that heterotrophic proteins responsible for denitrification dominate in particles over
4 chemoautotrophic processes that also result in the formation of nitrogen gas. This is consistent with the
5 work of Fuchsman et al (2011; 2012) who suggested that anammox is primarily a water column process
6 (free-living bacteria), and also consistent with other work conducted during our cruise suggesting a
7 dominance of denitrification over anammox at the time of our sampling (Ward et al. 2009).

8 How do we reconcile two biomarkers that appear to advocate opposite interpretations? The
9 observations are not necessarily at odds. As early as 1994 Azam et al. (1994) proposed a complex
10 microbial loop within the Arabian Sea ODZ comprising of active free-living and particle-attached bacteria
11 working together to effectively transfer material between the dissolved, suspended and sinking pools.
12 Close et al (2014) suggested a similar thing based on their lipid data, and Roullier et al (2014) suggested
13 that the attenuated flux in the Arabian Sea was partly the result of an efficient microbial loop that
14 effectively reconstituted and utilized the energy of the sinking flux. This is a compelling hypothesis that
15 requires further research. What are the growth efficiencies of heterotrophic communities in
16 oxygenated waters relative to those of the heterotrophic-autotrophic community in an ODZ? If the ODZ
17 community growth with less respiratory loss, this might account for the appearance of
18 chemoautotrophic carbon in the sinking particles and might also be the mechanism leading to the
19 'enhanced flux'.

20 It is worth noting that the (M1) Oxygen Effect and (M2) Efficiencies & Chemoautotrophy mechanisms
21 are not easily dissected and discerned from each other. For example, since the ship-board incubations
22 measured the accumulation of DIC, a change in the growth efficiency of the microbial community as a
23 function of oxygen content would result in the same observation (less DIC accumulation) as a true
24 oxygen effect would. Similarly, since we did not develop a peptide marker for aerobic respiration, we
25 cannot compare the abundance of the denitrification peptide marker against an oxic counterpart. Thus
26 we cannot say whether there is relatively less protein associated with denitrification in the ODZ relative
27 to aerobic respiratory proteins in the oxygenated waters.

28 Our bacterial ABC transporter protein data provide clues pertinent to this issue. ABC transporter
29 proteins are ATP-requiring enzymes used to transport compounds across membranes. They are among
30 the most commonly detected proteins in the ocean (Tanoue et al. 1995; Wang et al. 2011) and are
31 critical for the heterotrophic function of acquiring organic compounds from the environment. Thus,
32 they are a good marker for heterotrophic processing. The ATP transporter peptide we evaluated was
33 quite abundant at all stations (150-250 fg/mgdw) but in general there was more of this peptide at the
34 oxic station 3 relative to the two stations within the ODZ (Figure 6). This is suggestive that oxic station 3
35 might have more active heterotrophic communities on the particles than at the ODZ sites (though
36 concentrations do not equate directly to rates). Thus, the ABC transporter protein data are consistent
37 with more heterotrophy at station 3, but they do not preclude an efficient microbial loop at the ODZ
38 stations, where energy transfer can be achieved using solutes such as nitrite and ammonium (e.g. the
39 anammox process) that do not require ABC transporters. Thus, both the (M1) Oxygen Effect and (M2)
40 Chemoautotrophy mechanisms are viable given our data.

M3: **Zooplankton**

One of the more intriguing mechanisms that might influence the flux is the presence and activity of zooplankton. Their actions may alter the flux in a variety of ways. If the feed in surface waters and then migration into the ODZ for protection from fish, and they defecate in the ODZ, this would result in deliver of packaged particles that sink without having to pass the upper portions of the ODZ where remineralization is fastest (Cavan et al. 2015; Wishner et al. 2013). An argument against this is that if it occurs within the ODZ it should also occur within oxic water columns (e.g. Cavan et al. 2015). Alternatively, if zooplankton feed and defecate in surface waters and are inactive in the ODZ, then sinking particles would simply pass them by and not be re-ingested or repacked.

In addition to providing fecal material, zooplankton deliver dissolved materials (ammonium) that can promote chemoautotrophy (anammox), thus indirectly leading to 'enhanced' fluxes. Our data set is very limited in its ability to address the role of zooplankton. Even though many sediment traps were deployed, our vertical resolution is too low to evaluate whether there is a 'spike' in the flux at the depth that the zooplankton migrate to. We also have no zooplankton-specific biomarker to help evaluate whether their fecal material is a more important component of the sinking flux within the ODZ.

In a recent study, Roullier et al (2014) used an underwater vision profiler (UVP) to collect high resolution data of the particle flux within the Arabian Sea ODZ. They observed increases in the sinking flux that were associated with zooplankton assemblages living at the deeper boundaries of the ODZ, and suggest that zooplankton-derived injections of sinking particles are an important component controlling the deep flux. This data was collected deeper than our sediment traps and thus while their data clearly support a zooplankton contribution to the issue, they do not help explain why we (and others) observe attenuated fluxes above the zone where the zooplankton aggregated, within the heart of the ODZ.

M4: **Ballast effects of Mineral Protection and Sinking Speed**

Similarly to an oxygen effect, there is abundant evidence that mineral protection is an important mechanism promoting organic matter survival and burial in long-term sediment records (M4a) (Keil & Mayer 2014; Kennedy & Wagner 2011; Mayer 1994). A variety of experimental approaches have also shown mineral protection occurs for some fresh material sorbed to mineral surfaces (for example; Arnarson & Keil 2005; Le Moigne et al. 2013). In the water column, a mineral protection mechanism would rely either on biominerals created by plankton, or the delivery of lithogenic minerals from land. Aeolian dusts from Africa deliver mineral (and pollutants; Dachs et al. 1999) to the Arabian Sea where they are thought to sensitively influence the dynamics of sinking particles (Barkmann et al. 2010). We evaluated the potential effects of dust inputs by adding dust to shipboard incubations at a variety of oxygen contents (Figure 7) and observed immediate reduction in DIC accumulation rates. This suggests that aeolian sources of mineral to the Arabian Sea ODZ may directly influence the rate at which organic matter is remineralized, thus enhancing the flux. Our experiments were conducted by adding large quantities of dust (~4x greater) relative to the maximal seasonal input (Barkmann et al. 2010), suggesting that we may have observed the maximal effect.

To seek corroboration between the incubations and the sediment trap samples, we analysed the sediment trap material by XPS. Interestingly, no aluminium was detected in any sample, suggesting that terrestrial inputs of lithogenic material were minimal during the time of our sampling. Silica and calcium were both detected at 5-10 wt% of the surface material. The only differences observed for the biogenic markers was that the calcium content at station 2 (ODZ) was lower than at stations 1 or 3. This suggests that the sinking particles at station 2 were slightly richer in Si-rich diatom material relative carbonate compared to the other two stations.

Overall, our data are inconclusive about the effect of mineral on the remineralization rate of the organic matter; incubations suggest a strong effect, but direct measurements of the sinking particles suggest relatively minor contributions of biogenic mineral and no detectable Aeolian dust. These results do not exclude this as an important mechanism, and other modelling and data analysis efforts have suggested that it must be important in the Arabian Sea (Armstrong et al. 2002; Barkmann et al. 2010; Howard et al. 2006; Klaas & Archer 2002). It may simply be that our sampling period (transition to the inter-monsoon) was the incorrect period to observe a strong effect.

Mineral inputs can potentially control more than just the reactivity of whatever organic material is sorbed to it, the abundance of mineral in the sinking particles plays a large role controlling the sinking speed (M4b) (Burd et al. 2010; Jackson & Burd 2002). Given a single and constant degradation rate, any change in sinking speed will change how long the particle spends in the ODZ and thus influence how much it is remineralized there. Complicating matters is the fact that the ocean contains many different types of particles that aggregate and disaggregate and sink at different speeds. Riley et al (2012) has suggested that fast sinking particles can typically account for the carbon demand of the deep sea, and that more slowly sinking particles are effectually remineralized within the water column. Use of the Martin attenuation coefficient does not help in this regard because it combined the two terms, but the Ballast model allows some insight (Armstrong et al. 2002; Klaas & Archer 2002; Le Moigne et al. 2012). If ballasting is an important control on sinking speed, and sinking speed controls the flux attenuation in the ODZ, then samples from the ODZ should have proportionally more mineral compared to station 3. Our data show the opposite trend; samples from station 3 (more oxygenated) have higher percentages of inorganic material (Figure 3). This is inconsistent with ballast-driven sinking speeds being the primary driver of the reduced attenuation in the ODZ. However, as with everything else we measured, the data have the caveat that we did not measure sinking speeds directly, nor did we separate the material into pools with different sinking rates. In other studies where that has been done, the deep flux has been attributed to ballasted organic matter with fast sinking speeds or to fast-sinking materials derived from zooplankton (Cavan et al. 2015). (moved here and slightly rephrased to consolidate as per referee 1)

Conversely, organic material has the potential to minimize any sinking speed effect of mineral ballast (Azetsu-Scott and Passow 2004). As particles sink they interact with other components in the water such as exopolymers, and if these materials become associated, sinking speeds can slow and even become negative (buoyant). Thus, the impact of ballast on organic matter reactivity and sinking speed remains an area ripe for further research. To summarize, direct evidence of a ballasting effect on the collected sinking particles is inconclusive, but lab studies with added lithogenic material show an inhibition in degradation rates, suggesting further research on this topic is warranted.

1   *M5:* **Addition of Recalcitrant Organic Material**

2   One poorly evaluated possibility is that ODZ regions, for whatever reason, are prone to having refractory

3   material within them, thus providing sinking particles with material that is naturally resistant to

4   degradation. We assessed this by measuring terrestrial lignin phenols in the trap material. Our

5   assumption was that the lignin would be highly refractory and that if this mechanism was important we

6   would detect more lignin at the ODZ stations relative to station 3 further south. This is somewhat

7   logical, as a) the lignin found in the open in the ocean is generally thought to be refractory (Goni et al.

8   2009; Meyersschulte & Hedges 1986), b) station 1 is closest to the Indus River - a known and important

9   source of lignin to the Arabian Sea (Cowie 2005; Cowie et al. 1999; Vandewiele et al. 2009), and c)

10 station 2 is in a region where the dust deposition is roughly 2-3x that of station 3 (Grand et al. 2015).

11 However, the lignin yield was quite low, comparable to that found in the dissolved pool of the equatorial

12 Pacific (Meyersschulte & Hedges 1986) and we did not observe any differences in the quantities or

13 compositions of the minimal lignin contribution to the sinking particles at the three stations and the

14 contribution of lignin to the total organic matter was far less than 0.1%, implying that refractory organic

15 material from land was not an important component controlling the flux.

16 An additional component that we did not evaluate is the possibility that the phytoplankton community

17 above the ODZ waters natively create 'selectively preserved' organic matter that is strongly resistant to

18 remineralization such as algeanans (Gelin et al. 1996; Gelin et al. 1999). However, visualizations of the

19 sinking material using a dissecting scope aboard ship did not result in any note of differences between

20 the various stations in the physical structure or composition of the sinking material.

21 *M6:* **Changes in Temperature**

22 Matsumoto (2007) suggested that colder oceans more effectively transfer carbon to the interior

23 because degradation is temperature-dependent and Marsay et al (2015) showed evidence of this in the

24 North Atlantic. Could temperature impacts fluxes through an ODZ? At first glance, it seems unlikely

25 given that the three major ODZ regions of the ocean are in tropical waters and thus should have higher

26 attenuation rates. The median temperature of the upper 500 meters in the Arabian Sea during our

27 sampling was uniform at 18.5 $^{\circ}$C and there was no difference between stations. Comparing our flux

28 attenuation terms to those in Marsay et al (2015) for approximately the same temperature (see their

29 figure 2), we observe that our attenuation coefficients of 0.59, 0.63 and 0.98 are all much lower than the

30 'expected' value of ~1.2. This implies that the temperature effect on sinking flux attenuation is not the

31 explanation for our Arabian Sea data.

32 **A Heuristic Model for Organic Matter Cycling in an ODZ**

33 No single parameter we measured or mechanism explored seems to singularly control the flux through

34 the Arabian Sea ODZ, but the mechanisms (M1) Oxygen Effect and (M2) Growth Efficiency &

35 Chemoautotrophy have the strongest support within our data set and based on literature. The effect of

36 (M3) Zooplankton and of mineral ballast (which occurs as part of several mechanisms) appears to be

37 most important deeper within the ODZ (deeper than our sediment traps were deployed; Roullier et al.

38 2014), and the role of (M6) Sinking Speed remains unclear. The role of (M4) Mineral Protection seems

1   plausible and is supported by model efforts (Barkmann et al. 2010; Howard et al. 2006) but since no
2   lithogenic minerals were detected by XPS in our samples, mineral protection remains to be further
3   evaluated and might likely only be important under certain circumstances. The only mechanism that we
4   can rule out appears to be that of (M5) Refractory terrestrial inputs, but we note that we did not
5   evaluate algeanans.

6   A conceptual model for how an ODZ system might funnel carbon to the deep sea thus starts with the
7   upper ODZ being a region of intense microbial activity where respiratory reactions are either slowed by
8   the lack of oxygen (M1 Oxygen Effect) or are highly efficient at retaining energy within the system (high
9   growth efficiency; M2). Disentangling these two possibilities is of importance if we are to better
10 understand the forces controlling carbon fluxes in a changing ocean, and also important for
11 understanding the role of the changing oxygen content of the oceans (Stramma et al. 2010). Bacterial
12 growth efficiencies are known to vary widely from <5% to ~60% (del Giorgio & Cole 1998) and this is
13 thought to be controlled by a combination of factors including source materials and maintenance energy
14 costs. To our knowledge, these things have not been evaluated in ODZ regions and comparisons
15 between oxic waters and ODZs have thus not been made. As a thought exercise, assuming an aerobic
16 growth efficiency of 10%, to half the attenuation and double export out of a hypothetical ODZ with
17 similar inputs, the microbial efficiency of the bacterial community in the ODZ need only to double to
18 20%. Similarly, the oxygen effect need not be large; a halving of the degradation rate would result in a
19 doubling of the flux. Both these terms (growth efficiency and remineralization rate) are very poorly
20 explored for ODZ systems.

21 Assuming a higher growth efficiency relative to oxic waters, the ODZ microbial community could then
22 funnel energy to its chemoautotrophic community. The major chemoautotrophs in ODZ regions are
23 thought to be slow growing anammox bacteria (Lam & Kuypers 2011) which might grow slowly but also
24 keep biomass within the ODZ until they are grazed or otherwise transferred into the sinking pool. This
25 combination of reduced respiration, increased efficiency and chemoautotrophy probably explains most
26 observations of upper ODZ regions including the presence of relatively high amounts of non-sinking
27 loosely aggregated material (Roullier et al. 2014). The factors controlling how this material is
28 transferred (or not) to the sinking pool remain to be explored. The inputs of dust is likely to enhance the
29 flux by sorbing and protecting dissolved organic matter (Burdige 2007) and could also change sinking
30 speeds by providing ballast, but again, this remains to be directly demonstrated.

31 Deeper within the ODZ two processes appear likely to be important; the presence of a deep zooplankton
32 population (Roullier et al. 2014; Wishner et al. 2008) likely repackages suspended material and adds to
33 the sinking flux, and the remineralization of slowly sinking organic matter results in sinking rates that
34 increase as a function of depth (Berelson 2002). The overall observation of 'enhanced' fluxes is thus the
35 result of a complex series of processes, each of which may dominate at any given time or depth.

36 To evaluate this conceptual model, and to begin to place values on each of the potential mechanisms, it
37 is necessary to change our approach to evaluating sinking particles in ODZ regions. Particles need to be
38 sampled and/or evaluated with higher vertical resolution than is currently done using sediment traps
39 (e.g. Roullier et al. 2014), and new and existing methods for evaluating sinking speeds and particle

1 dynamics (McDonnell et al. 2015) need to be applied to ODZ regions. The sinking, suspended and free-
2 living/dissolved components of the carbon and microbial community should be evaluated together, and
3 additional biomarkers for evaluating different sources and reactivates need to be developed and
4 applied. Examinations of zooplankton dynamics must to be incorporated into these microbial and
5 geochemical studies of carbon flow. Finally, it would be useful to simultaneously evaluate both the
6 remineralization rates and the sinking speeds of different types of particles in order to better
7 understand how each factor influences carbon export.

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6.0   Author contribution

17 R. G. Keil and A. H. Devol managed the project and R.G. Keil wrote the manuscript with the assistance of
18 A. H. Devol. J. Neibauer oversaw all laboratory analyses, processed samples on all the mass
19 spectrometers, and helped with manuscript writing and proof reading. C. Biladeau measured the amino
20 acids and conducted the mineral SA and XPS analyses as part of her undergraduate degree in
21 Oceanography and interpreted early data sets as a part of her educational experience. K. van der Elst
22 collected the sediment trap samples, helped with incubation experiments and made substantial
23 improvements to the sampling plan whilst at sea.

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1 **Table 1.** Meta and elemental data for the samples. Sta denotes the station number, T.D is the trap diameter in meters, Deploy is the deployment time in
2 hours, wt%In is the weight percentage of inorganic mass.

Lat	Long	Sta	Date	Depth (m)	T.D. (m)	Deploy (h)	Mass flux (g/m²/yr)	C flux (g/m²/yr)	N flux (g/m²/yr)	d15N	d13C	wt% OC	wt%TN	C/N(a)	wt%In
19.41	66.66	1	2007-09-24	80	2	43.4	46.5	11.4	1.4	5.7	-22.3	24.6	3.0	9.6	55.8
19.41	66.66	1	2007-09-26	250	2	43.4	37.4	5.5	0.7	6.3	-22.1	14.8	1.9	9.2	73.4
15.00	64.00	2	2007-09-30	100	2	38.8	52.7	11.5	1.7	7.0	-20.8	21.8	3.2	7.9	60.7
15.00	64.00	2	2007-10-02	250	2	44.1	39.4	6.4	0.9	7.3	-22.0	16.2	2.3	8.3	70.8
15.00	64.10	2	2007-10-04	333	2	49.8	34.1	5.5	0.8	7.6	-21.7	16.0	2.4	7.8	71.1
15.25	64.02	2	2007-10-05	3600-3200	1.25	-				7.0	-22.0	10.0	1.2	9.7	82.0
15.25	64.00	2	2007-10-07	80	1.25	33.7	63.2	13.2	2.2	9.2	-21.2	20.9	3.5	6.9	62.3
15.25	64.00	2	2007-10-07	330	2	34.1	40.4	6.1	1.0	7.5	-21.7	15.2	2.6	6.8	72.7
15.25	64.00	2	2007-10-08	3600-3200	1.25	-				7.0	-22.0	9.1	1.2	8.8	83.6
15.15	64.00	2	2007-10-09	250	2	39.5	49.5	7.7	1.2	7.4	-22.0	15.6	2.3	7.8	71.9
11.00	68.00	3	2007-10-11	80	1.25	13.1	56.8	11.9	2.0	9.2	-22.2	20.9	3.5	6.9	62.3
11.00	68.00	3	2007-10-11	333	2	23.6	25.8	3.0	0.4	6.0	-20.8	11.8	1.7	8.3	78.8
11.00	68.00	3	2007-10-13	80	1.25	46.3	54.5	11.4	1.9	6.2	-22.6	21.0	3.4	7.2	62.2
11.00	68.00	3	2007-10-13	333	2	46.9	23.0	2.0	0.3	6.3	-22.0	8.9	1.3	8.3	84.0
11.00	68.00	3	2007-10-14	3600-3200	1.25	-				6.3	-22.6	10.0	1.2	9.3	82.0
11.00	68.00	3	2007-10-15	500	1.25	21.3	11.1	1.1	0.1	7.0	-22.0	10.3	1.3	9.2	81.4
11.00	68.00	3	2007-10-15	1700-1300	1.25	-				5.9	-23.3	9.8	1.2	9.9	82.3
11.00	68.00	3	2007-10-16	250	2	48.5	28.9	3.8	0.5	5.1	-22.7	13.0	1.7	8.7	76.6

3
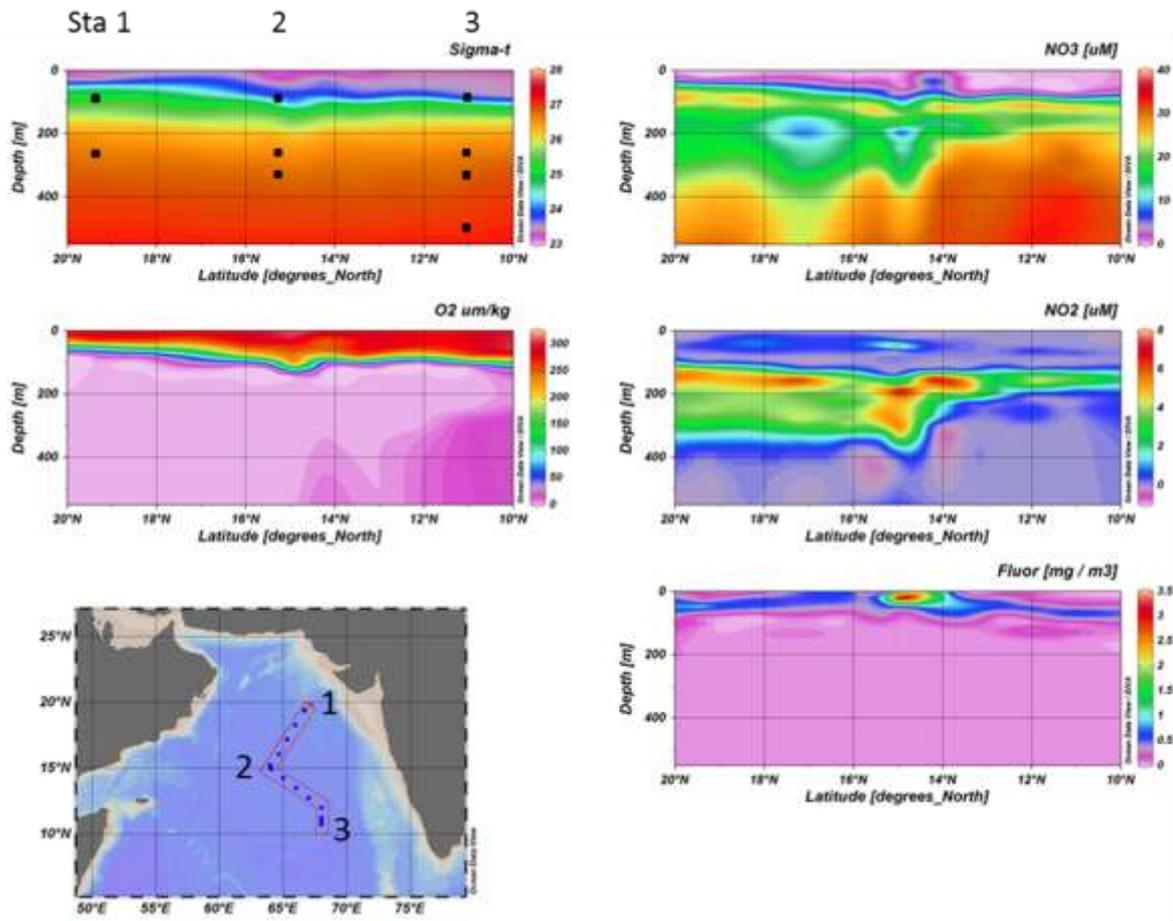
Figure 1. Spatial contours of water column parameters during the sediment trap deployments, clockwise from upper left; density, nitrate, nitrite, chlorophyll fluorescence, a map of the region including CTD stations (and with the trap deployment stations labelled 1-3), and oxygen. Squares in the upper left panel mark where sediment traps were deployed. A 2x denotes two traps deployed at these depths. Nutrient data previously reported by Bulow et al. (2009).
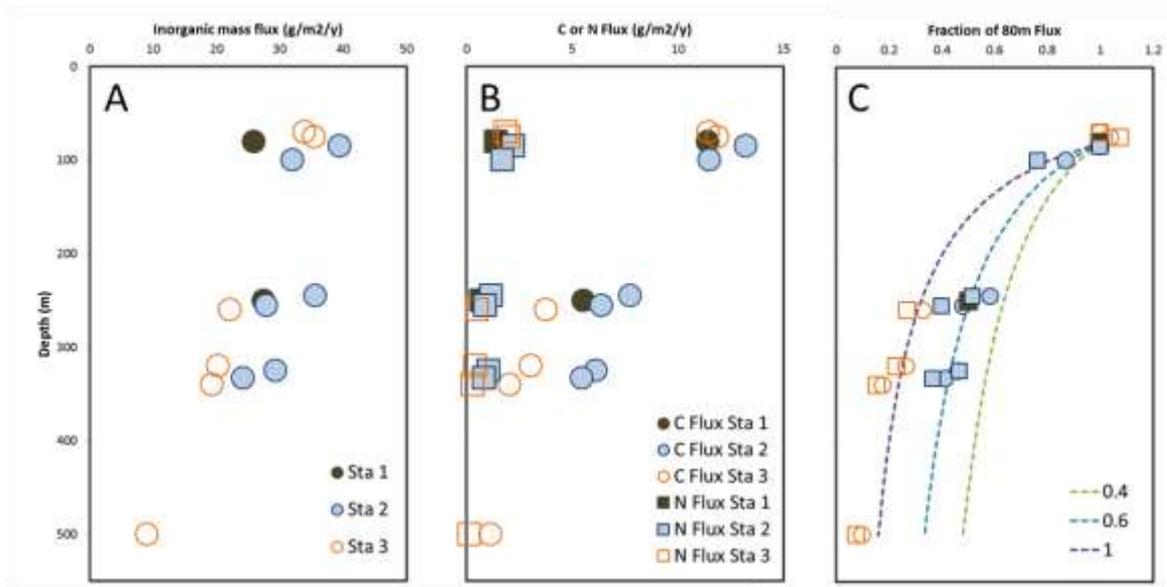
Figure 2. Sediment trap fluxes for inorganic material (A), organic C and total N (B) and the fraction of the 80m organic C or total N flux observed in deeper traps. Dashed lines in C denote Martin curves with attenuation coefficients between 0.4 and 1.0. At stations 2 and 3 multiple traps were deployed at nearly the same depth. Individual symbols represent the average of duplicate analyses of each trap sample. That is, replication is shown at the 'trap' level, and the variation within duplicate analyses of an individual trap sample is encapsulated within the size of the symbol.
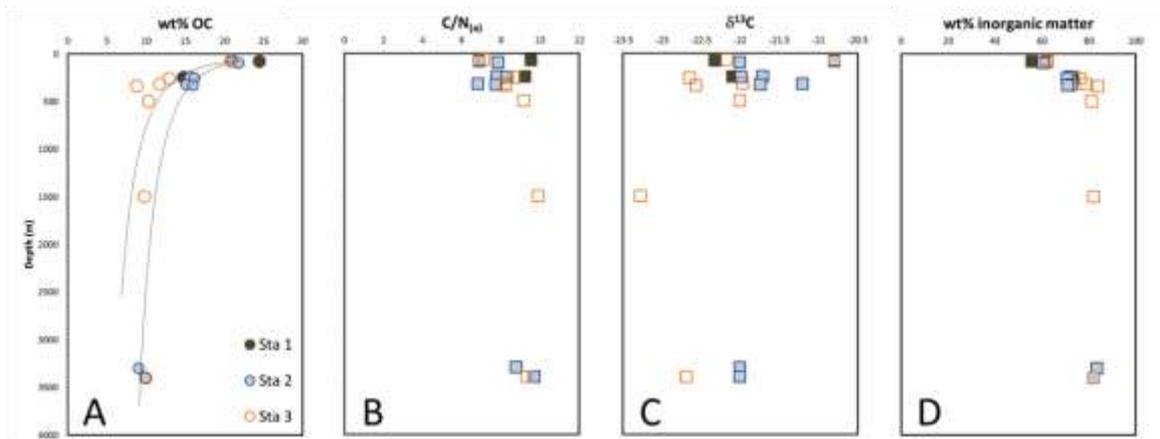
1

2   **Figure 3.** Weight percent organic carbon (A), atomic ratios of organic carbon to total nitrogen (B),
3   the stable carbon isotopic composition of the bulk organic matter (C) and the percentage of
4   inorganic material (D). Power functions in the left-most figure were added to aid the eye in
5   discerning possible differences between the three stations. Samples from deeper than 500m were
6   collected via slow net haul (see methods).
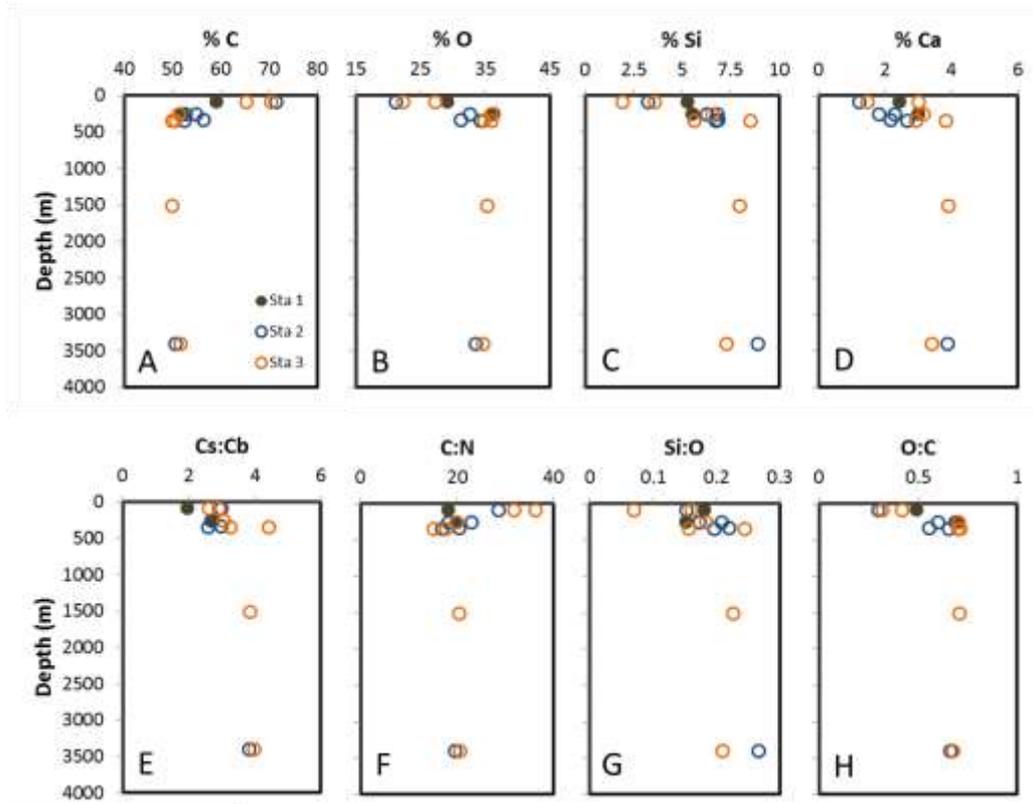
Figure 4. Atom percentages of different elements identified by XPS on the surfaces of the sinking particles; A) carbon, B) oxygen, C) silicon, D) calcium. E) Weight percentage ratio of carbon on the surface of the particles to bulk carbon measured by elemental analysis, F) atomic C:N ratio of carbon and nitrogen at the surface, G) atomic silica:oxygen ratio, H) atomic oxygen:carbon ratio. (Color scheme for symbols same as in Figure 3.)
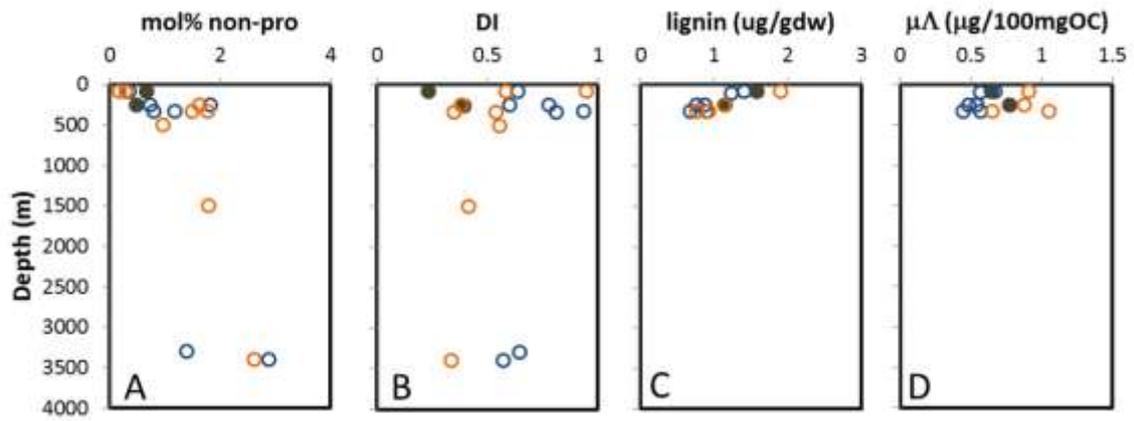
Figure 5. A) mole percentage of non-protein amino acids, B) amino acid degradation index, C) lignin phenol yield per gram dry weight of sinking material, and D) $\mu\Lambda$, the lignin yield in micrograms per 100 mg organic carbon. (Colour scheme for symbols same as in Figure 3.)
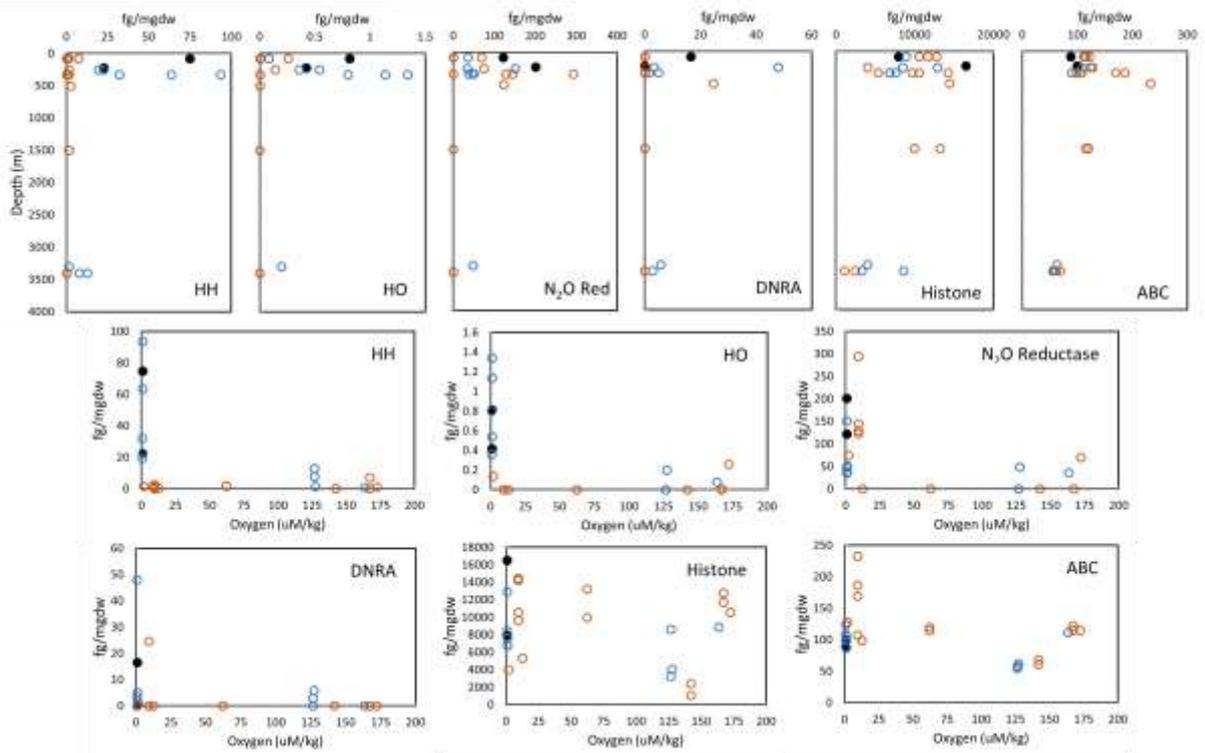
Figure 6. Target peptide quantifications. Upper row shows peptide quantifications as a function of depth, and the lower middle panels as a function of oxygen. HH combines data from 10 peptides specific to three forms of the anammox-specific enzyme Hydrazine Hydrolase; HO shows results from 4 peptides specific to the anammox enzyme Hydroxylamine/Hydrazine oxidoreductase; N₂O reductase data reflect 3 peptides specific marks the final step of denitrification; DNRA denotes 3 petides specific to Cytochrome c nitrite reductase (nrfA), a key enzyme in dissimilatory nitrate reduction to ammonium. Histone identifies two peptides specific to the eukaryote-specific H4 tetramer; ABC identifies 2 peptides specific to the general class of ABC transporter proteins commonly found in active (living) bacteria. (Colour scheme for symbols same as in Figure 3.).

1
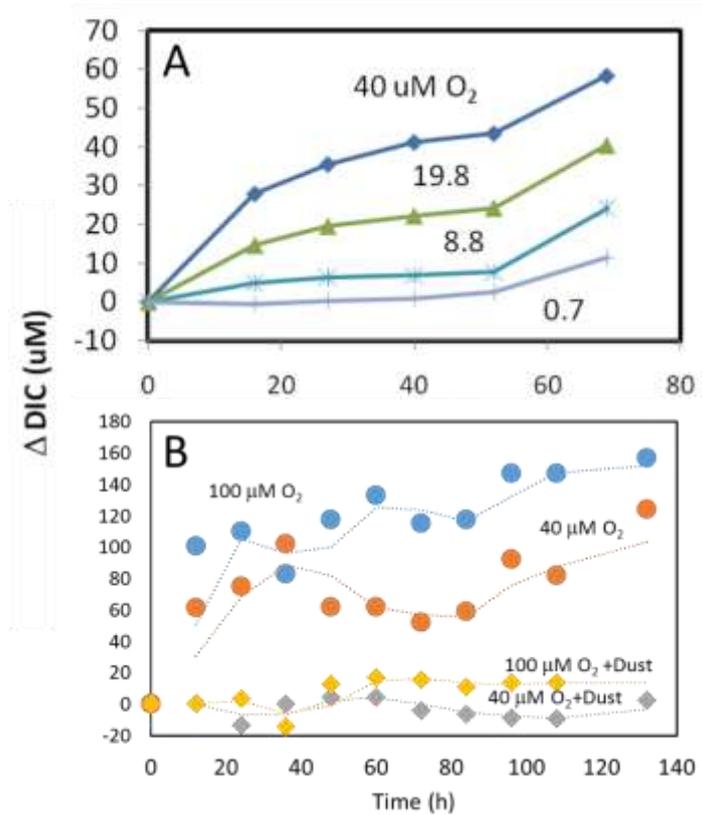
Figure 7. Incubation studies evaluating the change in DIC under different initial oxygen conditions (A) and with or without added dust from the Sahara desert (B). Sinking particles from station 3, 80m were added to incubation bags and alkalinity, pH and nutrients were measured. DIC calculated assuming that the only changes to the alkalinity were driven by changes in nutrient concentrations (Van Mooy et al 2002). Dashed lines denote a running average of 2 points.