

OXYGEN MINIMUM SEAFLOOR ECOLOGICAL (MAL) FUNCTIONING

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ABSTRACT

Although organic matter (OM) settling on the seafloor is generally rapidly recycled, a key ecological process, large scale burial events manifests itself in the marine sedimentary record as organic carbon (C_{org})-rich layers. Presently, this prevails under certain oceanic settings such as the oxygen minimum zones (OMZ) where OM accumulates in underlying sediments. A basic question that remains is to what extent does accumulation reflect a shunting of ecological processes: a niche unconquered? Experimenting with eastern Arabian Sea OMZ sediment we demonstrate that C_{org} accumulation here is not due to trophic satiation or low tolerance of biota to severe oxygen depletion but that sediment C_{org} has very low bioavailability that probably impairs biological transformation.

In the first set of experiments, the impact of oxygenation on the benthic ecological functioning was examined by following the fate of ^{13}C -labelled diatoms in intact sediment cores incubated for 7 days under normoxic versus suboxic bottom water conditions. Tracer organic matter assimilation (by bacteria and fauna) and respiration was evident and similar under both treatments and demonstrates that the benthic community was not food saturated or hindered by severe oxygen depletion.

In a second set of experiments, the bioavailability of *in situ* OMZ organic matter was determined directly through CO_2 production rates measurements in bottle sediment-water slurry incubations. In contrast to fresh tracer algal carbon which had a half-life 0.07 years, OMZ surficial sediment OM half-life was ~ 67 years already in very early diagenesis. However, although evidently excluded from immediate first-hand biotic transformation, this represents a niche on its own: a rapid shift from the “fast (biological)” to the “slow (geological)” carbon cycle along the continuum of OM recycling. Furthermore, in the a third set of experiments; we compared OM bioavailability in sediments with contrasting geochemical characteristics, including an ancient C_{org} -deposit. These results suggest that while this rapid shift may be common or characteristic of large scale accumulation events, the trigger mechanisms may not be uniform.

Keywords: oxygen minimum zone (OMZ), Arabian Sea, ecosystem functioning, benthic ecology, fauna, bacteria, carbon recycling, carbon burial, early diagenesis, stable isotopes

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INTRODUCTION

Across ecosystems, the recycling of elements is fundamental to energy flow and life. Similarly, a key ecological process occurring on the seafloor, the largest habitat on the planet, is the recycling of organic matter (e.g. Berner 1980, Middelburg et al. 1993). Organic matter (OM) escaping water-column remineralization fuels seafloor life (transformation into living biomass) that in turn constitutes the benthic players that carry out the recycling through basic catabolism. However, mass burial or preservation of OM as evidenced in marine sedimentary record (e.g. black shales and sapropels) has also been identified as crucial in the evolution and sustenance of the planet (e.g. Middelburg & Meysman 2007; Burdige 2007 and references therein). Representing a net removal of carbon dioxide from the atmosphere and accounting for the accumulation of oxygen in the atmosphere, organic material burial is a subject of global importance which calls for a better understanding of the modulating factors (Burdige 2007; Arndt et al. 2009; Cowie & Levin 2009; Lomstein et al. 2009). This is directly linked to a pressing issue in current marine ecology, the relationship between seafloor community structure and ecosystem functioning (Heip et al. 2009).

Present day seafloor environments with evidence of elevated sediment OM accumulations such as those underlying oxygen minimum zones (OMZ) found in the Arabian Sea can provide important insights (e.g. Cowie 2005 and references therein) and a basic question that remains is to what extent does C_{org} accumulation reflect “ecological malfunctioning”; i.e. to what extent can this OM accumulation under low oxygen conditions below the OMZ be considered a niche unconquered? Sediment rich in OM can potentially support high standing stocks of recycling agents but food availability above community carrying capacity may lead to accumulation of OM. Alternatively, very low bottom water oxygenation such as that in the Arabian Sea OMZ ($< 4 \mu\text{M O}_2$ in the core of OMZ, Cowie & Levin 2009, Ingole et al. 2010) may restrict benthic activity but under these relatively permanent settings (e.g. Reichart et al. 1998), adapted or specialized biota may be expected to have evolved (e.g. Childress & Seibel 1998, Middelburg & Levin 2009), as also implicated by drop in biodiversity of the fauna (e.g. Levin 2003; Levin et al. 2009, Ingole et al. 2010). If not among eukaryotes, adaptation is expected to prevail at least among the ubiquitous, omnipotent players: bacteria; their flexibility/diversity has also allowed them to extend the biosphere deep into the earth’s crust but also inhabit extreme environments (e.g. Jorgensen & Boetius 2007). However, it is as yet unclear whether OMZ organic matter accumulation reflects a case in which even microbial OM transformation is hampered (“batteries not included”, Lane 2006) resulting in rapid/immediate OM transfer out of the fast-biological cycle into the “slow (geological)” carbon cycle.

From a biogeochemical point of view, the question of what variables control OM preservation in marine sediments is one of the most complex and controversial issues (Hedges et al. 1999; Burdige 2007; Zonneveld et al., 2009). The Arabian Sea with its permanent OMZ extending from 100 to 1200 meters water depth and high productivity resulting in C_{org} -rich underlying sediments constitutes an ideal setting to examine the impact of severe

oxygen depletion on basic seafloor functioning (OM recycling) and its role in determining sediment carbon balance (e.g. Cowie & Levin 2009). OMZ systems are often viewed as the present-day analog of settings that could have led to formation of ancient C_{org} -rich deposits such as e.g. the most recent sapropel in the eastern Mediterranean with similar sediment C_{org} content (S1, deposited > 5 ka; de Lange et al. 2008 and references therein). Ultimately and from a biological point of view, it is the biota that are responsible for oceanic organic carbon recycling so that, among other factors, the bioavailability of the OM may be central in regulating the carbon balance in the sediment. This is often evaluated indirectly utilizing different sediment chemical parameters of OM reactivity or degradability (e.g. pigment or amino acid concentration and composition) that do not necessarily reflect OM bioavailability (e.g. Pusceddu et al. 2009, Woulds & Cowie 2009) and call for direct measurements.

Here we experimentally examine eastern Arabian Sea OMZ sediment ecological functioning and determine directly the bioavailability of indigenous OM. The introduction of deliberate ^{13}C tracer addition experiments on the fate of OM in major benthic compartments as well as respiration products has improved our understanding of seafloor functioning. It is clear that, from shallow to deep-sea sediments, fresh OM is rapidly assimilated and respired with (differential) participation of prevailing biota (e.g. Blair et al. 1996, Moodley et al. 2002; Witte et al. 2003, Woulds et al. 2007 and references therein). In this study we experimented with eastern Arabian Sea OMZ sediment; we adopted three approaches that combined demonstrate that C_{org} accumulation here is not due to trophic satiation or low tolerance of biota to severe oxygen depletion but that sediment C_{org} has very low bioavailability that probably impairs biological transformation. First, a series of the manipulative pulse-chase isotope experiments were conducted: intact sediment cores maintained under oxic and suboxic conditions were amended with fresh OM, the fate of which was measured after 7 days. Retarded or limited benthic OM transformation could indicate trophic satiation due to residing in very C_{org} -rich sediment and oxygenation related response would unravel the direct impact of oxygenation. Second, bioavailability of the OMZ indigenous OM was determined directly by measuring CO_2 production rates in bottle sediment-water slurry incubations. Finally, in a set of standardized slurry incubations with freeze-dried material, we compared the half-life of OMZ organic matter with that of recent intertidal, coastal subtidal and ancient C_{org} -rich deposits (Mediterranean sapropels).

MATERIAL AND METHODS

During an Indo-Dutch cruise onboard ORV *Sagar-Kanya* (SK-211) in October 2004, sediment samples were collected using a NIOZ box-corer (30 cm diameter) that retains bottom water, collecting relatively undisturbed sediment samples. Two stations were chosen based on earlier detailed analysis and designation of OMZ boundaries (Prakash Babu et al. 1999): the chosen OMZ station (17°30'N and 71°12'E; 756 m water depth) is located at the centre on the low oxygen area having high organic carbon content and bottom temperature around 11°C. For comparison outside any influence from the OMZ, a coastal shallow station was chosen (17°30'N and 72°44'E; 50 m

water depth in the shelf region on the west coast of India off Goa, Fig. 1). For experiments addressing sediment community functioning, several acrylic cores (14.5 inner diameter, 30 cm long) were sub-sampled from the boxcore and stored on board in the dark in a temperature-regulated fridge at 11°C. Unfortunately, due to logistic limitations, cores from the shallow station (bottom water temperature around 20°C, Naqvi et al. 2000; Ingole et al. 2010) was also maintained and incubated at 11°C. This may strongly underestimate absolute shallow water sediment community functioning but does not prevent certain amount of comparison with OMZ sediment structure and functioning excluding the impact of higher bottom water temperature (e.g. Moodley et al. 2005a). Details of the shallow station community functioning will be presented in a separate paper and here comparison with the OMZ is primarily that of biomass standing stock and that of indigenous OM bioavailability as determined in bottle sediment-water slurry incubations.

In the different replicate cores pre-designated for either normoxic or suboxic conditions (2 replicates per treatment), the overlying water was gently bubbled with either air from an aquarium pump (oxic) or from a certified gas mixture (Hoekloos BV, The Netherlands) to obtain suboxic conditions (from a 50 liter gas cylinder holding a mixture of 0.5 % O₂, 300 vpm CO₂ and the rest N₂; atmospheric concentration of CO₂ added to prevent drastic changes in water pH). This gas mixture at the given salinity and temperature resulted in overlying water having an oxygen content of around 3.2 µM as determined with oxygen-optodes (Presens, Germany) following standard procedures of calibration. In the oxic- treatments, oxygen content in the overlying water was 259 µM. Temperature and oxygen levels were maintained also during transport to the institute, only briefly disconnected during transfer from ship to truck and truck to thermo-container. After installation in the thermo-container at the institute, samples were allowed to settle for another few days before initiation of the experiments and again under controlled oxygen (i.e. sets of low & high oxygenation).

The whole core incubations (Fig. 2) were conducted for 7 days, in the dark at 11°C after adding tracer algal carbon (axenic, ¹³C-enriched *Skeletonema costatum* (a cosmopolitan diatom), added in amounts equivalent to 63.6 mmolC.m⁻²) using a long glass pipette to introduce them directly above the sediment (Moodley et al. 2005a). In order to reduce artificial introduction of dissolved OM (Moodley et. al 2005a, Andersson et al. 2008), we did not use freeze-dried algal material but frozen intact cells, thawed out just prior to initiation of the experiment, and brought into suspension with local 0.2 µm filtered seawater. Each core was then connected to two CO₂ traps in series (sets replaced once after 3.5 days) to trap the exiting gas (e.g. Kristensen et al., 1992) upon flushing with either air or the low oxygen gas mixture to quantify total respiration of the tracer OM (sum of trap, overlying and pore-water). Prior to processing, the cores were visually examined for traces of fauna activity but also sediment texture, color and odor characteristics. After sampling for ΣCO₂ and DOC (respectively 4 and 20 ml transferred through a GFF filter into a helium pre-flushed vial sealed with a shrimp-cap with rubber septum), the overlying water was carefully removed and volume determined. The amount of tracer OM in the DOC pool in the overlying

water was determined as described in Andersson et al. (2008). The sediment was extruded and sliced into plastic buckets (0-1, 1-3, 3-5 and 5-7 cm; deepest layer finally excluded from the study because there was no evidence of tracer uptake). After careful homogenization, the bucket sediment was sub-sampled with a cut-off syringe as follows: 20 ml for pore water extraction (centrifugation), 10 ml for metazoan meiofauna ($> 38 \mu\text{m}$), 10 ml for foraminifera ($>38 \mu\text{m}$) and 10 ml for PLFA (polar lipid derived fatty acids to quantify bacteria tracer carbon uptake), and the rest for macrofauna ($> 300 \mu\text{m}$). Fauna samples were preserved in Bengal-rose buffered formaldehyde and PLFA sample frozen for later freeze-drying and extraction (e.g. Middelburg et al., 2000). Sample processing including determining fauna and bacteria tracer assimilation as well as respiration was done as described in Moodley et al. (2002). Ultimately, the amount of tracer carbon in a specific pool or benthic compartment was determined as the product of excess ^{13}C and carbon biomass or concentration, divided by fraction ^{13}C in the tracer OM. Fauna biomass, as organic carbon content, was measured directly (Moodley et al. 2005a) and bacterial biomass estimated from concentration of bacteria specific PLFA (Middelburg et al., 2000). The amount of tracer OM respired was used to calculate half-life of tracer OM as function of oxygenation (see below).

Background sediment characteristics were determined in sediment from separate replicate cores of upper 3 cm surface layers: granulometry (sediment not acidified) using a Malvern Particle Analyser, sediment C_{org} content and isotope signatures as described in Moodley et al. (2005b).

The second set of experiments was conducted to determine the bioavailability of the *in situ* OM at both the OMZ and coastal Arabian Sea station by direct measurement of C_{org} remineralization through CO_2 production rates in sediment-water slurry incubations using a modified method of Dauwe et al. (2001) that included a correction for carbonate dissolution but also direct measurement of ΣCO_2 (sum of that measured separately in headspace and water slurry phase, van Nugteren et al., 2009a). For this purpose, sediment from background cores were taken from surface (0-3 cm) and subsurface layers (12-15 cm), individually homogenized and from which 10 ml was used (using a cut of syringe for accurate sampling) together with 10 ml 0.2 μm filtered bottom water to form slurries in 80 ml glass incubations bottles. This indigenous OM remineralization was compared to that of fresh highly degradable (^{13}C -enriched) simple (glucose) and complex organic matter (freeze-dried diatoms) conducted in separate slurry incubations. The glucose and algal addition slurries had a tracer carbon amendment of approximately $50 \mu\text{gC ml}^{-1}$ wet sediment. After being thoroughly mixed by hand shaking, slurries were purged for 15 min with either N_2 or air for anoxic and oxic slurries respectively. Activity expressed as half-life was calculated as $-\ln(0.5)/k$ with k (decay constant) calculated as quotient of CO_2 production and C_{org} content per ml wet sediment (Hargrave & Philips 1981) For the fresh highly degradable tracer substrates, the amount remineralized was calculated based on excess ^{13}C - ΣCO_2 (Moodley et al. 2005a) and k calculated as quotient of this and the amount added.

Differences in sediment-water slurry protocols, incubation temperature but also the local concentration of microbial degradation agents complicate direct comparison of marine sediment OM reactivity values reported for contrasting marine sediments (e.g. Dauwe et al. 2001; Hulthe et al. 1998; Moodley et al. 2005b). This was overcome in a third set of experiments performed in the laboratory in the Netherlands. Freeze-died sediment (stored frozen) from previously incubated sediment-water slurries (Mediterranean S1 sapropel, Moodley et al. 2005b, recent intertidal and subtidal sediment, Van Nugteren et al. 2009a) including that used in this study (described above), was still available and was used to conduct a set of standardized incubations (May 2006): one gram of dry sediment was amended with 30 ml 0.2 μm filtered seawater (low nutrient deep Atlantic water) and intertidal sediment bacteria (approx. 10^6 cells; cultured in the laboratory as described in De Goeij et al. 2008) in 80 ml serum glass bottles and maintained for 17 days in the dark at 15°C. These standardized re-incubations were done with OMZ sediment, coastal Arabian and North Sea as well as intertidal sediment and sediment from S1 sapropel deposited > 5 ka. Once again, measured and calculated as described in van Nugteren et al. (2009a). Although not reflecting *in situ* activity it provides a good indication of the relative degradability of the indigenous OM in these very contrasting sediments.

RESULTS AND DISCUSSION

Oxygen minimum seafloor characteristics

Compared to the range encountered in contrasting modern benthic environments (1- 5 mol C_{org} m^{-2} in the 0-1 cm of eutrophic intertidal to oligotrophic deep-sea floor sediment), sediment sampled from the centre of the highly productive OMZ area had indeed extremely high OM content (14.4 ± 0.11 mol C_{org} m^{-2} , Table 1). This was also higher than the coastal station outside the influence of the OMZ (5.3 ± 0.03 mol C_{org}) but very similar to that recorded in the ancient C_{org} -rich deposits of the most recent eastern Mediterranean sapropels (11.7 – 16.1 mol C_{org} m^{-2} , see below). However, the OMZ seafloor community characteristics were against expectations: i.e. a relatively low biomass standing stock (25 mmol C m^{-2} compared to 162 mmol C m^{-2} at the station outside the OMZ, Table 1). This aberration is also clearly evident in terms of the fraction living carbon: the percent living carbon in the OMZ upper 1 cm sediment was < 0.2 %, while the upper cm of other stations had 2-5 % living carbon (Table 1). More locally, the coastal station off Goa, having about one third the amount of OM found in the OMZ supports a much higher biomass than that in the OMZ station. This difference between within and outside OMZ sediments remains when considering the upper 5 cm ((Table 1). Bacteria made up the majority of the biomass both in the OMZ and the coastal station (Table 1).

The OMZ sediment closely resembled another organic-rich sediment in terms color and texture, some eastern Mediterranean S1 sapropels (L. Moodley personal observations): in this case very liquid, oily-like dark

green-brown sediment throughout the entire core; very fine but felt grainy to touch due to presence of planktonic foraminifera tests (shells). There were no black sediment layers or black spots and no scent of hydrogen sulfide (H_2S) in any layer. This was unexpected given that sulphate reduction is the major pathway of OM recycling in ocean margin sediments (e.g. Burdige 2007, Middelburg & Levin 2009), even more so under prevailing OMZ settings of low oxygenation and high OM content. However, this is in full accordance with earlier observations of enigmatic very limited sulphate reduction in Arabian Sea OMZ sediment compared to other OMZ sediment and settings (Pedersen & Schimmiel 1991, Passier et al. 1997, van der Weijden et al. 1999, Law et al. 2009). In contrast, the coastal sediment had a more typical gradation of sediment color (thin surface oxic, yellow layer and grey below with black spots here and there) but again no strong sulfide scent except faintly in the 1-3 cm layer. However, in contrast to OMZ sediment, high concentrations of H_2S can be characteristic of coastal waters and sediment in the western Indian shelf (Naqvi et al. 2000) that directly impacts sediment community structure and functioning (Panchang et al. 2006; Nigam et al. 2009).

Intact sediment-core incubations

In the intact sediment-core incubations examining community functioning, tracer OM recycling was clearly evident under both oxic and suboxic conditions (Table 2). After 7 days, tracer OM was recovered in bacteria and in different fauna components and, as in earlier studies, with the majority of recycling recorded as benthic respiration ($12-13 \text{ mmol C.m}^{-2} \approx 20\%$ of the added carbon) producing an average tracer organic carbon half-life of 0.065 years, similar under oxic and suboxic incubations (Table 2). A significant fraction of tracer OM was recovered in dissolved pool (DOC) in the overlying water (2 – 4 % of the added carbon). As in other marine sediments, bacteria and fauna readily assimilated algal carbon (combined, $904 - 1371 \text{ } \mu\text{mol C.m}^{-2}$ in the upper 5 cm $\approx 1-2\%$ of the added carbon) ruling out that prevailing OM accumulation is due to food satiation of the benthos (Table 2). This is corroborated by and in accordance with the low biomass standing stock encountered in these organic carbon-rich sediments (Table 1), which on itself is indicative of restricted flow of resident OM to the biota. These results suggest that the seafloor community may in fact be food limited in this apparent oasis of OM. However, with on average $25.5 \pm 1.4\%$ of the added carbon recovered in biota, DOC and ΣCO_2 , a larger fraction of the added particulate organic matter was still present at the end of the 7-day incubation period. Non-trophic limitations such as the very liquid sediment of the OMZ site constituting an unstable seabed potentially unfavorable to fauna would not necessarily explain the relatively low bacteria biomass (unstable seabeds like in the case of fluid muds are known to significantly reduce fauna populations in the favor of bacteria, e.g. Aller & Stupakoff 1996). Rapid dilution of the added tracer carbon, especially in this very liquid sediment, directly and through fauna activity may inhibit fauna uptake but simultaneously promote bacteria uptake (e.g. Van Nugteren et al. 2009b). However, there is no evidence of bacteria being favored in either treatment (Table 2b). Alternatively, the remaining sedimentary pool may represent the less reactive fraction of the added algal OM suggesting that lowered nutritionally quality is

very rapidly (within 7 days) produced/attained as also indicated by a large part of the tracer carbon entering the DOC pool evidently not remineralized (2-4 %, Table 2a). At present, this remains unresolved but it is clear that the short-term fate of OM was not strongly affected by low oxygenation: total tracer OM recycling (sum of assimilation, DOC and respiration as mmol C.m^{-2}) was significantly different between treatments (ANOVA, $p = 0.045$) but values were very similar (on average 15.2 and 16.7 mmol C.m^{-2}) as were tracer OM half-lives (on average 0.069 versus 0.064 years) under suboxic and oxic treatment respectively (Table 2a). Compared separately, total biotic tracer assimilation ($\mu\text{mol C.m}^{-2}$ in the upper 5 cm) was not significantly different between oxygen treatments (ANOVA, $p > 0.05$). Clearly, however, variation in assimilation was highest in the oxic cores (Table 2a). This may be because largest biomass variation was found in the oxic cores as a result of the high patchiness in fauna and organic compounds in Arabian Sea OMZ sediment (Woulds & Cowie 2009, Jeffreys et al. 2009, Ingole et al. 2010). Alternatively, adaption to low oxygen may result in biota being sensitive to high oxygenation so that low densities may have resulted from mortality induced by exposure to high oxygen. However, mortality would be expected to be more homogenous and therefore not a major source of variation in biomass standing stock. Additionally, cores were pre-incubated in experiment specific oxygen levels so that down-core migration would have been a way to avoid “lethal” high oxygenation for biota restricted to low oxygen (oxygen penetration depth is generally limited to a few mm). An alternative and probably better check on the impact of oxygenation, less sensitive to biomass variation, would be to analyze biotic activity per unit biomass (Table 2b). Once again, there is no evidence that biota are limited under severe oxygen depletion and some compartments may even be favored by low oxygenation: there was no significant difference for total recycling (sum of tracer OM in DOC, respiration and biota per unit biomass), bacteria or macrofauna tracer OM assimilation (ANOVA, $p > 0.05$) and both metazoan meiofauna and foraminifera assimilation was higher under sub-oxic conditions (ANOVA, $p < 0.05$). Overall, these observations strongly suggest that the biota is not restricted by the low oxygenation and implies that the relatively high organic carbon content in OMZ sediment is not consumed by the seafloor biota or remineralization process for other reasons than oxygen depletion.

Bioavailability of indigenous organic matter versus highly degradable carbon

Insight into the role of OM bioavailability or degradability in restricting OM transformation and thereby potentially promoting OM accumulation was obtained by determining bioavailability of indigenous OM: remineralization was directly measured as ΣCO_2 production in bottle sediment-water slurry incubations. In strong contrast to the remineralization of added algal OM (half-life of 0.06-0.08 yrs, Table 3), resident surface OMZ organic matter has extremely low bioavailability (half-life of 67 years) similar under oxic and anoxic conditions (Table 3). Although the remineralization rates of fresh algal OM and glucose were similar at the coastal station outside the OMZ influence, indigenous OM half-life was very much shorter outside the OMZ (14 versus OMZ 67 years, Table 3). Additionally, OMZ subsurface sediment had even longer half-life but in contrast to surface sediment, exposure to

oxic conditions stimulated OM degradation and half-life was longest under anoxic conditions (157 years, Table 3) which is in full accordance with the prevalence of high C_{org} content in these subsurface sediments ($11.5 \text{ mol } C_{org} \text{ m}^{-2}$, Table 5). This all reveals that OMZ indigenous OM is of low bioavailability which may be the prime cause of OM accumulation and restricted OM flow to the biota. The biomass standing stock can be taken as indicative of the bioavailable OM (Jorgensen & Boetius 2007). The relatively very low bacterial biomass found in the OMZ slurry sediment ($6\text{-}25 \text{ } \mu\text{gC ml}^{-1}$ sediment in OMZ subsurface and surface layers respectively versus $\sim 100 \text{ } \mu\text{gC ml}^{-1}$ sediment in the surface layer of the coastal station, Table 3) and observations of relatively low biomass in sediment below the OMZ zone on the Pakistan margin and western Indian continental margin of the Arabian Sea (Woulds et al., 2009, Ingole et al., 2010) support limited *in situ* bioavailability of OM which is in accordance and verified by the relatively long half-life values (Table 3). This is further supported by rapid microbial assimilation (tracer assimilation as recorded in bacteria specific PLFA) and respiration of the readily degradable tracer OM (algal OM and glucose) under both oxic and anoxic conditions (Table 3), again indicating limitation of bioavailable carbon. Bacterial biomass in subsurface OMZ sediment was extremely low ($6 \text{ } \mu\text{gC ml}^{-1}$ sediment) and may in part account for elevated half-life values of tracer OM mainly under anoxic conditions (Table 3). Moreover, tracer dynamics may differ according to carbon compound complexity; relatively more carbon is assimilated than respired in the case of complex algal carbon versus glucose (Table 3). Irrespective of carbon compound complexity, the surface sediment microbial community is evidently not restricted by severe oxygen depletion. The picture emerging from the whole core and bottle slurry manipulation incubations is that low bioavailability of indigenous carbon impairs biotic transformation thereby potentially promoting OM accumulation and that direct oxygen on the biota plays a secondary role. This supports that the lability of organic matter may be a key factor controlling the preservation of organic carbon (e.g. Chen et al. 2005; Arndt et al. 2009).

Conform that the fraction of refractory OM is expected to increase with time resulting in the most resistant fraction being buried (e.g. Middelburg & Meysman 2007), longest OM half-life was found in subsurface sediment under *in situ* anoxic conditions (157 yrs, Table 3). However, surface layer sediment OM had already a half-life of ~ 67 years indicating that pre-depositional processing and/or OM production under OMZ specific settings results in the relatively refractory OM with high preservation potential. At this stage, it is important to note that OMZ surface sediment OM half-life was not shortened by oxic conditions, which indicates that OM accumulation here cannot be attributed directly to post-depositional anoxic conditions and hints again towards the key role of pre-depositional processes. However, extended diagenesis evidently also alters OM dynamics: degradation of buried OMZ organic matter (sediment 12-15 cm below the seafloor) was stimulated upon re-exposure to oxygen (half-life lowered from 157 to 43 years, Table 3). Redox oscillation has been noted to enhance OM recycling (e.g. Aller 1994, Hulthe et al. 1998). However considered together, this also means that OM accumulation during subsurface deposition conditions was not necessarily related to low or no oxygen as observed here for the surface layers.

Processes/mechanisms resulting in surficial sediment OM with redox-independent resistance to microbial or fauna transformation have yet to be unraveled to explain how a large pool of OM is evidently largely excluded from rapid recycling. The mysterious limited sulphate reduction in Arabian Sea OMZ sediment (Pedersen & Schimmiel 1991, Passier et al. 1997, van der Weijden et al. 1999, Law et al. 2009) rules out OM sulfidization, often implemented as a key mechanism to explain OM preservation (e.g. Kohlen et al. 1990). However, the low bioavailability of OMZ sedimentary OM can potentially explain the related “malfunctioning” of retarded sulphate reduction, an otherwise dominant degradation pathway in ocean margin sediments (e.g. Burdige 2007, Middelburg & Levin 2009). The finding of OM remineralization in anoxic OMZ slurries may seem contradictory with limited sulfate reduction (Law et al. 2009) but it is important to note that rates are relatively very low ($0.01 - 0.04 \mu\text{mol C ml}_{\text{ws}}^{-1}\text{day}^{-1}$), both under oxic and anoxic conditions, compared to “normal” sediment ($0.07 - 0.44 \mu\text{mol C ml}_{\text{ws}}^{-1}\text{day}^{-1}$, Table 4), with OM half-lives as short as 1.2 years in intertidal surface sediment compared to ~ 67 years in OMZ surface sediment. Although slurry results should be considered potential rates because small-scale gradients are disturbed and dissolved-particulate ratios altered (Burdige 1991), this does not alter the main observation that OMZ surface sediment organic matter can be characterized as having strikingly very low bioavailability (Table 4).

Comparison of organic matter degradability in contrasting sediments

Pigments, especially chlorophyll-a, are often used as indicators of labile pool of OM (e.g. Pusceddu et al. 2009, Woulds & Cowie 2009) but even these very reactive components have surprisingly relatively long half-lives in sediment below the OMZ zone on the Pakistan margin of the Arabian Sea (3-10 years, Woulds & Cowie 2009) compared to 0.01 – 0.25 years measured in phytodetritus and “normal” surficial marine sediments (e.g. Sun et al 1993, Stephens et al. 1997, Chen et al. 2005, this study tracer algal carbon) implying that OMZ “bulk” organic matter half-lives may be even much longer. Modeling chlorins in OMZ sediment on the Oman margin produced half-lives of ~ 74 and ~ 680 years for surface and buried sediment respectively (Shankle et al. 2002). The relatively long half-lives are in accordance with the very existence of these C_{org} -rich sediment layers underlying the OMZ zone. In the present study, direct measurement of original half-life values of ~ 67 yrs for surficial OMZ sediment is indeed strikingly much longer than values reported for “normal” surficial sediments examined using similar methods (1-14 yrs, Table 4). However, direct comparison is hampered by difference in incubation conditions (Table 4). Therefore a larger set of sediments (coarse grained intertidal sediment to very fine grained recent and ancient deep-sea sediment, Table 5) were incubated under standardized conditions (temperature, freeze-dried material and the same bacterial inoculums). Longest half-lives were found for OM in sediment collected from the centre of the eastern Arabian Sea OMZ and in organic-rich sapropels from the eastern Mediterranean. Shortest half-life was found for OM in intertidal estuarine sediment (0.2 yrs) with similar values in coastal eastern Arabian and shallow North Sea (Table 5). Although confirming the low degradability of OMZ organic matter, OM half-lives were drastically shorter in the re-incubations (in subtidal and intertidal sediment factor 4-17 shorter, S1 sapropel <

factor 2 shorter and eastern Arabian Sea sediment factor 4-10 shorter). This may be due to the high concentration of degrading agents (all dried sediment inoculated with same large number of bacteria that under in situ conditions may differ, see Table 1 & 3) but also does not exclude that sample handling procedure (e.g. freeze-drying) enhanced OM degradation. At the same time, relatively smaller difference between sapropel original (8-13 years, Moodley et al. 2005b) and re-incubations (4-6 years, Tabel 5) suggest that the original sapropel oxic remineralization rates were most likely overestimated probably because there was no correction made for the fraction dissolved inorganic carbon originating from possible carbonate dissolution which can be very high, especially in buried sediment incubated under oxic conditions, e.g. > 80 % in recent subsurface coastal sediment (van Nugteren et al. 2009a). This, however, does not alter the main message of the sapropel study that degradation of OM in this ancient subsurface layer was evident only in the presence of oxygen (Moodley et al 2005b) which is in accordance with very existence of these layers in the absence of oxygen. But at the same time, as evidenced in this study with OMZ subsurface sediment, this does not necessarily reflect depositional redox or OM dynamics. Irrespective, the longest re-incubation half-lives were found in OMZ and sapropel OM (5-10 years compared to < 2 yrs for other sediment (Table 5) and reinforce the role of low OM reactivity in OM accumulation in OMZ systems. However, on the other hand, further sediment characteristics (see below) point out that different processes/factors were involved in triggering/modulating their OM accumulation.

As already discussed, the striking limited sulphate reduction in Arabian Sea OMZ sediment strongly contrasts with other OMZ sediment and Eastern Mediterranean sapropels. OM sulfidization may have contributed to promoting OM accumulation during sapropel formation (Passier et al. 1999) which on its own suggests that sapropel depositional OM reactivity may have been higher than OM in present-day OMZ sediment examined in this study. While having very similar C_{org} content, the contrast is further evident in distinct differences in sediment bulk OM characteristics especially in $\delta^{15}N_{tot}$ (Table 5). However, while the characteristic light values of $\delta^{15}N_{tot}$ in sapropel layers (range from -0.3 ‰ to +2.7 ‰) can be taken to reflect shift to specific primary producers involving nitrogen fixation rapidly reaching the seafloor as important trigger mechanism in sapropel formation (e.g. Sancetta 1994, Struck et al. 2001 and references therein; as also suggested for some Cretaceous black shales, e.g. Meyers et al., 2009), the heavier values ($\sim +7$ ‰) noted in OMZ sediment in this study as well as in sediment below the OMZ zone on the Pakistan margin of the Arabian Sea (Cowie et al. 2009) are within the range of “normal” marine sediment (Table 5) and are on their own, not particularly indicative of any aberrant OM source. Sediment C/N ratios were in both cases (OMZ & sapropel) higher than marine phytoplankton or undegraded phytodetritus; the even higher values in sapropel layers are conform more extensive post-depositional diagenesis (Passier et al. 1999, Bouloubassi et al. 1999), evidently limited in the examined OMZ sediment.

Synthesis

A large pool of OM in sediments underlying the Arabian sea OMZ is evidently excluded from rapid biotic degradation. The three sets of complementary experiments presented have revealed that this cannot be attributed to trophic satiation or low tolerance of biota to severe oxygen depletion but must be due to low bioavailability of deposited OM in this OMZ system. Apparently, pre-depositional or very diagenesis in OMZ setting results in low bioavailability. In a reactive continuum framework (Middelburg 1989; Boudreau & Ruddick 1991), this implies that a labile fraction of OM is transformed into a more refractory fraction. This constitutes a shunt of OM from the “fast” (biological) to the “slow” (geological) carbon cycle. This shunted OM recycling in OMZ settings implies that material refractory on early diagenesis time scales, but labile on geological time scales, is buried in OMZ sediments. Similarly, it has also been estimated for some Cretaceous black shales that the reactivity of organic matter was already extremely low at the time of its deposition (Arndt et al. 2009). This initial low reactivity of OMZ organic matter may also explain the absence of sulphate reduction in Arabian Sea sediments (Passier et al., 1997; van der Weijden et al., 1999; Law et al., 2009), and is consistent with the strikingly low content of potentially reactive components in sediment of this relatively productive OMZ setting (e.g. phytopigments and lipids, Sinninghe Damsté et al. 2002, Woulds & Cowie 2009; Cowie et al. 2009; Jeffery et al. 2009). Consistently, Vandewiele et al. (2009) reported that enzymatically available amino acids contributed only a small fraction to the pool of total hydrolysable amino acids in Arabian Sea OMZ sediments, indicating that bioavailability of proteins in OMZ sediments is low (Mayer et al., 1995). If pre-depositional transformation processes in the OMZ lower the availability and reactivity of organic matter and thus enhance organic carbon preservation and burial, the question then arises what make these OMZ settings unique in terms of pre-depositional processing. Van Mooy et al. (2002) reported preferential consumption of nitrogen-rich organic particles settling through OMZ. Such a preferential consumption of nitrogen-rich particles in OMZ is consistent with the elevated C/N ratios of sedimentary organic matter in OMZ and sapropel sediments (Table 5) and might also explain low initial reactivities of organic matter in OMZ because nitrogen-rich material is considered of higher quality for organisms. Another, perhaps related, explanation may be that in OMZ prokaryotic processing of settling particles is enhanced at the expense of metazoan consumption with the result that the remaining organic matter deposited on the seafloor is less bioavailable.

Overall, these complementary experiments with related C_{org} -rich sediments suggest that large scale burial events may in fact be initiated by a rapid shift of OM recycling from the fast biological cycle to the slow geological cycle but also that trigger mechanisms may not be uniform; clearly more experimental observations are required.

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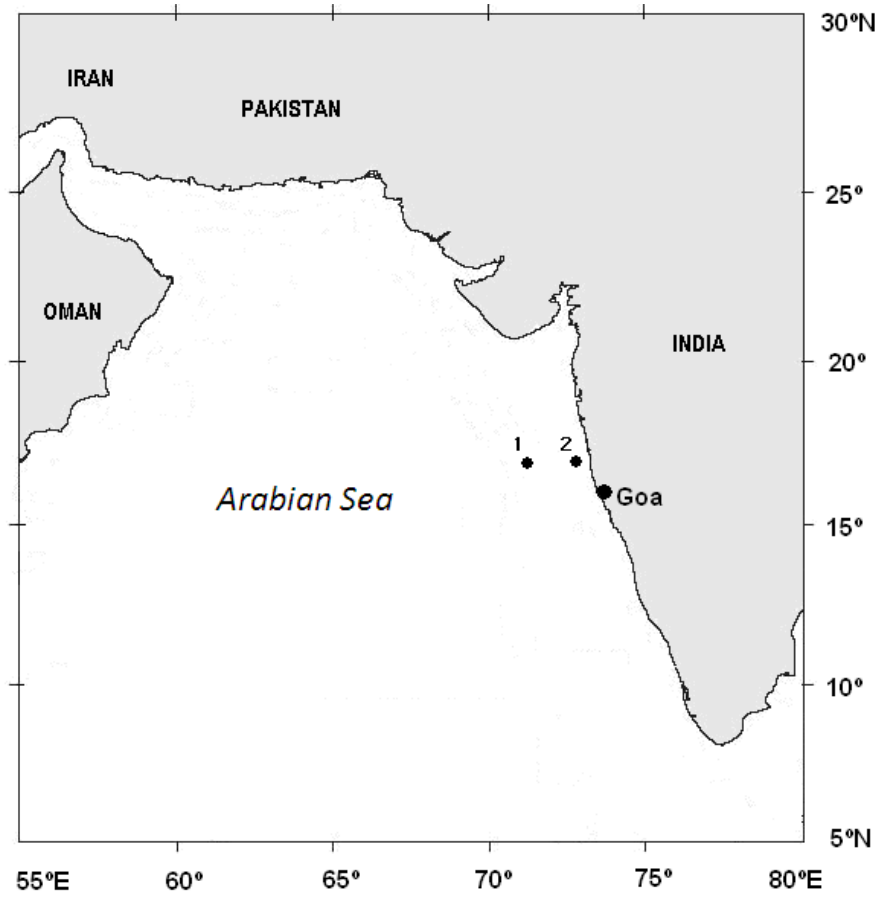


Figure 1. Location of the sampling sites in the eastern Arabian on the western Indian continental margin. Station 1 is in the centre of the OMZ zone (750 m water depth) and 2 is the 50 m deep coastal station.

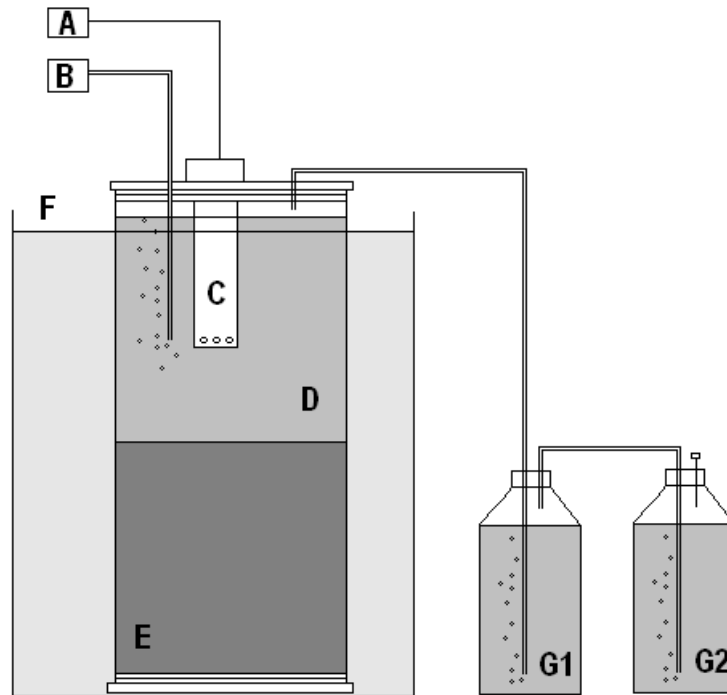


Figure 2. Schematic presentation of the setup used in the incubation experiment with intact sediment cores (inner diameter 14.5 cm). A: Stirrer speed controller. B: Air or gas mixture to obtain normoxic or suboxic overlying water. C: Magnetic stirrer. D: Overlying water. E: sediment. F: water bath. G: NaOH solutions to trap CO₂; remaining air exited the second trap through a needle that pierced the rubber septum in the cap of trap G2.

Table 1. Characteristics of eastern Arabian Sea OMZ sediment compared to sediments from contrasting benthic environments (intertidal to deep-sea). Organic carbon content (mol C.m^{-2}) and total biomass (bacteria + macrofauna + meiofauna and foraminifera in mmol C m^{-2}) recorded in the upper cm (within brackets 0- 5 cm values in Arabian Sea sediment). The contribution of bacteria to total biomass is presented in the last column.

Sediment Origin	Water depth (m)	C _{org} Content	Total Biomass	% Bacteria
<u>Eutrophic Intertidal to Oligotrophic Deep-sea</u> *	0 – 3559	1.4 – 5.5	22 – 253	48 – 99
<u>Eastern Arabian Sea</u> **				
Coastal Station:	50	5.33 ± 0.03	162 ± 18 (479 ± 284)	89 ± 4 (91 ± 3)
OMZ Station:	756	14.4 ± 0.11	25 ± 18 (128 ± 25)	85 ± 7 (82 ± 11)

*Range found in 7 stations after Moodley et al. 2005a, ** This study sampled in October 2004 off Goa, India. Values are average ± sd (n = 4).

Table 2. OMZ seafloor functioning. **(a)** Fate of tracer algal carbon (63 mmol Cm^{-2}) after 7 days incubation as recorded under oxic versus suboxic conditions in the overlying water and upper 5 cm of sediment cores collected from the centre of the eastern Arabian Sea OMZ. Total biota (sum bacteria + fauna incl. foraminifera) assimilation ($\mu\text{mol C m}^{-2}$), community respiration (sum overlying water and pore-water, mmol Cm^{-2}), amount of tracer carbon recovered in the DOC pool in the overlying water (mmol Cm^{-2}) and the sum of as benthic recycling of tracer OM (mmol Cm^{-2}). In the last column, tracer C_{org} half-life (years). **(B)** Tracer processing as a unit of biomass ($\mu\text{mol C.mmolC}^{-1}.\text{m}^{-2}$): total recycling (sum respiration, DOC and assimilation) and assimilation per different biotic compartments. $n = 2 \pm 1 \text{ sd}$.

(A)

Oxygenation	Assimilation ($\mu\text{mol C m}^{-2}$)	Respiration (mmol Cm^{-2})	DOC (mmol Cm^{-2})	Recycling (mmol Cm^{-2})	Half-life (yrs)
OXIC	904 ± 1089	13.1 ± 0.1	2.7 ± 0.5	16.7 ± 0.49	0.064 ± 0.00
SUBOXIC	1371 ± 271	12.3 ± 0.1	1.5 ± 0.2	15.2 ± 0.02	0.069 ± 0.00

(B)

Oxygenation	Recycling	Bacteria	Macrofauna	Meiofauna	Foraminifera
OXIC	143.4 ± 22.3	5.08 ± 5.46	13.85 ± 13.31	0.49 ± 0.39	1.81 ± 0.89
SUBOXIC	111.7 ± 24.0	4.72 ± 3.76	35.94 ± 0.64	9.59 ± 3.67	9.71 ± 0.06

Table 3. Organic matter recycling in eastern Arabian Sea OMZ and coastal surface sediment (in brackets the bacterial biomass in slurry sediment based on concentration of bacteria specific PLFA) of indigenous (*in situ*) organic matter (OM) versus fresh ¹³C-labelled complex (diatoms) and simple (glucose) substrate under oxic and anoxic conditions as measured in bottle slurry incubations (7 days dark incubations, 11°C). nm = no measurement.

Sediment Layer	OM Source	Half-life (yrs)		Bacteria Tracer C-uptake $\mu\text{gC.ml sed}^{-1}$	
		Oxic	Anoxic	Oxic	Anoxic
OMZ Surface ($25 \pm 5 \mu\text{gC.ml sed}^{-1}$)	<i>In situ</i>	67.4 ± 5.5	66.7 ± 3.9	-	-
	Diatoms	0.06 ± 0.011	0.07 ± 0.001	1.02 ± 0.43	2.12 ± 0.17
	Glucose	0.04 ± 0.002	0.04 ± 0.003	0.45 ± 0.26	0.74 ± 0.01
OMZ Subsurface ($6 \pm 1 \mu\text{gC.ml sed}^{-1}$)	<i>In situ</i>	42.6 ± 3.9	157 ± 0.03	-	-
	Diatoms	0.08 ± 0.012	0.25 ± 0.002	1.06 ± 0.07	1.01 ± 0.102
	Glucose	0.05 ± 0.002	0.09 ± 0.003	0.54 ± 0.03	0.11 ± 0.01
Coastal Surface ($100 \pm 17 \mu\text{gC.ml sed}^{-1}$)	<i>In situ</i>	13.9 ± 5.2	nm	-	-
	Diatoms	0.07 ± 0.002	0.07 ± 0.007	4.37 ± 0.002	3.15 ± 0.33
	Glucose	0.04 ± 0.001	0.03 ± 0.000	3.07 ± 0.442	2.99 ± 0.53

Table 4. Oxic versus anoxic OM remineralization rates ($\mu\text{mol C ml}_{\text{ws}}^{-1}\text{day}^{-1}$) and OM half-life (years) as measured in contrasting sediment with indigenous microbial populations using identical bottle slurry methods. Temperature of the original incubations are given in brackets. nm = no measurement.

Site	Sediment	Remineralization Rates		Half-life	
		Oxic	Anoxic	Oxic	Anoxic
Subtidal North Sea ¹ (12°C)	Surface	0.26 ± 0.01	0.21 ± 0.03	4.3 ± 0.13	5.3 ± 0.64
	Subsurface	0.08 ± 0.00	0.13 ± 0.00	20.2 ± 0.68	12.0 ± 0.39
Intertidal Estuary ¹ (15°C)	Surface	0.44 ± 0.01	nm	1.2 ± 0.02	nm
Coastal Arabian Sea ² (11°C)	Surface	0.07 ± 0.02	nm	13.9 ± 5.2	nm
OMZ Arabian Sea ² (11°C)	Surface	0.04 ± 0.00	0.04 ± 0.00	67.4 ± 5.5	66.7 ± 3.9
	Subsurface	0.04 ± 0.002	0.01 ± 0.007	42.6 ± 3.9	157 ± 0.03

¹after van Nugteren et al. 2009a, ²this study (see further Table 5 for more details)

Table 5. Organic matter half-lives (years, $n = 2 \pm 1$ sd) in contrasting sediments as determined in standardized (temperature, bacterial inoculums) oxic, bottle sediment-water slurry incubations. Characteristics of the contrasting sediment include granulometry as median grain size (μm) and % silt (fraction $< 63\mu\text{m}$ within brackets), original OM carbon content (1 cm layer), C/N ratio, stable carbon and nitrogen isotope signatures.

Sediment Origin	Granulometry	C_{org} mol m^{-2} (%)	C/N (mol)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}_{\text{tot}}$ (‰)	Half-life Re-incubations
<u>Subtidal North Sea¹</u>						
Surface Sediment	49.9 (62)	6.7 (0.99)	8.9	-21.5	+10.7	0.98 ± 0.03
Subsurface Sediment	54.1 (58)	8.1 (0.78)	9.6	-22.1	+9.2	1.16 ± 0.08
<u>Intertidal Scheldt Estuary²</u>						
Surface Sediment	110.6 (18)	2.9 (0.24)	9.4	-23.4	+13.1	0.20 ± 0.0
<u>Eastern Med. Sapropels³</u>						
SL 33	34.6 (72)	12.2 (2.17)	13.6	-22.1	+0.7	5.10 ± 0.6
SL 33	21.7 (82)	12.6 (2.11)	15.0	-22.1	+0.4	4.44 ± 0.1
SL 35	30.6 (71)	16.1 (3.95)	15.3	-21.6	-0.3	6.26 ± 0.5
SL 125	10.5 (91)	11.7 (1.77)	15.4	-22.2	+2.7	5.26 ± 0.8
<u>Coastal Eastern Arabian Sea⁴</u>						
Surface Sediment	37.6 (75)	5.3 (1.93)	9.6	-19.1	+9.1	1.35 ± 0.0
Subsurface sediment	30.7 (83)	6.4 (1.76)	10.1	-19.5	+8.5	1.79 ± 0.4
<u>OMZ Eastern Arabian Sea⁴</u>						
Surface Sediment	53.0 (55)	14.4 (4.83)	10.5	-20.5	+7.0	7.79 ± 0.3
Subsurface Sediment	63.7 (50.0)	11.5 (2.84)	10.8	-19.9	+6.5	10.44 ± 1.0

¹Shallow (59 m water depth) site in the eastern North Sea (57° 50 N 10° 01 E) where surface is upper 2 cm and subsurface is 18-20 cm below the seafloor. ² Intertidal surface sediment (upper 2 cm) collected during low tide from a mudflat (southwest Netherlands, 51° 26 N, 3° 57 E, ¹&²van Nugteren et al. 2009a). ³Sapropel sediment from cores collected in the eastern Mediterranean (see Moodley et al. 2005b) containing sapropels 22-32 cm below the seafloor (water depth: 1560 – 2765 m). ⁴ This study, surface is upper 3 cm and subsurface is 12-15 cm below the seafloor (see Table 1).