Organic matter cycling in hypoxic environments: the role of oxygen availability and benthic faunal communities

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The candidate confirms that the work submitted is his/her own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Continental margins receive significant amounts of organic matter (OM) from terrestrial and marine sources, and it is estimated that over 80 % of all organic carbon (OC) preservation in marine sediments takes place in these areas. The least well understood aspect of OM cycling and burial in marine sediments is the role of benthic fauna living on and in the sediments. Seafloor communities influence marine sedimentary OM cycling and burial via a number of activities including digestion, bioturbation or burrowing, respiration, irrigation and ventilation, and through microbial stimulation. In turn, several factors are known to influence benthic biological processing of OM: oxygen, OM quality and quantity, temperature, and faunal size and abundance. Thus, dynamic relationships exist between benthic faunal communities, sediment geochemistry and oxygen availability, yet these remain poorly understood or quantified. Results from previous studies indicate that benthic communities usually intercept and rapidly ingest most of the OM flux delivered to the seafloor but that the response varies between faunal groups such as bacteria, foraminifera and megafauna. In this study, whole-community experiments were conducted at sites with a natural range of biogeochemical characteristics, across the Indian Margin oxygen minimum zone (Arabian Sea) and the Gotland Basin (Baltic Sea). In order to assess how short-term faunal OM processing varies with oxygen availability, shipboard incubation experiments were conducted under both ambient and manipulated oxygen concentrations. ^{13}C and ^{15}N-labelled phytodetritus (chlorella) was added to incubations to mimic seasonal OM fluxes. The added isotopically-labelled OM was traced into different pools including fractions of the faunal community, sediments, pore waters and overlying waters. Faunal uptake of added OM was determined by isotopic enrichment of organic carbon ($\delta^{13}OC$) and nitrogen ($\delta^{15}N_{org}$) of faunal body tissue, bacterial assimilation was assessed through ^{13}C analysis of specific bacterial polar lipid fatty acids (PLFAs), and respiration was measured from ^{13}C enrichment of dissolved inorganic carbon (DIC, ΣCO_2). Results suggest that respiration is the dominant fate of OM at the seafloor in marine sediments. Organic matter processing is dominated by bacteria or foraminifera where oxygen is depleted and organic matter quality is low. Biological sedimentary organic matter processing is evenly shared between macrofauna, foraminifera and bacteria where oxygen is not limited and organic matter quality is high. This study is one of the first to conduct such isotope tracing experiments in conjunction with oxygen manipulation. Oxygen availability was found to be the over-riding control on organic matter preservation and short term cycling at the seafloor in both regions.

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1. INTRODUCTION

1.1. Project Rationale

Continental margins receive significant amounts of organic matter (OM) from terrestrial and marine sources, and it is estimated that over 80 % of all organic carbon (OC) preservation in marine sediments takes place in these settings (Berner, 1982). The cycling and burial of OM in these regions is therefore significant in the global cycles of carbon (C), nitrogen (N) and other major bioelements, and in ocean productivity and climate (Berner, 1982, 1989; Walsh, 1991). Furthermore, marine sedimentary OM burial is one of few processes by which C is buried over geological timescales, but it is both poorly quantified and characterised. Thus a greater understanding of the factors that govern this process is crucial to our understanding of the global C and N cycles.

Much research has been conducted to determine the controls on OM distribution and preservation in marine sediments, and has identified several factors including O_2 availability and/or exposure time (e.g. Canfield, 1989; Cowie et al., 1999; Dauwe et al., 2001; Demaison and Moore, 1980; Hartnett et al., 1998; Hulthe et al., 1998; van der Weijden et al., 1999), differential OM sources and reactivity (e.g. Dauwe et al., 1999; Hedges et al., 1988a, b; Lee et al., 2000; Schulte et al., 2000), sorptive preservation and organic-mineral interactions (e.g. Calvert et al., 1995; Hedges and Keil, 1995; Keil and Cowie, 1999; Mayer, 1994; Pedersen et al., 1992), primary productivity and/or sediment accumulation rates (e.g. Betts and Holland, 1991; Canfield, 1994; Henrichs and Reeburgh, 1998; Pedersen and Calvert, 1990), and biological processing (e.g. Aller, 1982; Cowie and Hedges 1996; Levin et al., 1997; Moodley et al., 2002, 2005; Sun et al., 1999, 2002; Thomas and Blair, 2002;). While there have been numerous reviews of the relationships between sedimentary OM burial efficiency and local oceanographic conditions, the relative importance of these factors remains unresolved. Many of the factors are interrelated, making them difficult to deconvolve, and their relative influences are likely to vary between environments (e.g. coastal margins vs. the open ocean). Consequently, it is often an interplay of factors that generates observed cross-margin OM trends.

The least well understood aspect of OM cycling and burial in marine sediments is the role of benthic fauna living on and in the sediments. Continental margins are food-limited environments where seasonal pulses of phytodetritus from the surface ocean form an important food supply to benthic communities (Billett et al., 1983; Pfannkuche et al., 1999;

Pfannkuche et al., 2000). OM quality, OM availability, and oxygen concentrations are known to heavily influence the presence, size, composition and behaviour of benthic faunal communities (Levin, 2003; Levin et al., 2000; Woulds et al., 2009). In turn, benthic organisms are known to affect the distribution, composition and preservation of sedimentary OM (Aller, 1982; Bianchi et al., 1988; Michaud et al., 2010; Sun, 2000; Sun et al., 1993). Seafloor communities influence marine sedimentary OM cycling and burial via a number of activities including digestion (Lauerman et al., 1997), bioturbation or burrowing (Levin et al., 1997; Sun et al., 1999; Thomas and Blair, 2002), respiration (Aberle and Witte, 2003; Witte et al., 2003a) irrigation and ventilation (Aller and Aller, 1998; Sun et al., 1999; Sun et al., 2002), and through microbial stimulation (Aller, 1982; Levin et al., 1997; Sun et al., 1999). Thus, dynamic relationships exist between benthic faunal communities, sediment geochemistry and oxygen availability, yet these remain poorly understood or quantified.

Early studies concerning the role of benthic fauna in marine sedimentary OM cycling revealed that faunal biomass is not a sufficient proxy for biological OM processing (Pfannkuche et al., 1999). As a consequence, ^{13}C and ^{15}N stable isotopes have been widely used to investigate the feeding habits of benthic communities and have been shown to be excellent source indicators that can be used to reconstruct food webs (Fry and Sherr, 1984; Minagawa and Wada, 1984; Peterson and Fry, 1987). Many organisms have a diverse range of food sources with overlapping isotopic signatures. However, natural ^{13}C and ^{15}N stable isotopes occur in too low natural abundances to resolve these signatures confidently. In order to trace a multitude of benthic processes and biogeochemical cycles, artificial enrichments of these isotopes are used to allow direct tracking of OM through benthic systems, and their incorporation into naturally occurring compounds or substrates (e.g. bicarbonate, glucose, algal detritus and ammonium) (Cowie and Woulds, 2011).

Results from previous studies indicate that benthic communities usually intercept and rapidly ingest the OM flux delivered to the seafloor (Blair et al., 1996; Cahet et al., 1990; Cahet and Sibuet, 1986; Lauerman et al., 1997; Levin et al., 1997) but that the response varies between faunal groups such as bacteria, foraminifera and megafauna (Armenteros et al., 2010; Boetius and Lochte, 1996; Lochte and Turley, 1988; Woulds et al., 2007). The majority of previous studies have generally been restricted to single faunal processes (e.g. digestion or irrigation) or single species in artificial microcosms with only a fraction of the natural benthic community, yielding a range of contrasting results. However, whole-

community studies are usually limited by the natural conditions at the study site, and are thus unable to deconvolve the influences of biomass, species composition, OM availability and oxygen concentration on biological C processing.

In order to make direct comparisons of OM cycling between contrasting environments and benthic faunal communities, a more comprehensive approach is required. Whole-community isotope tracer experiments suggest that foraminifera and bacteria dominate the uptake of added isotopic label, and thus OM remineralization, in marine sediments (Moodley et al., 2000; Moodley et al., 2002). Conversely, other studies have found that macrofauna are key players in faunal OM processing in terms of OM transport, burial, uptake, and respiration (Heip et al., 2001; Levin et al., 1997; Witte et al., 2003a; Witte et al., 2003b; Woulds et al., 2007). In addition, several factors are known to influence benthic biological processing of OM: oxygen (Woulds et al., 2007), OM quality and quantity (Buhring et al., 2006b; Sayles et al., 1994; Woulds et al., 2007), temperature (Moodley et al., 2005; Woulds et al., 2007), and faunal size and abundance (Middelburg et al., 2000; Woulds et al., 2007). To date, few experimental studies have addressed more than one factor, and so it is not yet clear how these influences interact with each other to provide a cumulative effect. Thus, further work is required to determine how key variables such as O_2 concentrations, OM quality and community structure combine to affect biological processing of OM in marine sediments.

1.2. Research Approach

In order to further understand the effects of fauna on sedimentary OM cycling, whole-community experiments were conducted under varying oxygen concentrations conditions at sites with a natural range of biogeochemical characteristics. The development of whole-community experiments was vital in addressing the role of benthic fauna in OM cycling and burial, in order to develop comprehensive models of seafloor OM cycling, by measuring organic matter pathways in benthic environments across both shelf and deep sea sediments (Middelburg et al., 2000; Moodley et al., 2005; Woulds et al., 2007).

In this study, the interaction between benthic fauna and sedimentary OM cycling was investigated using whole-community pulse-chase tracer experiments. While microcosm experiments have been conducted across a range of environments, they often only study a single faunal group (e.g. macrofauna, Sun et al., 1999) or a single environmental factor (e.g. oxygen, Forster et al., 1995). Thus they are not necessarily good representations of the natural environment. More accurate experiments can be conducted on intact marine

sediments, without selecting or excluding faunal groups, and are termed "whole-community" experiments.

Given that the majority of organic matter supply to the seafloor occurs as seasonal pulses of phytodetritus, the whole-community experiments were conducted by adding a known quantity of phytodetritus (chlorella) to mimic these pulses. In order to track the pathway of OM in the system, the added phytodetritus was pre-enriched in ^{13}C and ^{15}N to enable chemical tracing. Thus, ^{13}C- and ^{15}N-enriched chlorella was added to intact sediment cores containing whole faunal communities, both in-situ and to sediment cores incubated aboard ship. The added isotopically-labelled OM was traced into different pools such as fractions of the faunal community, sediments, pore waters and overlying waters. Faunal uptake of added OM was determined by isotopic enrichment of organic carbon ($\delta^{13}OC$) and nitrogen ($\delta^{15}N_{org}$) of faunal body tissue, bacterial assimilation was assessed through ^{13}C analysis of specific bacterial polar lipid fatty acids (PLFAs), and respiration was measured from ^{13}C enrichment of dissolved inorganic carbon (DIC, ΣCO_2). In addition, natural sediments were sampled for geochemical parameters at both bulk and molecular levels.

Experiments were conducted in both the Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin), at sites displaying large natural contrasts in bottom-water oxygen concentrations, sediment geochemistry, OM availability and benthic faunal communities. In order to assess how faunal activity varies with oxygen availability, incubation experiments were conducted under both ambient and manipulated oxygen concentrations.

1.3. Research Questions And Hypotheses

1.3.1. Research Questions

- What is the short-term fate of OM in Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin) sediments?
- To what extent are benthic fauna responsible for determining the fate of OM?
- How does faunal-OM interaction depend upon
    - oxygen availability,
    - temperature,
    - depth,
    - benthic community size and/or composition?
- What classes of fauna are the key players in the short-term OM processing?

- How does the distribution and degradation state of sedimentary pigments vary across the Baltic Sea (Gotland Basin)?
- How do pigment suites relate to local sediment geochemistry and benthic communities in the Baltic Sea (Gotland Basin)?

1.3.2. Hypotheses

- Benthic communities play a significant role in determining the short-term fate of organic matter in Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin) sediments.
- The role of benthic fauna in short-term organic matter cycling is strongly influenced by local oxygen conditions and organic matter quality in both the Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin).
- Biological sedimentary organic matter processing is:
    - dominated by bacteria and foraminifera where oxygen is depleted and organic matter quality is low (e.g. in the OMZ core of the Arabian Sea, and at the deep anoxic sites of the Baltic Sea).
    - evenly shared between macrofauna, foraminifera and bacteria where oxygen is not limited and organic matter quality is high (e.g. outside of the OMZ in the Arabian Sea, and at oxygenated sites in the Baltic Sea).
- Oxygen availability, OM supply and sedimentary texture determine pigment distribution and degradation state across the Baltic Sea (Gotland Basin).

1.4. Thesis Structure

- Chapter 1 provides the scientific rationale of this study and the research approach, identifies research questions, sets the hypotheses to be tested, and outlines the thesis structure.
- Chapter 2 is a review of the literature, providing background information on the global carbon cycle, marine hypoxia, benthic ecology, organic matter cycling and research approaches.
- Chapter 3 introduces the study sites and provides details of the methods employed across the study.
- Chapter 4 describes the distribution and degradation state of sedimentary pigments across the Gotland Basin of the Baltic Sea and how this relates to sediment geochemistry and benthic faunal communities.

- Chapter 5 examines the role of benthic fauna in the short-term processing of OM in both the Arabian and Baltic Sea.
- Chapter 6 builds a carbon processing budget, complete with respiration and microbial processing, and reviews carbon processing patterns from previous studies.
- Chapter 7 states the research achievements, summarises the key findings of the study and identifies areas for further research.

2. LITERATURE REVIEW

2.1. The Global Carbon Cycle

The global carbon (C) cycle is made up of three active carbon reservoirs (the oceanic, atmospheric and terrestrial systems) and a sub-surface geological reservoir that includes carbon stored in carbonate, and in oil- and gas-bearing rocks (Figure 1). The active reservoirs are linked by many processes (e.g. photosynthesis, respiration, weathering, biological pumping, riverine transport, ocean-atmosphere interactions) in which carbon may undergo multiple changes in chemical form.

The oceanic reservoir is the largest in terms of C content which is stored in three forms: as dissolved inorganic C (i.e. dissolved CO_2, HCO_3^- and CO_3^{2-} ions), dissolved organic C and as particulate organic matter (Post et al., 1990). Carbon in the ocean plays a key role in determining atmospheric CO_2 through physical mixing and circulation, via chemical buffering or as a result of biological processes. Primary production is the process by which organisms living in surface waters use the dissolved forms of carbon during photosynthesis, to produce both inorganic and organic compounds. The mechanism of biological pumping occurs when these products are transported to the deeper ocean waters as sinking dead organisms or faecal pellets towards the seafloor. Here, the organic matter may undergo remineralisation and/or bacterial decomposition, meaning only a small amount is ultimately deposited on the seafloor. Burial of organic material in seafloor sediments is a crucial way in which carbon from the surface active carbon reservoirs is transferred to the sub-surface geological reservoir.

There is overwhelming evidence that human activities (e.g. increasing CO_2 emissions, land use changes) are significantly altering the global carbon cycle and these changes are intrinsically linked to other climatological and biogeochemical processes. Alarming observations have been made across numerous ocean parameters, including: rising global ocean surface temperatures, increasing ocean acidification, declining oxygen concentrations and disrupted ocean currents (Diaz and Rosenberg, 2008; Doney et al., 2009; Levitus et al., 2009). However, there is no comprehensive understanding of how anthropogenic climate change is influencing marine biota and their role in the global carbon cycle. While it has so far been difficult to predict the response of the oceanic biological communities to these changes, it is generally thought that these changes may

significantly affect the role of the oceans as a carbon sink in the future (Sarmiento et al., 1998).

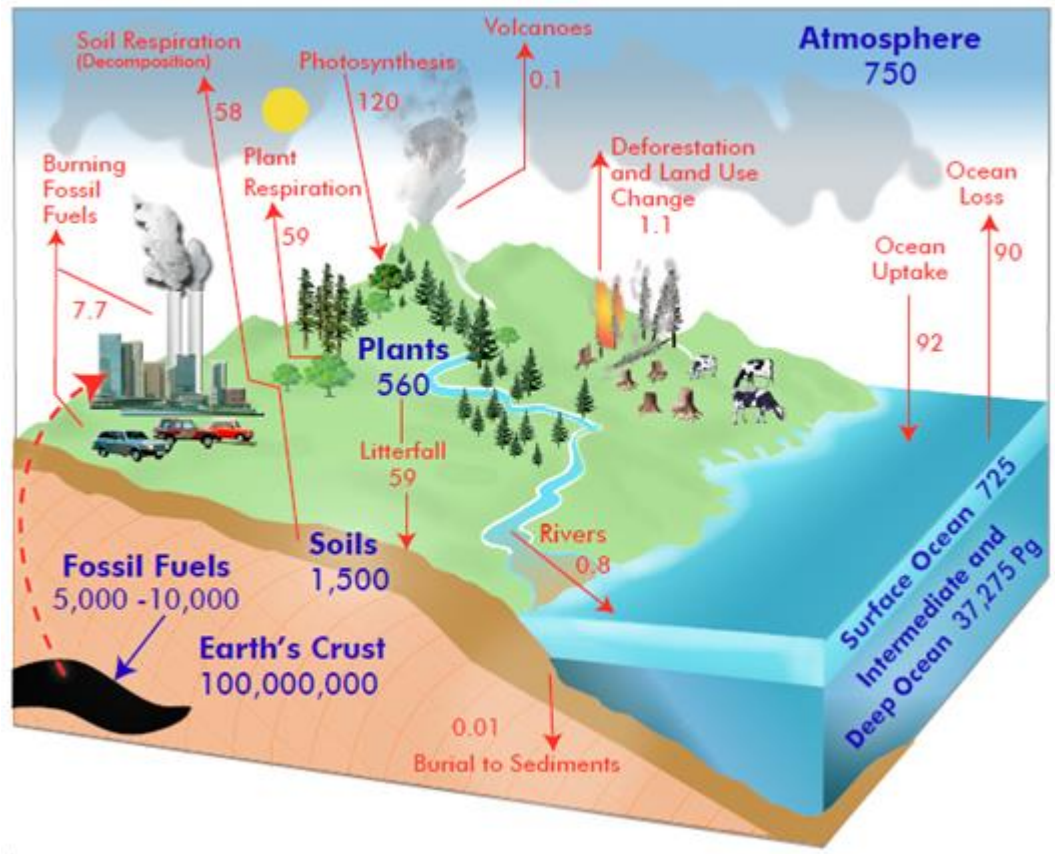


Figure 1. The global carbon cycle, including notable carbon pools and fluxes. Pool sizes (blue) and fluxes (red) are given in Pg per year (GLOBE Carbon Cycle Project, www.globe.gov/projects/carbon).

2.2. Marine Hypoxia

2.2.1. Overview

Hypoxia is a shortage of dissolved oxygen in a water mass which occurs due to an imbalance between oxygen production (i.e. photosynthesis), consumption (i.e. respiration), and atmospheric exchange processes. More than 400 coastal sites worldwide have been reported to experience hypoxia and its associated effects (Diaz and Rosenberg, 2008), and so hypoxia has emerged as a major threat to marine ecosystems. Many hypoxic sites correlate to major population centres or watersheds as indicated by the "human footprint" index produced by Sanderson et al. (2002) (Figure 2). Furthermore, there has been an increasing number of reports of hypoxic sites across a multitude of environments

including embayments, estuaries, fjords, oxygen minimum zones, continental shelves and large rivers (Zhang et al., 2010).

There is little consistency in the use of either units or thresholds of hypoxia in the scientific community, which can make comparisons difficult. However, the most frequently used units for dissolved oxygen are ml L^{-1}, mg L^{-1}, and μM and the usual definition of hypoxia is where dissolved oxygen is <2 mg L^{-1}, equivalent to 1.4 ml L^{-1} or 63 μM (Rabalais et al., 2010). Furthermore, the term anoxia is typically applied where dissolved oxygen is <0.01 mg L^{-1} (Diaz and Rosenberg, 1995). However, this term is somewhat debated and some authors state that the presence of sulphide is required for the term anoxia to apply.

Oxygen depletion may occur naturally, due to human activities, or as the result of the interplay between human and natural processes, which further increases the risk of hypoxia. Figure 3 shows the mechanisms by which dissolved oxygen is produced and consumed in coastal waters. Dissolved oxygen in surface waters is regulated by photosynthesis and ocean-atmosphere interactions. In deeper waters and seafloor sediments, dissolved oxygen is consumed by bacterial activity, re-oxidation of reduced compounds, OM degradation. Dissolved oxygen concentrations are further influenced by the physical processes of advection, turbulent mixing, upwelling, diffusion, bioturbation and irrigation. Natural hypoxia has been observed in the majority of coastal upwelling systems, including the western African, western Indian, eastern Pacific and Peruvian coastlines (Helly and Levin, 2004). Upwelling of nutrients to surface waters stimulates high productivity (i.e. phytoplankton growth) rates, and the subsequent decomposition of phytoplankton as it sinks through the water column leads to high oxygen consumption rates which are greater than production or re-supply. This excessive production of biomass in the water column is termed eutrophication, and often results in oxygen depletion. Further supply of nutrients to surface waters via airborne deposition, riverine and terrestrial inputs may further enhance eutrophication and thus, hypoxia. In addition, warm saline waters hold lower dissolved oxygen concentrations than cold, fresh waters. Furthermore, hypoxia is exacerbated in waters that are highly stratified or physically isolated from oxygenated water masses. Stratification may result from seasonal warming or intense precipitation (e.g. monsoons, flooding) and physical isolation may occur due to this stratification or physical restriction of water flow (e.g. by sills). Thus, water bodies with long residence times and restricted mixing with oxygenated water are prone to hypoxia. The degree of hypoxia in a given environment may vary in relation to

productivity rates and stratification (Naqvi et al., 2006; Rabalais et al., 2001). There are numerous anthropogenic influences on hypoxia at both local and regional scales. These include human-induced eutrophication, contaminated river inputs and warming associated with global climate change.

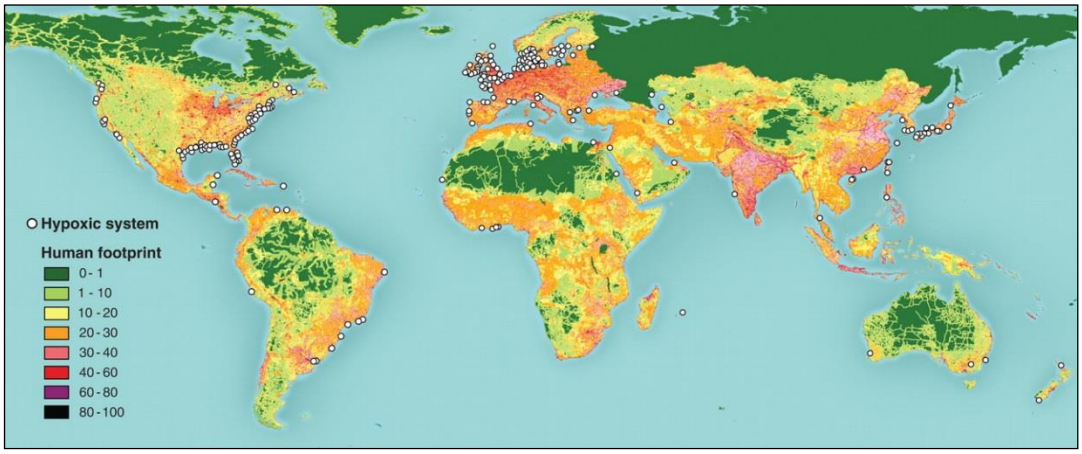


Figure 2. The global distribution of 400-plus coastal sites that have been reported as hypoxic. The Human Footprint Index was produced by Sanderson et al. (2002) (Diaz and Rosenberg, 2008).

The effects of hypoxia on aquatic systems are extensive and include severe ecosystem disturbance, through changes in food chain dynamics, faunal and floral mortality, habitat loss or compression, faunal migration, reduced biodiversity and altered biogeochemical cycles of nutrients (Bonsdorff, 2006; Diaz and Rosenberg, 1995; Karlson et al., 2002; Rabalais et al., 2001; Smith and Hollibaugh, 1989; Vahtera et al., 2007; Vaquer-Sunyer and Duarte, 2008). Algal blooms are rapid increases or accumulations of algae in response to an excess of nutrients, particularly phosphorus. The death of algal blooms results in the decay of large amounts of OM which consumes dissolved oxygen and further exacerbates hypoxia. Harmful algal blooms develop when harmful microalgae produce natural toxins which can lead to or the mass mortality of other aquatic organisms. Examples include microalgal groups of dinoflagellates (e.g. *Alexandrium* spp., *Ceratium* spp.), diatoms (e.g. *Corethron* spp., *Skeletonema costatu*), cyanobacteria (e.g. *Anabaena* spp., *Gloeotricha* spp.) and a non-microalgal group, ciliates (e.g. *Mesodinium* rubrum) (Landsberg, 2002). Decreasing bottom-water oxygen concentrations also have significant impacts on sediment biogeochemistry: favouring anaerobic rather than aerobic diagenetic pathways; altered sediment-water exchange fluxes, enhanced accumulation and burial of OM, changes in microbially-mediated biogeochemical processes (Middelburg and Levin, 2009).

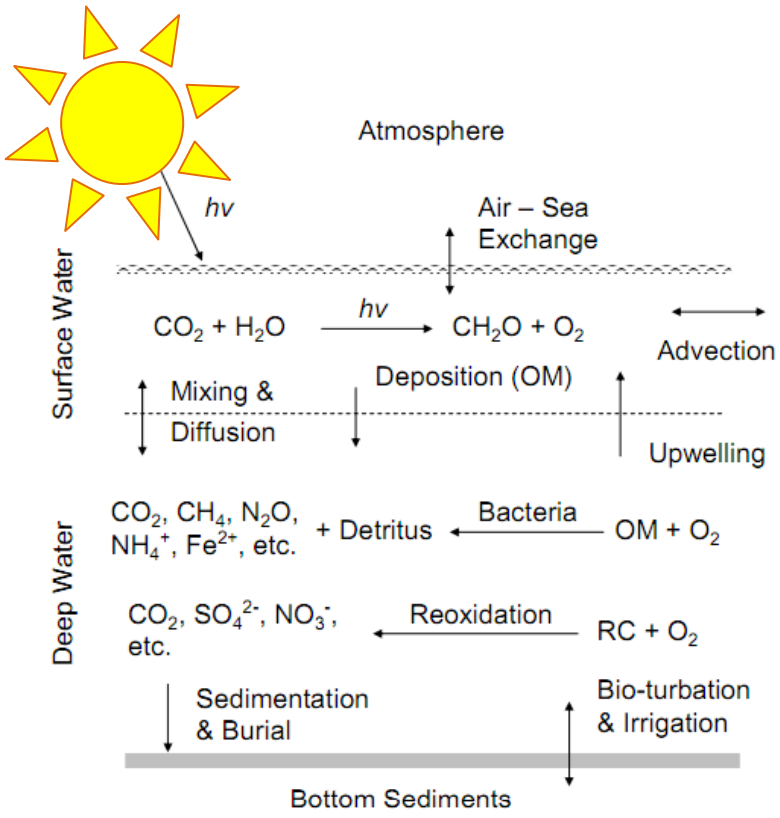


Figure 3. Mechanisms by which dissolved oxygen is produced and consumed in the water column (Zhang et al., 2010).

Oxygen concentrations are continuing to decrease in the majority of marine environments and this trend has been attributed to both growing anthropogenic stresses and global climate change. These changes are associated with increased stratification, increased evapotranspiration, altered wind regimes, changes in nutrient, organic matter and freshwater inputs, and reduced oxygen solubility due to ocean warming (Middelburg and Levin, 2009). Global climate models have forecast decreases of 1–7 % in oceanic dissolved oxygen concentrations as a result of the combination of predicted ocean warming, decreasing oxygen solubility in surface waters, disrupted ocean circulation and increasing atmospheric CO_2 levels (Keeling et al., 2010; Shaffer et al., 2009). These changes will have substantial impacts on benthic ecosystem dynamics and sediment biogeochemistry.

Figure 4 illustrates the complex interactions between anthropogenic activities, climate change, hypoxia and biological activity. As oxygen concentrations decline, it is important to gain a greater understanding of fauna-OM interactions and feedbacks under different oxygen scenarios, and the mediation of biogeochemical processes by benthic fauna that influence the sedimentary carbon and nutrient pools.

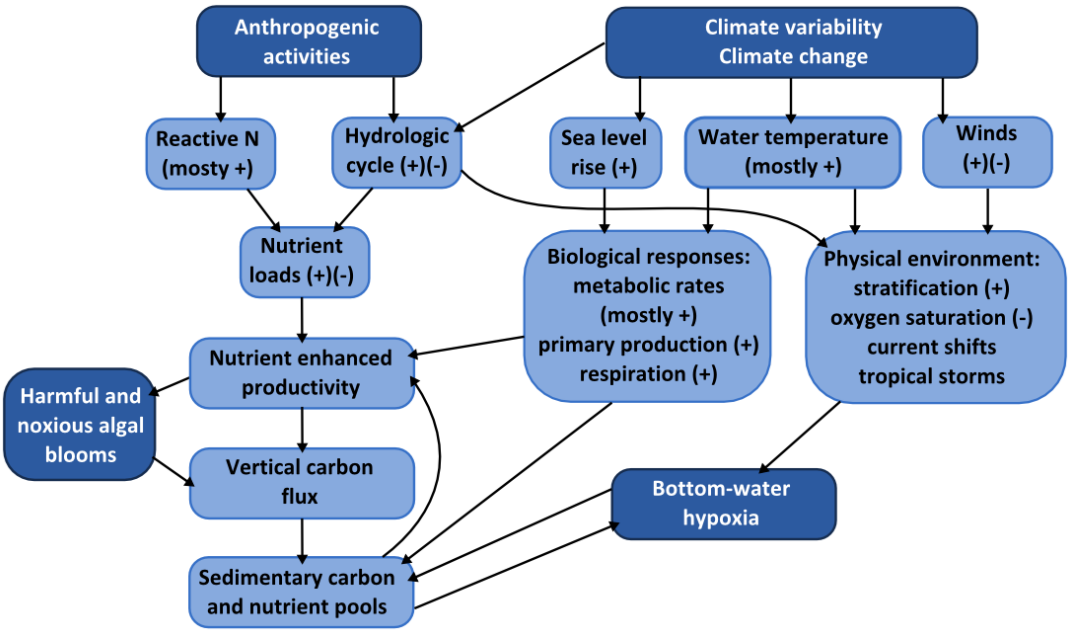


Figure 4. Potential oceanic biological, chemical and physical interactions as a result of anthropogenic climate change (modified from Rabalais et al., 2010).

2.2.2. Oxygen-Depleted Environments

The number of reports of hypoxic sites is increasing globally: from environments such as estuaries and bays, semi-enclosed seas and basins to oxygen minimum zones. The following examples of hypoxic environments have been selected to represent this range of environments (Figure 5): Chesapeake Bay, Black Sea, Northern Adriatic Sea, Baltic Sea, Eastern Tropical Pacific Ocean, South West African Cost and the Arabian Sea.

2.2.2.1. Estuaries

Estuaries (often also called bays, harbours, sounds, or inlets) are important habitats for many shellfish and fish species which are harvested commercially, hence estuarine hypoxia is of great concern. In the US, over 46 % of estuaries experience seasonal hypoxia, mostly along the eastern and Gulf coastlines (Gray et al., 2002). Estuarine hypoxia is usually seasonal due to increased temperature and salinity stratification during the summer months. However, hypoxia in these environments may also be:

- aperiodic - not annual, lasting days to weeks,
- episodic - i.e. intermittent, post-flooding or post-monsoon,
- restricted - to confined areas, e.g. a tributary (Levin et al., 2009a).

Estuarine oxygen depletion is typically the result of elevated terrestrial inputs of nutrients and freshwater-induced stratification. More comprehensive accounts of estuarine and bay hypoxia can be found in Diaz and Rosenberg (1995; 2001; 2008) Gray et al. (2002) and Levin et al. (2009a).

Chesapeake Bay (Figure 5) is a widely cited example of estuarine hypoxia, as hypoxia in the region is a known environmental problem and has been well documented (Boesch et al., 2001; Hagy et al., 2004; Kemp et al., 2005; Kemp et al., 2009). It is the largest and most biologically diverse estuary in the United States (Li et al., 2005) and serves as a commercial and recreational resource. The combination of a large watershed (Rabalais et al., 2010), a relatively shallow mean depth (Rabalais et al., 2010) and an oversupply of nutrients, from both point (e.g. waste water treatment plants) and non-point (e.g. agricultural run-off) sources, has steadily increased the duration and volume of bottom-water hypoxia (Hagy et al., 2004). Thus, hypoxic events in Chesapeake Bay are described as persistent, seasonal and stratified (Kemp et al., 1992). Further contributors such as modest tidal exchange, fresh water inputs, and riverine sediment loading have been exacerbated by a growing population, increased use of agricultural fertilizers and atmospheric deposition of nitrogen oxides. Local conditions have been worsened by overfishing and faunal diseases which have led to increased phytoplankton growth (Figure 6), habitat destruction, loss of shellfish and fisheries production, and summer crab depletion (Hagy et al., 2004; Kemp et al., 2005; Kemp et al., 2009; Officer et al., 1984).

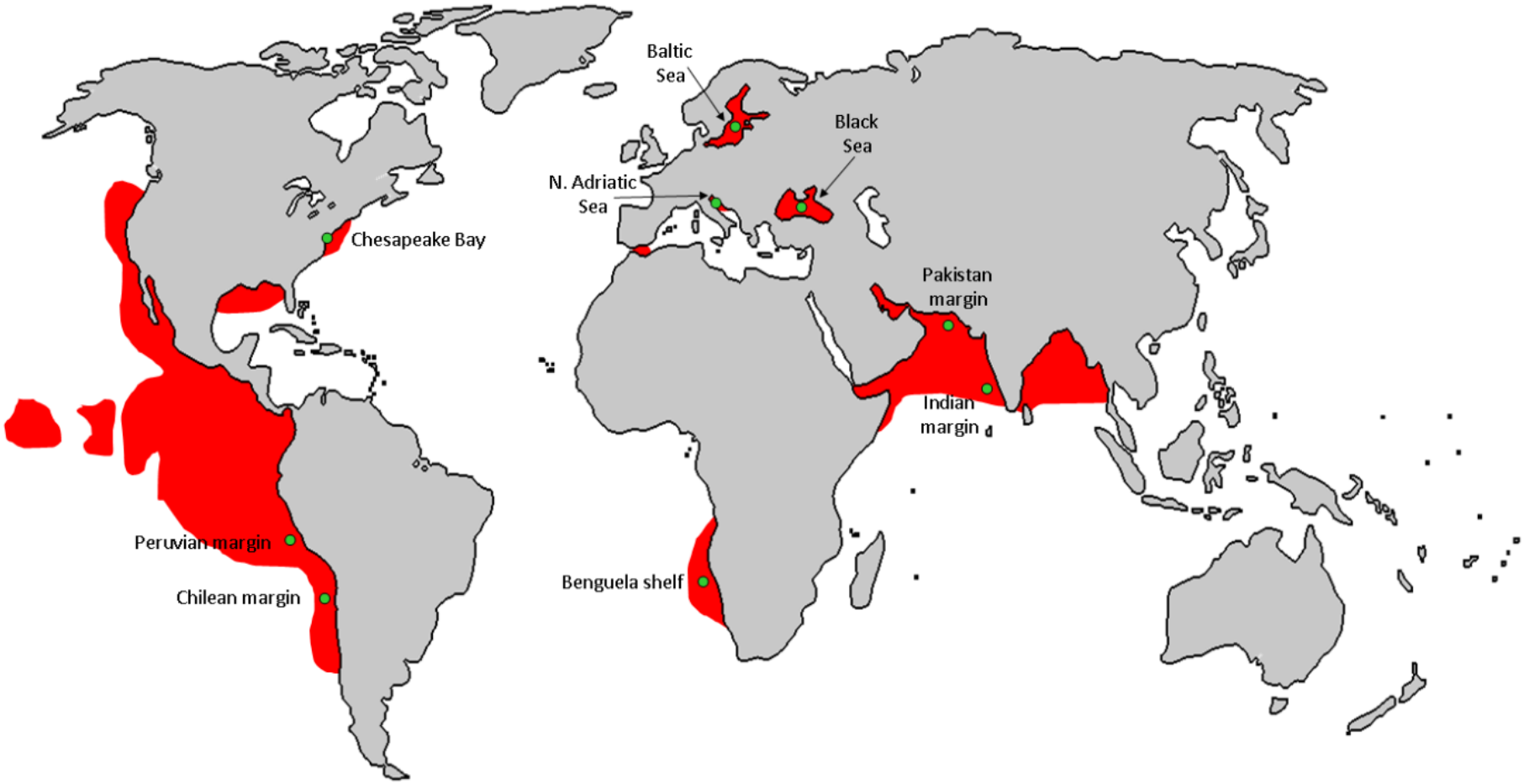


Figure 5. A map of the world identifying the locations of the example of oxygen-depleted environments given in the text.

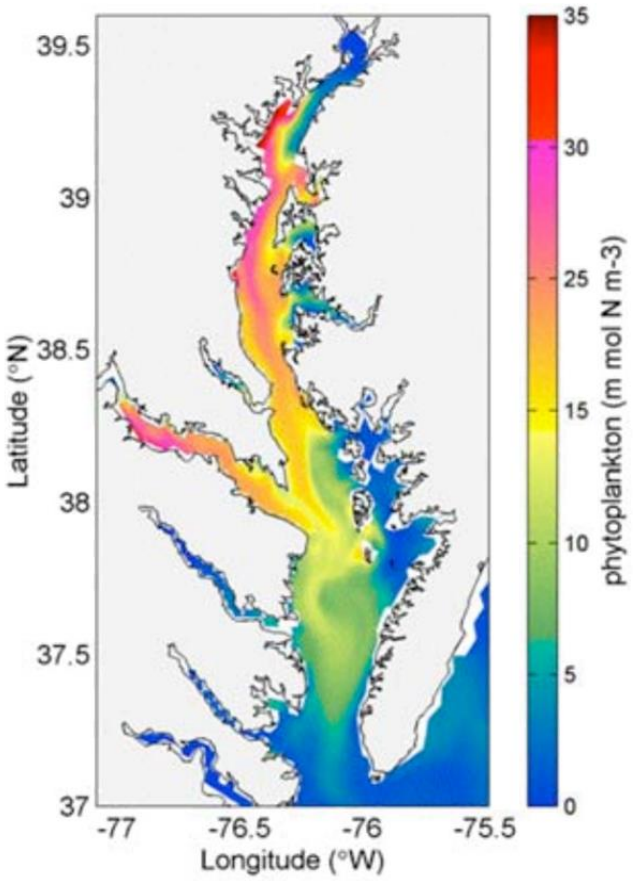


Figure 6. Modelled surface spring phytoplankton biomass in Chesapeake Bay, following a high run-off year in 1996 (Li et al., 2005).

2.2.2.2. Semi-Enclosed Seas And Basins

Many semi-enclosed waters (e.g. fjords, lochs and shallow seas) such as the Black Sea, Cariaco Basin, Adriatic Sea and Baltic Sea suffer from hypoxia and have been extensively studied (Karlson et al., 2007; Oguz et al., 2000; Riedel et al., 2008). In these environments the main cause of hypoxia is physical isolation, resulting in restricted exchange with the open ocean which leads to water column stratification. Water column stratification is further developed by shallow water depths which make the environment more susceptible to seasonal temperature fluctuations (Levin et al., 2009a). Thus, these environments are often subjected to intense summer hypoxia events.

The Black Sea (Figure 5) is the world's largest body of permanently anoxic water and receives inflow from 17 countries. Increased agricultural and industrial inputs from these countries have been the main cause of increasing hypoxia in the region. The effects of hypoxia on benthic communities are well-documented, including the widespread (40000 km^2) "dead zone" which is completely devoid of benthic fauna due to repeated mass

mortality events (Gregoire et al., 2008). Large annual algal blooms are produced as a result of high nutrient fluxes and further exacerbate the oxygen depletion. Conditions are worsened by additional nutrients in the form of fluxes of phosphates and ammonium from the basin sediments, which are released into the water column as neither adsorb to sediments under anoxic conditions (Levin et al., 2009a).

In the Northern Adriatic Sea (Figure 5), decreasing bottom water oxygen concentrations have been observed in both historical records and palaeo-environmental records, with continuous decline observed since the 1950s (Crema et al., 1991; Justić et al., 1987; Justić, 1988). These changes have been attributed to high productivity rates, long residence times and increasing nutrient loads from the Po River, Italy (Druon et al., 2004; Ott, 1992; Stachowitsch, 1991). Hypoxia in the region has become more severe since the 1950s and now lasts for prolonged periods of time (Barmawidjaja et al., 1995; Penna et al., 2004; Stachowitsch, 1984). The size of areas affected by hypoxia has ranged from 250 km^2 in 1974 to 4000 km^2 in 1989 in various locations, meaning that nearly all of the northern Adriatic Sea has experienced hypoxia (Riedel et al., 2008). Frequent and widespread mass mortality events have been observed within the benthic community since the early 1980s, and slow recovery was observed following large-scale loss of biodiversity during the 1983 hypoxia following a large summer algal bloom (Franco and Michelato, 1992; Riedel et al., 2008; Stachowitsch, 1991).

The Baltic Sea (Figure 5) is a semi-enclosed brackish water body covering an area of 412560 km^2, with a volume of 21,631 km^3, an average depth of 52 m and a maximum depth of 459 m. Its hypoxic zone has quadrupled in area since the 1960s and presently reaches up to 41000 km^2 annually (Conley et al., 2002). Most of the deep basins of the Baltic Sea are continuously hypoxic, while permanent anoxia can be found in the deepest parts of the Gotland Deep (Conley et al., 2002). The water column is permanently stratified, with two distinct water masses: a surface brackish water layer (7–8 PSU, Practical Salinity Unit) and a deeper saline water layer (11–13 PSU) (Zillen et al., 2008) . The presence of a strong halocline separates the surface waters from the bottom waters and thus prevents vertical mixing of the water column and ventilation of the oxygen-depleted bottom waters (Matthaus and Schinke, 1999; Rabalais et al., 2010). While hypoxia in the Baltic Sea is not a modern phenomenon, eutrophication is believed to be the main cause of decreasing oxygen concentrations in the last 100 years (Conley et al., 2009a; Jonsson et al., 1990). Anthropogenic airborne and waterborne nitrogen and phosphorus inputs have at least quadrupled in the last century (Larsson et al., 1985; Wulff et al., 2007).

This is mostly due to the fact that the watershed contains a population of over 85 million people and drains an area that is four times larger than the actual sea (Zillen et al., 2008).

Despite the ongoing hypoxia problems, the Baltic Sea is home to over 100 species of fish, 450 species of macroalgae, 1000 species of zoobenthos and 3000 species of plankton (HELCOM, 2012). When compared to other brackish water-bodies (e.g. Black Sea and Caspian Sea), the Baltic Sea has the lowest native species richness and the greatest number of invasive, or alien, species (Paavola et al., 2005). Furthermore, the Baltic Sea hypoxia is observed to have altered food chain dynamics and caused faunal habitat loss across the Baltic Sea, reduced benthic communities below the halocline and led to benthic "ecological deserts" that cover over 30 % of the seafloor annually (Karlson et al., 2002; Laine, 2003; Zillen et al., 2008). The Eastern Gotland Deep displays marked faunal zones: >50 species occur at oxygenated water depths (<30 m); 11–14 species exist in hypoxic waters (50–124 m); no species are found in anoxic waters (124–140 m). In a negative feedback, decreasing oxygen concentrations have been positively correlated with increasing phosphorus release from the sediments which add more nutrients to the already hypoxic waters (Conley et al., 2002). This occurs because phosphate sorbs strongly to iron oxides in oxic sediments but is released into the water column under anoxic conditions.

2.2.3. Oxygen Minimum Zones

Oxygen minimum zones (OMZs) are areas of permanent low-oxygen that typically occur at bathyl depths of between 200 m and 1000 m. As with hypoxia, there is little consensus within the scientific community about what oxygen concentration defines an OMZ. They are the largest low oxygen areas on Earth, coving approximately 30 million km^2 of open ocean in the eastern Pacific, off western Africa and in the northern Indian Ocean (Kamykowski and Zentara, 1990; Paulmier and Ruiz-Pino, 2009). 148000 km^2 of the continental margin sea floor is estimated to have bottom water oxygen concentrations <0.5 ml L^{-1}, and approximately 764000 km^2 has concentrations <0.2 ml L^{-1} (Helly and Levin, 2004). OMZs are typically stable features that occur at intermediate depths (100–1000 m) and persist at least for at least decades (Rabalais et al., 2010). The position of OMZ upper and lower boundaries are influenced by natural processes and cycles such as monsoons (Helly and Levin, 2004; Wyrtki, 1966). High surface water productivity, long residence times and restricted water circulation are responsible for the formation of OMZs. Furthermore, some regions also experience upwelling which causes higher

productivity rates and increases oxygen demand and thus contributes to hypoxia (Helly and Levin, 2004). The combination of high organic matter supply, from high surface water productivity, and low oxygen concentrations makes these areas major sites of carbon burial. OMZs are typically characterised by specialized low biodiversity benthic communities that have lower oxygen tolerance thresholds (Levin et al., 2000) achieved by physiological and morphological adaptations and the ability to utilize chemosynthesis-based nutritional pathways (Levin, 2003). The global climate model forecast of decreased oceanic dissolved oxygen (1 % to 7 %) (Keeling et al., 2010; Shaffer et al., 2009) is predicted to lead to the expansions of OMZs into shallower depths and severe, permanent oxygen depletion (Arrigo, 2007; Riebesell et al., 2007; Shaffer et al., 2009). Recent expansion of OMZs has already been observed in the Pacific Ocean and has been attributed to global climate change (Stramma et al., 2008).

The most widely studied OMZs are discussed in greater detail below:

- the Peruvian and Chilean shelves of the Eastern Tropical Pacific Ocean,
- the Benguela shelf on the South West African coast,
- and the Indian, Oman, and Pakistan margins of the Arabian Sea.

2.2.3.1. Eastern Tropical Pacific Ocean

Dissolved oxygen concentrations are well documented across the margins of the Eastern Tropical Pacific Ocean (Figure 5), ranging from hypoxic to anoxic (Figure 7). Hypoxia is associated with upwelling, and thus increased primary production. The occurrence of El-Niño attenuates hypoxic seasonality and leads to better oxygenated, winter-like conditions across the shelf throughout the El-Niño years. “Normal” hypoxic conditions in the OMZ are associated with the development of sulphide-oxidising bacterial mats (e.g. *Thioploca* and *Beggiatoa* spp.) during summer hypoxia.

On the northern Chilean shelf, permanent hypoxia is found to a depth of 400 m as a result of seasonal upwelling in shallow waters (Sellanes et al., 2003; Sellanes et al., 2007). Typically, macrofauna (>1 cm) are abundant but exhibit low diversity (Sellanes et al., 2007) and body sizes are reduced (Quiroga et al., 2005). During El-Niño events, meiofauna (<300 μm) increase in both abundance and biomass (Sellanes and Neira, 2006) and, in general, meiofaunal behaviour can be positively correlated with oxygen concentrations (Levin et al., 2009a). On the Peru margin however, three distinct benthic community states have been identified. Under anoxia-hypoxia (<10 μM O_2), few macrofauna exist and

biomass is dominated by nematodes. In intermediate oxygen concentrations (10–20 µM O_2) sulphide-oxidising bacterial mats (e.g. *Thioploca* spp.) dominate. Where oxygen >40 µM, i.e. during strong El-Niño years, macrofauna are dominant (Levin et al., 2009a).

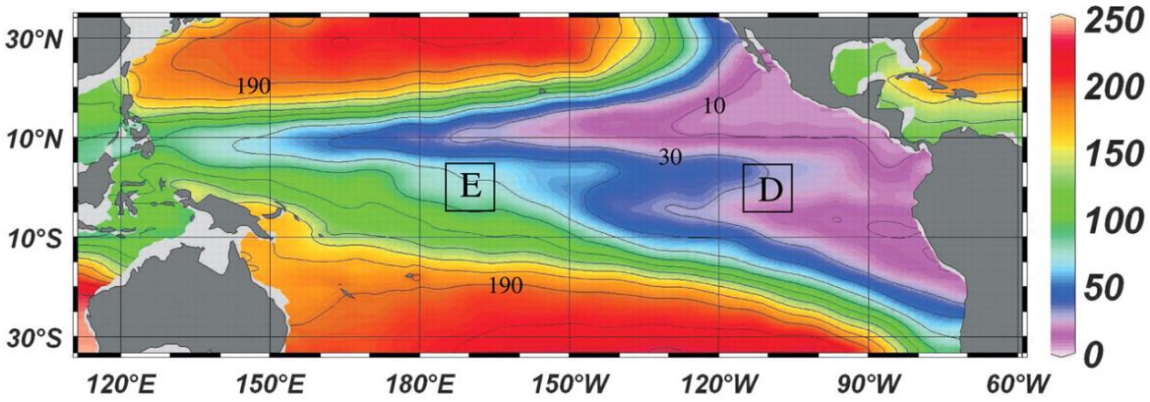


Figure 7. Mean dissolved oxygen concentrations (µmol kg^{-1}) at 400 m water depth across the eastern tropical Pacific Ocean (Stramma et al., 2008).

2.2.3.2. South West African Coast

The Benguela shelf, on the South West African coast, experiences hypoxia that extends to 350 m. It is predominately controlled by upwelling as a result of the Benguela Current. Bruchert et al. (2003) identified three zones: the relatively well oxygenated continental slope below the OMZ; the oxygen depleted OMZ; and the inner shelf which features severely oxygen-depleted bottom waters. To the north, the benthic community within the OMZ is dominated by molluscs while more southern waters are covered with sulphide oxidising bacterial mats. Species richness tends to be greater on the continental shelf compared to the inner shelf (Zettler et al., 2009).

2.2.3.3. Arabian Sea

OMZ formation across the Arabian Sea continental margins results from seasonal, monsoon-driven hypoxia combined with upwelling of nutrient-rich sub-surface waters and freshwater inputs along the eastern coastline. Low-diversity foraminiferal assemblages have been observed within the OMZ but they mostly present in the upper 1 cm of sediments (Larkin and Gooday, 2009). However, a low diversity, high biomass macrofauna community is also present at the lower OMZ boundary, typical of the "edge effect" discussed later (Levin et al., 2009b).

Isotope enrichment studies conducted by Woulds et al. (2009; 2007) reveal that carbon-processing pathways shift with changing oxygen concentrations. It was noted that under

oxygenated conditions macrofauna dominate ^{13}C consumption (when bacteria are not included) whereas in low oxygen conditions (<0.1 ml L^{-1}), foraminifera dominate. Similarly on the Indian margin, high abundances of benthic foraminifera have been observed in surface sediments within the OMZ (*Bolivina*, *Cassidulina*, *Lernella*, *Uvigerina* and *Eponides* spp.) and at 90–1200 m off Goa (Nigam et al., 2007). While many studies have quantified the effect of the OMZ on benthic communities, sulphide oxidising bacterial mats have not yet been reported. Further details of the Arabian Sea OMZ are detailed in Chapter 3; Materials and Methods (page 57).

2.3. Benthic Ecology

2.3.1. Communities

While there are distinctive groups within the benthic fauna community, there is no consistency in the literature about how these groups are defined in terms of size.

Megafauna are generally defined as large animals that are visible in seafloor photographs or can be caught in trawl samples. They typically include swimming animals i.e. mainly fish and decapods across OMZ margins. Megafauna are often absent within the cores of OMZs, but may have large concentrations at the boundaries, such as ophiuoids at 1000 m in the Arabian Sea ("edge effect", Levin et al., 2000).

Macrofauna communities in oxygen-depleted environments are generally dominated by annelids, typically polychaetes and oligochaetes, and sometimes by molluscs, usually aplacophorans, bivalves and gastropods (Diaz and Rosenberg, 1995; Gallardo et al., 1995; Gallardo et al., 2004; Levin and Gage, 1998; Levin et al., 2000). In terms of size, marine macrofauna are usually defined as those larger than 300 μm but smaller than 1 cm. They are often assigned feeding guilds, such as deposit feeder, suspension feeder, facultative feeder, carnivore or herbivore.

Metazoan meiofauna consist of smaller animals than those found in the macrofauna group and include ostracods (shrimps), copepods and nematodes. Within the meiofauna, nematodes are most abundant, and sometimes virtually the only metazoan taxa in OMZs. Metazoan meiofauna are often defined as smaller than 300 μm.

While foraminifera are meiofauna, they are not metazoan and thus are categorised separately. Foraminifera are testate protists ubiquitous in both marine and freshwater environments. They typically produce a shell, or test, with a single or multiple chambers

and may be elaborately structured. Tests are usually one of three basic types: made of organic material, agglutinated sediment particles or calcium carbonate.

Many OMZ environments contain large communities of endosymbiotic, sulphide-oxidising bacteria that are able to fix carbon for their host symbionts (Levin, 2003). They are capable of oxidising hydrogen sulphide (H_2S) as an energy source (Jorgensen and Gallardo, 1999). Furthermore it is thought that mats of filamentous sulphur bacteria may form the base of food webs as is suspected on the Chile OMZ (Gallardo et al., 1995). However, the Arabian Sea may be different – in 2008 no sulphide was detected and little evidence of sulphur bacteria was found (pers. comm. Dr Clare Woulds). The *Thioploca* species are colourless, sulphide-oxidizing, nitrate-reducing bacteria that are known to exist in both freshwater and marine sediments and appear to dominate the bacterial community in low oxygen environments (Gallardo et al., 1995; Gallardo et al., 2004). *Beggiatoa*, a species related to *Thioploca*, also has high densities and abundances in oxygen depleted settings (Jorgensen and Gallardo, 1999). The morphological difference between these two common bacteria is that *Thioploca* filaments occur in bundles within a sheath whereas *Beggiatoa* filaments appear singularly, without a group structure.

2.3.2. Spatial Heterogeneity

While only a fraction of the world's seafloor has been studied, it has already been made clear that there is great spatial heterogeneity in benthic faunal distributions, densities, compositions and abundances. Sediment characteristics, water depth, oxygen availability and organic matter inputs are just some of the numerous factors that have been identified as key controls on both the vertical and horizontal distributions of benthic fauna (e.g. Jumars et al., 1990; Rhoads, 1974; Schaff et al., 1992; Wishner et al., 1990). Spatial heterogeneity can be directly applied to sample sites, and is often determined by assessing similarities or differences between multiple cores obtained at a single sampling site. As benthic fauna distribution is patchy and abundances may vary on scales as little as 10 cm, it is necessary to consider spatial heterogeneity when making broad conclusions about a particular environment based on few data from limited sites. To mitigate this, cores for analysis are chosen from separate multi-core samples which are likely to be metres apart on the seafloor.

Typically, benthic fauna exhibit a horizontal spatial pattern whereby faunal communities within oxygen depleted waters (i.e. within the OMZ) display less structural and biological heterogeneity than communities either side of the OMZ (Levin, 2003). For example, Levin

et al. (2000) observed that across the Oman margin, faunal heterogeneity was greater outside of the OMZ than within it. A similar trend was observed in macrofauna communities on the Chile margin, where homogeneity corresponded to the oxygen minima (Gallardo et al., 2004). These trends are thought to occur as a result of decreased faunal diversity within the OMZ, notably the absence of large burrowers (Gallardo et al., 2004).

The vertical distribution of fauna within the OMZ has a more complex relationship with bottom water oxygen concentrations. Fauna have usually been observed to migrate upwards when oxygen is depleted: e.g. nematodes within the Chile OMZ (Neira et al., 2001b), and foraminifera within the California OMZ (Bernhard, 1992). However, this is not always the case – some studies have found faunal communities that migrate upwards as oxygen concentration increases: e.g. meiofauna (Neira et al., 2001a) and macrofauna (Levin et al., 2002) within the Peru OMZ, and benthic fauna within the core of the Oman OMZ (Smith et al., 2000).

2.3.3. Edge Effects

The term 'edge effects' was first used to describe the observation that benthic faunal density maxima coincided with the upper and lower boundaries of the Californian OMZ (Mullins et al., 1985). These boundary or edge effects, typically occur at OMZ boundaries (~0.5 ml L^{-1}), but may also occur within OMZs themselves (~0.1–0.2 ml L^{-1}) (Levin, 2003). Density maxima are thought to be the result of physiological thresholds due to oxygen limitation and/or changes in organic matter supply, i.e. opportunistic species live at their threshold oxygen concentrations in order to take advantage of abundant food supplies (Levin, 2003). Consequently, OMZ boundaries characteristically contain dense benthic populations, although more commonly at the lower than the upper boundary. Faunal density maxima have been observed in a number of environments, including the Peru OMZ (Rowe et al., 1991), the Black Sea (Zaika, 1999), the Oman margin OMZ (Levin et al., 2000), the Pakistan margin OMZ (Levin et al., 2009b; Murty et al., 2009). On the Peru OMZ edge effects, in the form of foraminiferal density maxima, have been noted on both the upper and lower boundaries (Resig and Glenn, 1997).

2.3.4. Oxygen Thresholds

While the bulk of marine fauna require oxygen to function, some marine organisms are seen to thrive in oxygen-depleted environments such as OMZs where there is high food

availability (Diaz and Rosenberg, 1995). It is thought that the critical oxygen threshold for the majority of benthic fauna is approximately 0.4–0.5 ml L^{-1} – below which, faunal communities experience changes in structure, diversity and behaviour, and ultimately mortality (Levin et al., 2000).

Oxygen thresholds vary between faunal groups. Generally, megafauna are the most sensitive group, followed by macrofauna then meiofauna (Levin, 2003). Megafauna are often absent within OMZs, typically where oxygen concentrations drop below 0.15 ml L^{-1} (Levin, 2003; Wishner et al., 1990) given that they are thought to migrate to less hostile environments. As they are not often present in oxygen depleted environments, they are not discussed further. In general, oxygen depletion has been found to reduce macrofaunal biomass and abundance (Gutierrez et al., 2000). Thus, it is no surprise that faunal diversity is lower within the OMZ and that dominance by a single or few taxa is common (Levin et al., 2000). Some macrofauna have adapted to tolerate permanent or prolonged oxygen depletion, most commonly by enlarged branchiae which increases the respiratory surface area in order to enhance oxygen diffusion (Lamont and Gage, 2000). Polychaetes commonly form elongate, filamentous branchiae (Levin et al., 2000) and one particular family of polychaetes, spionids, have been observed to increase their size and branching (Lamont and Gage, 2000). However, no consistent shifts in body size have been observed in macrofauna across the Oman margin (Levin et al., 2000) or the Peru margin (Levin et al., 2002). It has been suggested that oxygen exerts more of a control than OM over macrofaunal communities at 0.45 ml L^{-1}, below which faunal behaviour and structure is altered (Levin and Gage, 1998). However, threshold levels are thought to be lower than 0.15 ml L^{-1}, given that high biomass values have been found at 0.16 ml L^{-1} on the Oman margin (Levin et al., 2000), at 0.26 ml L^{-1} on the Peru margin (Levin et al., 2002) and at 0.10 ml L^{-1} on the Chile margin (Gallardo et al., 2004). On the other hand, while meiofauna in oxygen-depleted areas typically exhibit changes in structure, diversity and behaviour, they are still abundant at <0.1 ml L^{-1}. Nematodes in particular have been observed to have higher threshold levels. Cook et al. (2000) found that nematode abundance did not vary in relation to bottom-water oxygen concentrations in the OMZ of the Arabian Sea. This agrees with observations on the Peru margin (Neira et al., 2001a) where total meiofauna abundance was not reduced within the OMZ. Foraminifera are also generally tolerant of depleted oxygen conditions, where some species have been found with elevated densities within such environments (Bernhard, 1986; Gooday et al., 2000; Gooday et al., 1998; Gooday et al., 2009). There are significant differences in tolerance between the three most

basic test types (organic, agglutinated, and calcareous): calcareous foraminifera appear to be more tolerant of low oxygen environments, with lower thresholds than both agglutinated and organic foraminifera, but the mechanisms for this are little understood (Gooday et al., 2000). Furthermore, foraminifera are the only group that consistently reduces body size in response to reduced oxygen (Bernhard et al., 2008; Bernhard et al., 1997). The common species of bacteria found in OMZ regions (*Beggiatoa* sp. and *Thioploca* sp.) are known to be tolerant of extremely low oxygen concentrations and are able to oxidise hydrogen sulphide as an energy source. Thus no oxygen thresholds have been set for sulphur bacteria. In fact, in the Arabian Sea thick mats of *Thioploca* sp. have been found within the core of the OMZ (Jorgensen and Gallardo, 1999).

2.4. Organic Matter: Distribution And Preservation

Continental margins receive significant amounts of organic matter from terrestrial and marine sources, and it is estimated that over 80 % of all organic carbon preservation takes place in these areas (Berner, 1982). The cycling and burial of OM in these regions is therefore significant in the global cycles of carbon, nitrogen, and other major biogenic elements, and in ocean productivity and climate (Berner, 1982, 1989; Walsh, 1991). For example, long-term carbon burial largely controls the atmospheric accumulation of oxygen, on geological timescales (Berner, 1982). Furthermore, buried OM is the main potential source of fossil fuels and can also be used to reconstruct records of palaeo-environments (Cowie et al., 1999). Therefore, it is crucial to identify and understand the factors which control the sources, distribution and preservation of OM along continental margins – both non-biological and biological.

2.4.1. Non-Biological Factors

Much research has been conducted to determine the controls on OM distribution and preservation, and has identified several non-faunal factors including sediment accumulation rates, primary productivity, differential carbon sources and reactivity, sorptive preservation and organic-mineral interactions, O_2 availability, water depth, winnowing and re-deposition (Calvert et al., 1995; Cowie et al., 1999; Hedges and Keil, 1995; Mayer, 1994; Schulte et al., 1999; van der Weijden et al., 1999). While there have been numerous reviews of the relationships between sedimentary OM burial efficiency and local oceanographic conditions, the relative importance of the proposed factors is debated (Table 1). Many of the factors are interrelated, making them difficult to deconvolve, and their relative influences are likely to vary between environments (e.g.

coastal margins vs. the open ocean). Consequently, it is often an interplay of factors that generates observed cross-margin OM trends.

Table 1. Examples of papers that address four of the key non-faunal factors that control OM distribution and preservation.

Non-faunal factor	Example references (observations or experimental data)
Oxygen availability and/or exposure	(Canfield, 1989, 1994; Cowie et al., 1999; Cowie et al., 1995; Dauwe et al., 2001; Demaison and Moore, 1980; Glenn and Arthur, 1985; 1998; Moodley et al., 2005; Paropkari et al., 1992; Thiede and Vanandel, 1977; van der Weijden et al., 1999)
Organic matter source and/or reactivity	(Canuel and Martens, 1996; Danovaro et al., 2001; Dauwe et al., 1999; Hedges et al., 1988a, b; Lee et al., 2000; Schulte et al., 2000)
Sorptive preservation	(Calvert et al., 1995; Canfield, 1994; Hedges and Keil, 1995; Keil and Cowie, 1999; Keil et al., 1994; Mayer, 1994; Pedersen et al., 1992; Ransom et al., 1998)
Primary productivity and/or sediment accumulation rate	(Betts and Holland, 1991; Canfield, 1994; Henrichs and Reeburgh, 1987; Muller and Suess, 1979; Pedersen and Calvert, 1990; Stein, 1986)

2.4.1.1. Sediment Accumulation And Primary Production

High sediment accumulation rates have been positively correlated with enhanced OC burial efficiency across a variety of environments (Canfield, 1994; Henrichs and Reeburgh, 1987). It has therefore often been proposed that the supply of OC, largely influenced by primary production rates, controls the accumulation of OM in marine sediments (Calvert et al., 1992; Pedersen and Calvert, 1990). With enhanced OM production and thus high burial rates of reactive organic compounds, a large proportion of OC will be preserved in the sediments (Pedersen and Calvert, 1990). Elevated primary productivity, and thus rapid sedimentation leads to faster burial of OM that would usually be destroyed during extensive exposure to the overlying waters, and thus shorter exposure times (Muller and Suess, 1979). However, enhanced sedimentation may lead to decreased sediment OC concentrations due to the diluting effect of clastic debris (Paropkari et al., 1992). At zero dilution, only OM is deposited and so organic-rich sediments will be found despite the extent of degradation (Canfield, 1994).

While OM preservation is positively correlated with burial rates (Figure 8), strongly linked to sedimentation rates, it has been observed that O_2 concentration plays an additional role (Canfield, 1994). Low oxygen conditions tend to produce higher C preservation rates than would be expected from sedimentation rates alone. However, other reviews of available data (Betts and Holland, 1991) also found a strong correlation between OC burial efficiency and sediment accumulation rates, but O_2 availability had only a minor influence. These opposing observations are most likely due to differing environmental conditions across a range of settings.

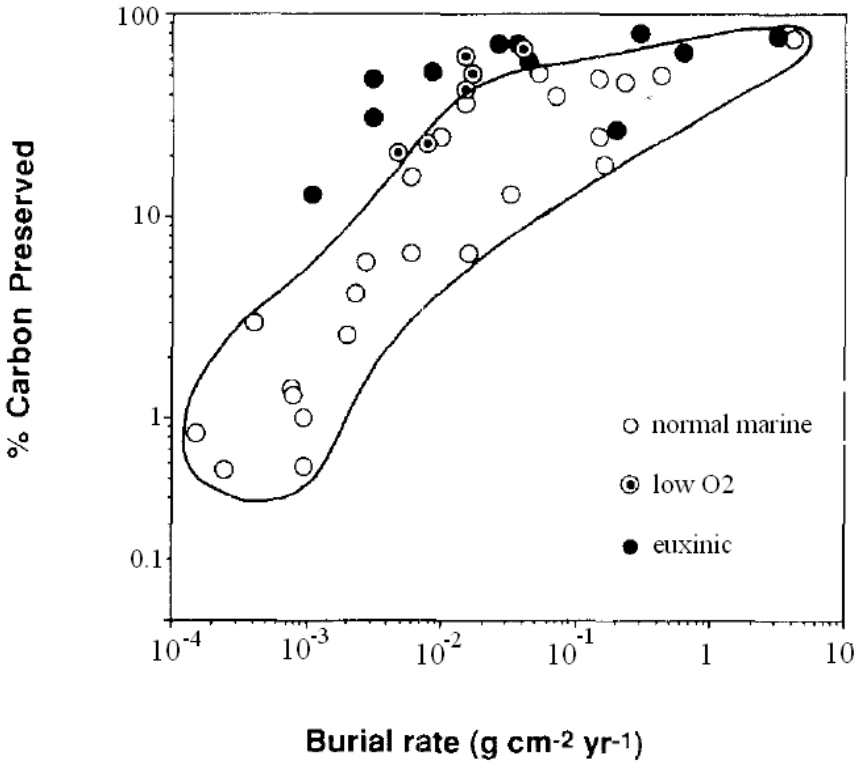


Figure 8. Percentage carbon preserved vs. against burial rate (Canfield, 1994).

2.4.1.2. Organic Carbon Source

Different OM compounds exhibit very different susceptibilities to mineralisation by microbial attack. Work by Hedges et al. (1988a) demonstrates that lignin is one of the least degradable classes of organic compounds when undergoing active decomposition in margin sediments. As a result, the ratio of marine (lignin-free) to terrestrial (lignin-rich) OM supplied to marine sediments can influence OC preservation. The relative stability of lignin has previously been used to monitor waste decomposition stages, where low cellulose to lignin ratios indicate highly decomposed, well-stabilized refuse (Bookter and Ham, 1982). Lee et al. (2000) observed that pigments are generally very reactive

compared to other biochemical classes. In contrast, carbohydrates have often been observed to be relatively un-reactive, sometimes even preferentially preserved (Danovaro et al., 2001). Yet degradation has been found to be selective amongst carbohydrates (Hedges et al., 1988a). Furthermore, selective lipid enrichment has been observed in Pakistan margin sediments (Schulte et al., 2000).

2.4.1.3. Sorptive Preservation

It is thought that sediment texture plays a key role in determining sedimentary OC concentrations (Calvert et al., 1995; Pedersen et al., 1992). Fine grained sediments have been found to have higher concentrations of OC, due to the similar hydrodynamic transport properties of both organic and fine particles, and sorption of OM onto mineral surfaces (Hedges and Keil, 1995; Mayer, 1994). This relationship is due to the fact that fine particles have greater surface area to volume ratios. A strong correlation between preserved OC and particle surface areas has been observed, typified by a constant ratio of OC to sediment surface area of 0.5–1 mg C m^{-2} (Hedges and Keil, 1995; Keil et al., 1994; Mayer, 1994). This has been termed the 'monolayer hypothesis', where the premise is that OM is adsorbed onto the surface of mineral grains in a single molecule thick coating (Mayer, 1994). Sorptive interaction with mineral grains means OM fills interstices on mineral surfaces, providing protection from large bacterial enzymes (Canfield, 1994). This mechanism, 'sorptive preservation', should depend only on the surface area (SA) of the sediment grains and therefore act independently of depositional environments (Canfield, 1994). However, the 'monolayer hypothesis' has since been disproved (Ransom et al., 1998) and while the loading of OM onto mineral surfaces still holds, it is thought that spatial variations in OM preservation is attributed to sensitive balance between sorptive preservation and O_2 availability (Hedges and Keil, 1995; Keil and Cowie, 1999; Ransom et al., 1998). Ransom et al. (1998) noted that in Californian margin sediments, sediment characteristics have more influence over OM preservation than both bottom-water O_2 concentrations and OM source. The authors observed that organic carbon appears to be preferentially sorbed onto smectite-rich clays rather than chlorite-rich clays, and that preservation is not significantly influenced by oxygen concentration. While factors including sediment texture, hydrodynamic sorting and reworking play key roles, their importance appears increase where O_2 exposure is short, as indicated by enhanced OM preservation (estimated by OC:SA values) in sediments within the OMZ of the NE Arabian Sea (Keil and Cowie, 1999). This has been further illustrated by Vandewiele et al. (2009)

who observed that many stations showed either an excess or deficiency of OC relative to "monolayer equivalent" loading (Figure 9).

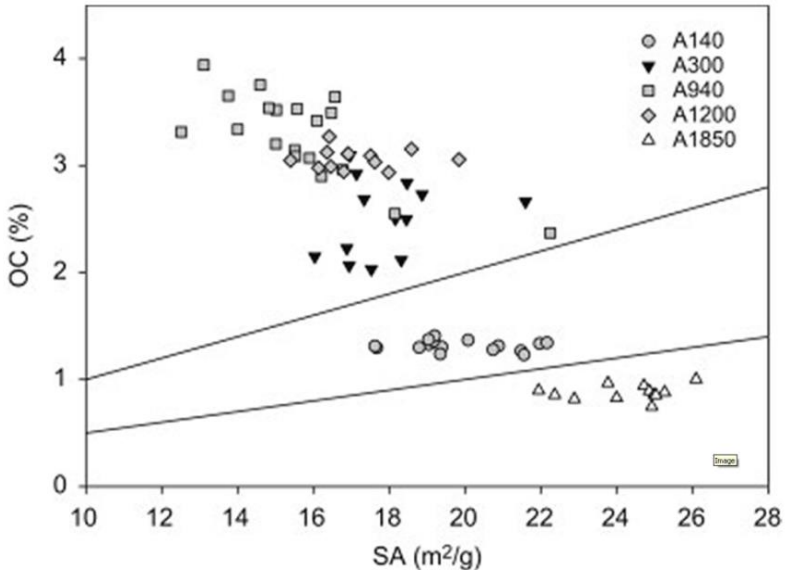


Figure 9. Sedimentary organic carbon content vs. mineral surface area across the Pakistan margin of the Arabian Sea: upper OMZ (140 m); OMZ core (300 m); lower OMZ (900, 1200 m); and below OMZ (1850 m). Lines show the boundaries for "monolayer equivalent" coverage (from Vandewiele et al., 2009).

2.4.1.4. Oxygen Availability

It is generally accepted that the absence**,** or low concentration, of oxygen in bottom waters promotes preferential OM accumulation and preservation in marine sediments, forming OM-rich facies (Canfield, 1989, 1994; Demaison and Moore, 1980; Paropkari et al., 1992; Thiede and Vanandel, 1977). This has been observed across many modern anoxic environments including the Baltic Sea, Black Sea, and Arabian Sea margins (Cowie et al., 1999; Demaison and Moore, 1980; Glenn and Arthur, 1985; Levin et al., 2000). It is reasoned that when less efficient anaerobic decomposition exceeds aerobic decomposition, such as in a euxinic water-column, higher concentrations of OC are preserved in marine sediments (Demaison and Moore, 1980).

Some studies suggest that the overall time of exposure to O_2, rather than bottom-water O_2 concentrations, is the primary control on sedimentary OM preservation (Cowie et al., 1995). Exposure time is largely governed by sediment accumulation rate, water column height, and the oxygen penetration depth into the sediments (Hartnett et al., 1998; Hedges et al., 1999). Experimental field studies by Hulthe et al. (1998), Dauwe et al. (2001) and Moodley et al. (2005) indicate that O_2 availability is important in determining both the

amount and degradation state of natural OM in marine sediments. Re-exposure of turbidites on the Madeira Abyssal Plain to oxygenated water caused an oxidation front to burn down through the sediment, causing a substantial reduction in preserved sediment OC compared to that previously preserved in anoxic conditions (Cowie et al., 1995). Further evidence for the influence of O_2 includes OC maxima found in sediments within, and immediately below, OMZs on various continental margins (Cowie et al., 1999; Demaison and Moore, 1980; Hartnett et al., 1998; Keil and Cowie, 1999; Schulte et al., 2000; Thiede and Vanandel, 1977).

Other studies argue that the presence or absence of O_2 has little influence on the preservation of OC in sediments (Calvert et al., 1992; Henrichs and Reeburgh, 1987; Pedersen and Calvert, 1990; Pedersen et al., 1992). For example, Calvert and Pedersen (1992) cast doubt on the effect of O_2 on OC values, highlighting that that elevated OC concentrations are not always found in euxinic environments (e.g. the Black Sea). Therefore another process, such as sorptive preservation, must be the primary control. On the Arabian Sea margins, OC concentrations found outside of the OMZ in oxidised bioturbated sediments have been at least as high as OC concentrations in laminated reduced sediments within the OMZ (Cowie et al., 1999; Levin et al., 2000). Furthermore, Sun (2000) conducted a lab study comparing OM degradation rates under different oxygen concentrations and found that decay rates were greater in the presence of oxygen than in its absence.

2.4.1.5. Summary

It should be noted that the relative importance of OM preservation controls greatly across and between different continental margins. Cowie and Hedges (1992) show this in their comparison of coastal margins with comparable OM sources, productivity and sedimentation rates, but with distinctly different bottom-water redox conditions. The study found no measurable differences in the composition or burial efficiency of OM, even with contrasting O_2 availability. Furthermore difficulties arise as many of the preservation controls are interdependent, such as OM supply and O_2 availability, and therefore are difficult to deconvolve. For example, both primary productivity and water depth influence sedimentation rate, which in turn influences the oxygen exposure time of the organic matter, but OM degradation is also a result of sinking time — i.e. water column depth. A synopsis by Canfield (1994) made three main observations:

- the most important control on OM preservation is the rate of sediment deposition, with less time for decomposition resulting in higher preservation at greater deposition rates (Henrichs and Reeburgh, 1987; Stein, 1986)
- at sediment deposition rates greater than 0.04 cm yr^{-1} (assuming a porosity of 0.6), O_2 concentrations have little or no influence
- at sedimentation rates below 0.04 cm yr^{-1} enhanced preservation is found in sediments deposited in O_2 depleted or euxinic environments.

Later work by Hartnett et al. (1998) showed that carbon burial efficiency was strongly correlated with oxygen but that this relationship broke down at low oxygen exposure times. It was hypothesised that the variation in OM distribution in these conditions was due to faunal activity (Figure 10). Clearly, there is much still to be understood about the controls on sedimentary OM distribution, between and across continental margins. It can be said though, that OM preservation is ultimately the result of numerous processes acting simultaneously, where some are independent of and others are directly related to O_2 availability. This work aims to deconvolve the interaction between both the non-biological factors (e.g. oxygen, sportive preservation) and the influence of benthic fauna as discussed below.

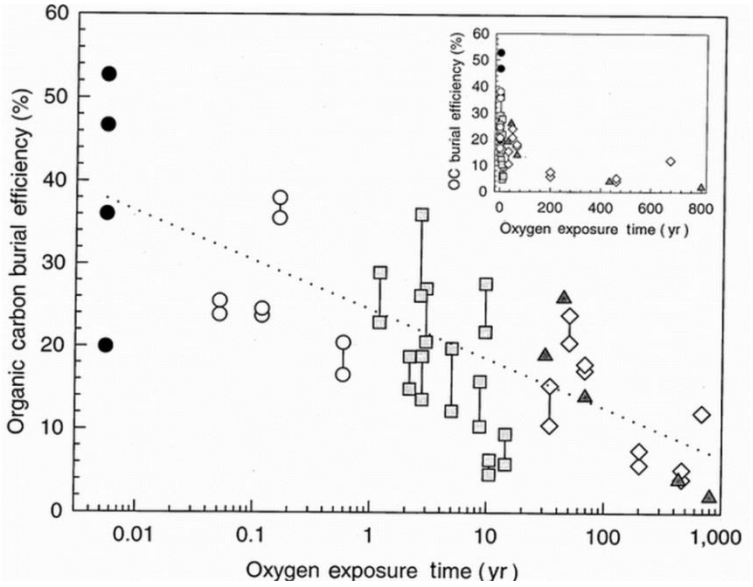


Figure 10. The relationship between OC burial efficiency and O2 exposure time. Data is from: Mexican shelf, 100–150 m (○); Mexican OMZ, 150–1000 m (●); Washington shelf and upper slope, 100–600 m (□), Washington lower slope, 600–2500 m (◇); California margin, 1500–3500 m (s) (from Hartnett et al., 1998).

2.4.2. Biological Factors

Fauna are known to influence sedimentary OM distribution and preservation via a number of processes including burrowing, bioturbation, digestion, and microbial stimulation (Aller, 1982). These named examples are discussed below in more detail.

2.4.2.1. Faunal Burrowing And Bioturbation

Organic matter transportation by fauna may occur vertically into or out of the sediment as a result of ingestion and subsequent egestion, or horizontally due to ploughing across the sediment surface. With regards to vertical movement, it may result in the downward transport of fresh reactive OM to oxygen-depleted sediments, which in turn serves to slow decay and thus enhance preservation (Sun et al., 1999; Thomas and Blair, 2002). However, the opposite may occur, where previously buried OM is brought back to the surface, further exposed to oxygen and more susceptible to decay. In addition, the extent and type of bioturbation is dependent on faunal type, and thus is a consequence of varying burrowing depths, rates, shapes, sizes and directions (Demaster et al., 1994). Some burrowing fauna have been observed to flush bottom water through their burrows which results in re-oxygenated sediments. This re-exposes previously buried OM to oxygen which has been shown to increase OM decay rates (Aller, 1994; Sun et al., 2002). It is hard to isolate the mode of faunal bioturbation and its effects of OM preservation due to the range of burrowing modes. Thus, there is still uncertainty about whether bioturbating fauna enhance or limit OM preservation.

2.4.2.2. Digestion

The alteration of OM during digestion is an important process that influences both the availability and quality of OM. For example, OM can be altered by physical breakdown in the gut passage and thus makes it more readily available to secondary feeding by fauna or enzymatic breakdown by bacteria (Aller, 1982). In addition, digestion is a selective process which varies both between fauna and organic matter compounds. For example, some fauna appear to preferentially assimilate nitrogenous compounds from available OM (Cowie and Hedges, 1996), while others exhibited preferential uptake of certain carbohydrates, amino acids (Thomas and Blair, 2002; Cowie and Hedges, 1996) or lipids (Sun et al., 1999).

2.4.2.3. Microbial Stimulation

In addition to typically dominating benthic biomasses, microbial organisms are also usually responsible for most faunal OM processing (Moodley et al., 2002; Moodley et al., 2005). Their role may be enhanced by the activities of larger benthic fauna, such as sediment reworking and bioturbation (Kristensen, 2001). Faunal activity can oxidise sediments and increase the surface area of OM particles which further exposes OM to microbial decay (Aller, 1982; Sun et al., 2002; Levin et al., 1997). Reworking of sediments by larger benthic fauna redistributes labile OM, making it more readily available to microbial communities (Aller, 1982; Kristensen, 1988).

2.4.3. Factors Influencing Benthic Faunal Processing

2.4.3.1. Oxygen

While oxygen is known to be limiting factor on the distribution of benthic fauna in OMZs, it has also been found to influence the way in which benthic fauna process organic matter. Woulds et al. (2007) found that bottom-water dissolved oxygen concentrations in the Arabian Sea have a strong influence on benthic faunal OM processing. Short term OM processing was observed to be dominated by macrofauna at oxygen concentrations >7 μmol L^{-1} (0.16 ml L^{-1}) but switched to foraminiferal dominance at 5 μmol L^{-1} (0.11 ml L^{-1}). This shift occurred even though macrofauna dominated the biomass, suggesting that oxygen availability exerts a threshold-type control. While foraminiferal OM uptake was reduced at hypoxic sites, bacterial uptake (measured through phospholipid fatty acids) did not significantly change as a result of differing oxygen concentrations. These observations are consistent with the well-acknowledged notion that oxygen availability influences the distribution of benthic fauna in OMZs (Levin et al., 2000) and that larger-sized fauna are less tolerant of low oxygen availability. Thus, an oxygen threshold for OM processing has been suggested to lie between 5 and 7 μmol L^{-1} (Woulds et al., 2007). However, it is important to note that this oxygen threshold hypothesis proposed by Woulds et al. (2007) has been formed from the results of relatively few studies and therefore calls for additional work. Furthermore, oxygen thresholds are likely to vary across environments and differ between individual species (Levin, 2003; Levin et al., 2000). This could potentially be further investigated using ^{13}C tracing experiments conducted with deliberately manipulated oxygen concentrations.

2.4.3.2. OM Quality And Quantity

Experiments conducted by Buhring et al. (2006b) in the Mediterranean Sea traced the artificial addition of ^{13}C-enriched material through the benthic system. The study revealed that carbon assimilation increases with greater OM loadings, indicating that carbon flow pathways can differ in response to varying amounts of OM inputs, and thus comparisons of benthic faunal OM processing between experiments should only be made where a similar quality and quantity of OM are used (Buhring et al., 2006b). Faunal communities in the Arabian Sea have been observed to process greater amounts of OM at sites with larger amounts of naturally abundant higher quality OM than at sites with low quality and quantity OM (Woulds et al., 2007). The authors conducted further experiments pre- and post-monsoon which showed greater uptake rates post-monsoon, suggesting that benthic communities may have shifted into more efficient feeding modes following natural pulses of OM to the seafloor.

2.4.3.3. Temperature

Brown et al. (2004) proposed the Metabolic Theory of Ecology (MTE), built on an equation where the rate of a metabolic process is the function of body mass, temperature and the materials that fuel and maintain the metabolism. Furthermore, most biochemical reactions and metabolic rates are known to increase exponentially with temperature within the temperature range of "normal activity" which varies between and within species (Brown et al., 2004; Gillooly et al., 2001). ^{13}C tracing experiments conducted across a range of benthic environments (from estuarine to deep sea) by Moodley et al. (2005) reveal how both the speed and magnitude of respiration can be temperature dependent, as predicted by the MTE. The authors found that respiration of added organic matter in low bottom water temperatures (4–6 °C) was significantly lower than in warm bottom waters (14–18 °C), in both shallow and a deep-sea environments. Similar conclusions were reached by Woulds et al. (2007) where biological C processing rates decreased in relation to lower bottom-water temperatures (~23 °C to 4 °C) across the eastern Arabian Sea margin.

2.4.3.4. Faunal Size And Abundance

Also described by the MTE is the dependence of metabolic processes on body mass (Brown et al., 2004). However, the relationship is not straightforward: larger organisms have proportionally higher metabolic rates than smaller organisms; but they have relatively slow metabolisms when the body mass to size ratio is concerned (Gillooly et al,

2001). A positive correlation has previously been observed between faunal biomass and carbon uptake, implying that faunal size and abundance, and therefore benthic community structure, influences OM processing patterns (Middelburg et al., 2000; Woulds et al., 2007). ^{13}C labelled algae processing rates have been found in proportion to consumer biomass in estuarine (Middelburg et al., 2000) and deep sea environments (Woulds et al., 2007). However these trends may be due to higher gut capacities, and thus gut carbon content, of larger fauna (Woulds et al., 2007).

2.4.4. Classification Of Carbon Processing Patterns

In a comparison of isotopically labelled pulse-chase experiments conducted across the Pakistan OMZ with the results of previous studies, Woulds et al. (2009) identified three categories of benthic carbon processing patterns, as explained by environmental and biological variations. "Respiration dominated" carbon processing is characterised by respiration accounting for >75 % of biological C-processing, while metazoan macrofaunal, foraminiferal and bacterial uptake contribute <10 %. Typical sites tend to be (but not necessarily) cold, occur on lower slope and at abyssal depths (e.g. NE Atlantic, Porcupine Abyssal Plain), have low carbon inputs and low-biomass metazoan macrofaunal communities (0.06–1.2 g C m^2). This category of biological carbon processing is likely to include vast areas of the seafloor which are relatively deep, have low carbon inputs (Demaison and Moore, 1980) and low faunal biomass (Rowe et al., 1991). Under "active faunal uptake" carbon processing, respiration accounts for <75 % of biological C-processing, while metazoan macrofaunal, foraminiferal and bacterial uptake contribute 10–25 %. It encompasses a wide range of environments including sites from the upper OMZ, estuaries, and deep fjords. They are characterised by higher OM availability and faunal biomasses than the first category. Furthermore, this category may be refined (subject to data availability) as either macrofaunal- or foraminiferal-dominated where the latter is the result of lower O_2 concentrations. In "metazoan macrofaunal uptake dominated" carbon processing, macrofaunal uptake accounts for 42–85 % of biological C-processing as a result of large biomasses of metazoan macrofauna by comparison to the other two categories. Sites typically exhibit high OM inputs and are predicted to include the lower parts of OMZs where edge effects produce spikes in macrofaunal biomass.

Later, Woulds et al. (2016) added a fourth category, "bacterial uptake-dominated" carbon processing to account for studies where bacterial uptake of carbon exceeded that of usually-dominant respiration. In this category, bacterial uptake is the dominant fate of

biologically processed carbon, accounting for between 35 and 70 %. While respiration is no longer the dominant sink, it is still important, and may represent 25–40 % of the carbon budge. Faunal uptake is smaller, responsible for 5–20 % of the total OM processing. As a new category, bacterial uptake dominated sites have not been extensively recorded and have thus far only been observed in sandy sediments.

2.5. Faunal OM Processing: Methodological Approaches

In order to assess benthic faunal feeding and metabolic activities, conventional geochemical sampling methods, such as sediment and water sampling, have proven difficult given the spatial heterogeneity of benthic fauna. Consequently, various alternative techniques have been developed which use tracer materials to follow benthic faunal processes.

Cowie and Woulds (2014) identify key desirable properties of a tracer:

- mimics the natural compound of interest both physically and chemically;
- easily identified and measured;
- easily handled;
- relatively inexpensive;
- robust enough for the both the experiment duration and the subsequent sample storage.

Stable isotopes, radioisotopes, glass or coloured beads, and luminophores are examples of tracers that have been previously used to assess benthic faunal activity. However, the following text will only concern the use of stable isotopes as tracer materials.

2.5.1. Stable Isotopes

Isotopes are chemical elements that have the same atomic number (i.e. identical numbers of protons) but different atomic masses (i.e. different numbers of neutrons), and can be categorised as either radioactive or stable. In the radioactive form, the nuclei are unstable and undergo decay to a more stable form, by alpha, beta or gamma radiation. In contrast, stable isotopes do not undergo radioactive decay and may be the resultant form following decay of a radioactive isotope.

Carbon has two stable isotopes, ^{12}C and ^{13}C, of which the lighter isotope (^{12}C) is more abundant (98.9%). Nitrogen also has two stable isotopes, ^{14}N and ^{15}N, where the lighter

isotope dominates the natural environments (99.6%). In both cases, an isotopic signature can be calculated, which measures the ratio of the heavier isotope to the lighter isotope: i.e. ^{13}C:^{12}C and ^{15}N:^{14}N. This isotopic signature is reported in parts per thousand (per mil, ‰) and is defined against a standard reference material:

$$\delta^{13}\mathrm{C} = \left(\frac{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{sample}}{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{standard}} - 1 \right) \times 1000$$

$$\delta^{15}\mathrm{N} = \left(\frac{\left(\frac{^{15}\mathrm{N}}{^{14}\mathrm{N}}\right)_{sample}}{\left(\frac{^{15}\mathrm{N}}{^{14}\mathrm{N}}\right)_{standard}} - 1 \right) \times 1000$$

Where the standard for carbon is Pee Dee Belemnite (PDB; ratio ^{13}C:^{12}C = 0.0112372) and for nitrogen is atmospheric air (ratio ^{15}N:^{14}N = 0.0036765). Due to the difference in atomic masses between stable isotopes, they behave differently in biological and chemical processes. Heavier isotopes tend to reactive more slowly than lighter isotopes, leading to isotopic separation (or fractionation) between the initial and resultant product. As a result, the ratio of heavy to light isotopes changes and enrichment of the heavier isotope can occur. It is this enrichment that can be measured, and used to establish the nature and speed of biological and chemical reactions.

The tracking of stable isotopes is a safe and powerful tool in the study of biological and chemical pathways, as the both collection and analysis is relative simple and straightforward. As a result, stable isotopes can be used to ascertain the transfer and assimilation of elements such as carbon, nitrogen and phosphorous. For example, the natural abundances of ^{13}C and ^{15}N stable isotopes have widely been used to measure both faunal food sources and trophic levels, since the isotopic signature of a heterotroph is due to the isotopic signatures of its food sources and the subsequent fractionation that takes place in metabolic processes (Fry and Sherr, 1984). Therefore, stable isotopes have been shown to be excellent source indicators that can be used to reconstruct food webs, but are in too low natural abundances to trace though the multitude of benthic processes and biogeochemical cycles. Vast improvements in isotope ratio mass spectrometry (IRMS) mean stable isotopes (e.g. ^{13}C and ^{15}N) have become easier to handle and measure. As natural occurrences of ^{13}C and ^{15}N stable isotopes are low (1.1 % and 0.37 %, respectively), artificial enrichments of these isotopes are easy to track through benthic

systems as they are incorporated into naturally occurring compounds or substrates (e.g. bicarbonate, glucose, algal detritus and ammonium; Cowie and Woulds, 2014).

Currently most stable isotope tracer experiments involve the deliberate addition of isotopically-labelled material to incubated samples, which is then traced into various C and N pools — e.g. sediments, fauna, and both the organic and dissolved inorganic dissolved forms. Isotopically-labelled materials are those that have been artificially enriched in a particular isotope (in this case ^{13}C and ^{15}N) and depleted of its other forms. This allows the quantification of a variety of benthic processes, including respiration, assimilation and feeding guilds. We are therefore able to characterise C and N cycling on both long term and short term timescales and thus investigate the relationships between benthic faunal activities and OM cycling.

2.5.2. Microcosm Experiments

Microcosm experiments have been conducted across a range of environments, in order to examine the influence of fauna on organic matter cycling and burial. Some of these have focussed on the effects of benthic fauna on sedimentary cycling of carbon (Armenteros et al., 2010; Forster et al., 1995; Sun et al., 1999; Sun et al., 2002). Sun et al. (2002) used isotopically labelled algal cells in a series of microcosm experiments to investigate the influence of different physical mixing regimes (no mixing, episodically mixed and bioturbated) on the degradation and preservation of organic matter in surficial sediments. Similarly, Thomas and Blair (2002) used ^{13}C-labeled diatoms to study the effect of deposit feeders on organic matter distribution and composition, by tracing the isotopic signatures of amino acids derived from chosen species.

A major drawback of microcosm experiments is that they often only concentrate on a single factor (e.g. oxygen, Forster et al., 1995) or a single species (e.g. macrofauna, Sun et al., 1999; nematodes, Armentero et al., 2010) and therefore are not good representations of the natural environment. Furthermore, microcosm experiments are often conducted on homogenised sediments and with artificially selected organisms. While microcosm experiments allow the control of the factors such as oxygen concentrations, temperature and light, and are therefore replicable, the differences between the artificial system and the natural ecosystem may mean ecological realism is limited. In order to truly study the effects of fauna on sedimentary OM cycling, experiments are needed that consider the effects of the whole benthic community response to natural factors.

2.5.3. Whole-Community Pulse Chase Experiments

The majority of organic matter supply to the sea floor often occurs as seasonal pulses of fresh phytodetritus as a result of phytoplankton blooms. Whole-community pulse-chase experiments are set up to mimic these pulses by the addition of isotopically labelled organic substrate.

2.5.3.1. In-Situ Approaches

Early chemical measurements were conducted on recovered water and sediment samples, subsequently processed on board the ship or in the laboratory. However, during the sampling and analysis processes, sediment and water samples may face a combination of physical, biological and/or chemical changes. The development of in-situ technologies has facilitated in-situ studies of undisturbed environments (Viollier et al., 2003). A major advance was the introduction of benthic landers in the mid-1960s (Viollier et al., 2003), which enable measurements of a variety of fluxes across the sediment-water interface. Benthic chambers fitted with a range of micro-sensors, for example oxygen, H_2S, and pH electrodes, allow benthic biogeochemistry at the sediment-water interface to be profiled and accurately quantified at high resolutions, on scales smaller than a millimetre (Glud et al., 2000). Upon deployment on the sea floor, overlying water within the lander chamber is sampled at pre-determined time intervals. Concentration changes over time in the sampled water are used to calculate fluxes into and/or out of the sediment. Following the termination of the incubation, the lander is retrieved and the recovered sediments are sub-sampled and analysed alongside the water samples. This method has been used in a range of studies including flux analyses of oxygen (Berg et al., 1998), nutrients (Jahnke, 1990; Jahnke et al., 1990), trace metals (Ciceri et al., 1992), and pollutants (Chadwick et al., 1994; Chadwick et al., 1993). The development of autonomous benthic landers in the 1970s (Viollier et al., 2003) has allowed chamber incubations to be conducted in deep sea and abyssal environments. A pioneering study by (Smith, 1978) measured the sediment community oxygen consumption (SCOC) in abyssal waters using an autonomous benthic lander. Better still, the expansion to modular benthic landers (Figure 11), which include several chambers, presents the ability to conduct simultaneous experiments and therefore replicate measurements. A full history of the development and design of benthic landers is detailed by Tengberg et al. (1995).

(A) (B)

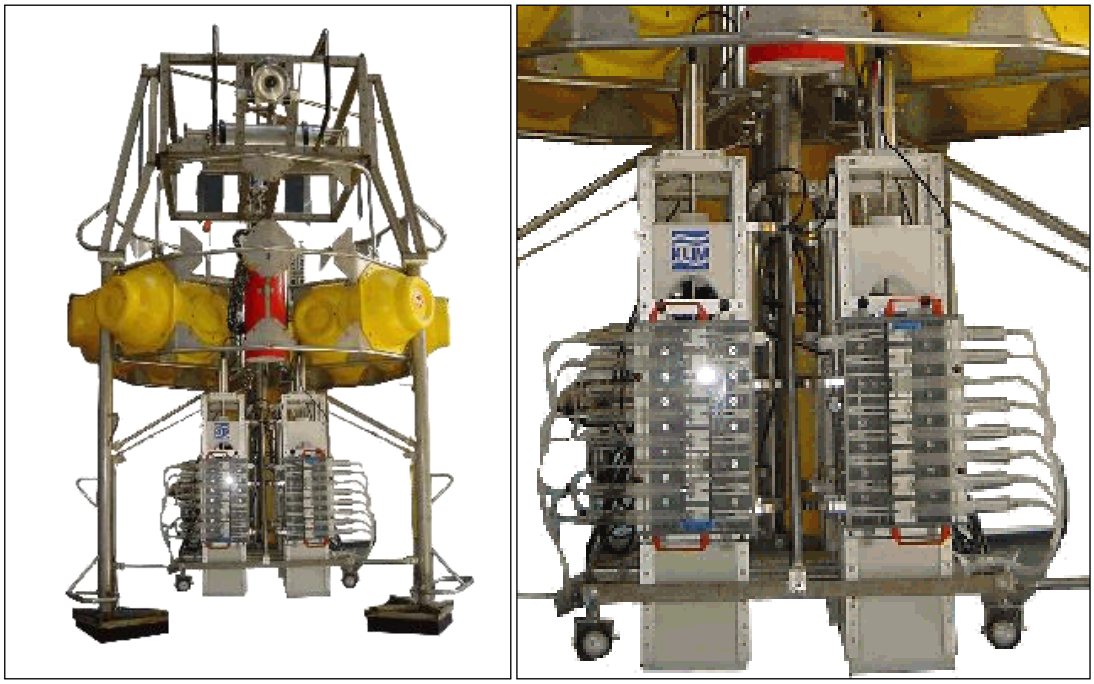


Figure 11. An example of a typical modular benthic lander (A) and a close up of the chambers (B). Photo courtesy of K.U.M. engineering.

Recent studies utilising benthic landers include such pulse-chase experiments, with modified chambers so that particulate tracers can be injected into and traced through the benthic system (e.g. Aberle and Witte, 2003; Moodley et al., 2002; Witte et al., 2003, Woulds et al., 2007; Sweetman and Witte, 2008). The development of stable isotope techniques and addition of ^{13}C and/or ^{15}N labelled organic substrates to benthic chambers has facilitated progress in measuring organic matter pathways in benthic environments across both continental margin and deep sea sediments (e.g. Middelburg et al., 2000; Moodley et al., 2005; Woulds et al., 2007).

When using benthic landers in pulse-chase experiments, several assumptions are often made. A simplification of the system is made by the assumption that steady state conditions prevail during the incubation period. Water column biogeochemistry and hydrodynamic processes are largely ignored if they cannot be measured independently. It is important to consider whether the size of the sample area is representative of the wider environment. It has been shown that in areas of high macrofauna abundance, a combination of a large benthic chamber with replicate deployments is needed in order to attain representative flux measurements (Glud and Blackburn, 2002). Benthic chamber

experiments may also induce hypoxia into the chamber environment due to the closure of the chamber lid for several days. This is a particular issue on OMZ margins and may be overcome by setting a programme that opens the lid at regular intervals. Chambers used in the Arabian Sea in 2003 were fitted with an 'oxystat' system which allowed the oxygen concentration in the chambers to be monitored and maintained throughout the experiment (pers. comm. Dr Clare Woulds).

2.5.3.2. Ex-Situ Approaches

In-situ experiments face both practical and logistical difficulties such as the monitoring and subsequent control of varying environmental properties (e.g. oxygen concentrations), and the accessibility issues of working with deep sea sediments. Further, complex technology is required to work in-situ, which has a relatively high failure rate and if equipment is damaged it is often impossible to fix during the cruise. Thus, in-situ experiments are 'high risk'. In order to overcome some of these challenges, ex-situ methods can be used. Shipboard experiments can be performed, identical or similar to those set up in-situ. Experiments set up aboard research vessels can be conducted on replicate cores, and allow greater experimental control, due to easier access to the experiment. For example, it is possible to deliberately manipulate experimental conditions, such as oxygen concentrations on board the ship which cannot be done in-situ.

Tracer studies conducted ex-situ involve controlled incubation of whole sediment cores, ideally overlain by bottom-water collected from the same sampling site, at ambient seafloor temperatures. Using work by Woulds et al. (2007) as an example, ex-situ isotope tracing experiments can be conducted by adding ^{13}C labelled food (e.g. diatoms, algae) to incubated cores under controlled temperatures and oxygen concentrations in order to assess the influence of oxygen availability on the role of benthic fauna on sedimentary carbon cycling. Cores are then sealed with specially designed core-tops, including a stirrer, and overlying waters are sampled for dissolved inorganic carbon and its $\delta\ ^{13}C$ at regular intervals across both 2 day and 5 day experiments. Following incubation termination, cores are sliced and sampled for pore waters with sediments either immediately sieved or freeze-dried for faunal extraction and further geochemical studies. A useful analysis is the quantification of ^{13}C in bacterial phospholipid fatty acids (PLFAs) in order to assess the uptake and assimilation of the isotopic label by the bacterial fraction of the benthic community (Boschker et al., 1998; Middelburg et al. 2000; Moodley et al. 2000).

2.5.3.3. Comparison Of Approaches

It has been argued that in-situ experiments afford more reliable results than those conducted ex-situ in the assessment of benthic biogeochemistry (Glud et al., 1994). While shipboard experiments provide greater access and control of experimental variables, studies have shown that some benthic micro-organisms are altered by the changes in atmospheric pressure induced by core sampling (Park and Clark, 2002). However, multiple cores taken from the same site may allow the assessment of local variability or patchiness in benthic processes and community levels as observed in many regions. Systematic differences have been reported between in-situ and ex-situ results in deep water environments, but Woulds et al. (2007) found that these potential artefacts in the data are not significant enough to affect analyses of the data and can be compensated by greater replication of experiments.

2.5.3.4. Limitations

While isotope labelling techniques afford the opportunity to study the role of benthic organisms in biogeochemical cycles, it is important to note that there are several problems. Using stable isotopes to isotopically enrich substrates is often expensive and requires careful handling. Furthermore, problems may be encountered in producing isotopically labelled OM that mimics natural compounds, especially in deep-sea settings. For example, the commonly used fresh labelled-algae are compositionally different to the degraded OM usually consumed by benthic fauna (Cowie and Woulds, 2014). When interpreting the results of isotope tracing experiments, it is crucial to assess (and subtract out) the baseline isotopic signatures, which have been shown to significantly vary within sampling areas (Vander Zanden and Rasmussen, 1999). The duration length of incubation experiments should be considered, as the tracer must have time to be consumed, processed and/or assimilated. Too short incubations may result in no label being transferred, and too lengthy experiments may lead to dilution and recycling of added label (Evrard et al., 2010). Fore-knowledge of the carbon and nitrogen cycling in the chosen environment may allow better estimates for determining the duration of tracing experiments. The resolution of time-series sampling should be high enough to allow sufficient tracking of the tracer through the system, as indicated by the results of (Evrard et al., 2008). Furthermore, the quantity of the tracer added has previously been shown to influence the uptake and processing of carbon, as addressed in section 2.4.3.2.

3. MATERIALS AND METHODS

3.1. Introduction to the Study Sites

Experiments were conducted in the Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin), both of which display large natural contrasts in bottom-water oxygen concentrations, sediment geochemistry, OM availability and benthic faunal communities (Figure 5).

3.1.1. The Arabian Sea (Indian Margin)

The oxygen minimum zone of the Arabian Sea (Figure 12) is one of the largest volumes of depleted water in the world (Helly and Levin, 2004), impinging on the western Indian continental margin between 150 and 1500 m water depth. OMZ formation across the Arabian Sea margins results from seasonal, monsoon-driven hypoxia combined with upwelling of nutrient-rich sub-surface waters and freshwater inputs along the eastern coastline. These nutrient-rich waters increase productivity in the euphotic zone and thus increase oxygen consumption while freshwater inputs increase stratification and hence reduce ventilation of bottom waters (Levin et al., 2009b). On the Indian margin, hypoxia on the upper shelf has been observed to have strengthened during last three decades which has been attributed to a large increase in both waterborne and airborne nitrogen inputs (Duce et al., 2008; Naqvi et al., 2009). These increases are primarily due to the extensive use of synthetic fertilisers in South Asia (Naqvi et al., 2006), and subsequent loss to rivers and the sea. Along the Pakistan margin, low-diversity foraminiferal assemblages have been observed within the OMZ but they are mostly present in the upper 1 cm of sediments (Larkin and Gooday, 2009). However, a low diversity, high biomass macrofauna community is present at the lower OMZ boundary, typical of the "edge effects" discussed later (Levin et al., 2009b). Isotope enrichment studies conducted by Woulds et al. (2009; 2007) reveal that carbon-processing pathways shift with changing oxygen concentrations. It was noted that under oxygenated conditions, macrofauna dominate ^{13}C consumption (when bacteria are not included) whereas under low oxygen conditions (<0.1 ml L^{-1}), foraminifera dominate. Similarly on the Indian margin, high abundances of benthic foraminifera have been observed in surface sediments within the OMZ at 150–1500 m (*Bolivina*, *Cassidulina*, *Lernella*, *Uvigerina* and *Eponides)* and 90–1200 m off Goa (Nigam et al., 2007). While many studies have quantified the effect of the OMZ on benthic communities, sulphide-oxidising bacterial mats have not yet been reported.

3.1.2. The Baltic Sea (Gotland Basin)

The Baltic Sea (Figure 13) is a semi-enclosed brackish water body covering an area of 412560 km^2, with a volume of 21631 km^3, an average depth of 52 m and a maximum depth of 459 m. Its hypoxic zone has quadrupled in area since the 1960s and presently reaches up to 41000 km^2 annually (Conley et al., 2002). Most of the deep basins of the Baltic Sea are continuously hypoxic including the Gotland Deep, Baltic Proper, and Gdansk Deep while permanent anoxia can be found in the deepest parts of the Gotland Deep (Conley et al., 2002). It is thought that the hypoxia in the Baltic Sea first appeared approximately 8000 cal. yr BP (Sohlenius et al., 2001), when it shifted from a fresh to brackish water body, recurred through the Holocene (Zillen et al., 2008) and became permanent in about 1900 (Fonselius, 1981). Evidence for past hypoxia comes from a combination of laminated sediments found in cores (Burke and Kemp, 2004) and the accumulation of trace elements (e.g. Mn, Mo, U, V, Cu and Zn) in these laminated sediments (Sternbeck et al., 2000).

Physical isolation from the North Sea, due to sills in the Skagerrak and Kattegat region, mean that displacement and renewal of deep oxygen depleted waters only takes place on average three times annually as a result of large inflows of higher salinity and oxygen-rich water from the North Sea (Stigebrandt and Gustafsson, 2003). The water column is permanently stratified, with two distinct water masses: a surface brackish water layer (salinity, 7–8 PSU) and a deeper saline water layer (salinity, 11–13 PSU) (Zillen et al., 2008). The presence of a strong halocline separates the surface waters from the bottom waters and thus prevents vertical mixing of the water column and ventilation of the oxygen depleted bottom waters (Matthaus and Schinke, 1999; Rabalais et al., 2010). While hypoxia in the Baltic Sea is not a modern phenomenon, eutrophication is believed to be the main cause of decreasing oxygen concentrations in the last 100 years (Conley et al., 2009a; Jonsson et al., 1990). Anthropogenic airborne and waterborne nitrogen, and phosphorus inputs have at more than quadrupled in the last century (Larsson et al., 1985; Wulff et al., 2007). This is mostly due to the fact that the watershed contains a population of over 85 million people and drains an area that is four times larger than the actual sea (Zillen et al., 2008).

Baltic Sea hypoxia is observed to have altered food chain dynamics and caused faunal habitat loss across the whole Baltic Sea, reduced benthic communities below the halocline and led to benthic “ecological deserts” that cover over 30 % of the seafloor annually (Karlson et al., 2002; Laine, 2003; Zillen et al., 2008). The Eastern Gotland Deep displays

marked faunal zones: >50 species occur at oxygenated depths (<30 m); 11–14 species exist in hypoxic waters (50–124 m); no species are found in anoxic waters (124–140 m). In a negative feedback, decreasing oxygen concentrations have been positively correlated with increasing phosphorus release from the sediments which add more nutrients to the already hypoxic waters (Conley et al., 2002). This occurs because phosphate sorbs strongly to iron oxides in oxygenated sediments but is released into the water column under anoxic conditions.

There has been great concern about Baltic Sea hypoxia since the 1980s, and schemes have been implemented in order to reduce nutrient inputs and improve water quality across the region. These include the reduction of point sources (e.g. industrial and municipal wastewaters), and some local improvements in coastal hypoxia have been observed (Rabalais et al., 2010). However, unless there are considerable long-term attempts to reduce nutrient loading to the Baltic Sea, the combination of its volume and the aforementioned positive feedbacks will continue to hinder remediation. In a further attempt to resolve the hypoxia problem, the Swedish Environmental Protection Agency and other national agencies have explored the possibility of oxygenating the bottom waters in order to reduce phosphorous release from the sediments (Conley et al., 2009b; Vahtera et al., 2007). This engineering scheme proposes to pump oxygenated surface waters into the hypoxic bottom waters and manipulate local currents. However, concerns have been raised because, while Baltic Sea biogeochemical cycles are mostly understood, the effects of such a large-scale remediation project need greater understanding. For example, there may be negative impacts on ecosystem dynamics and so these areas require further studies that investigate the relationships between benthic fauna and biogeochemistry,

3.2. Field Sampling And Experimental Methods

3.2.1. Arabian Sea

During September-November 2008, a pair of cruises aboard the R/V Yokosuka and the submersible Shinkai 6500 took place across the OMZ of the Indian margin of the Arabian Sea. Research scientists aboard the R/V Yokosuka included members of the University of Edinburgh (UK), Japan Agency for Marine-Earth Science and Technology (JAMSTEC, Japan), University of Tokyo (Japan), Nippon Marine Enterprises (NME, Japan), National Institute of Oceanography (NIO, India), University of Aberdeen (UK), National Oceanography Centre (Southampton, UK), Scripps Institution of Oceanography (USA) and

the University of Tübingen (Germany). Multiple shipboard and in-situ surveys and experiments were designed to investigate biogeochemical cycling, sedimentary processes and benthic ecology at sites with contrasting redox conditions. 23 sample stations were visited across two different offshore transects, during which some depths were sampled more than once, either as multiple dives at a given site, or at the same depth at each transect. Three sites were studied in detail, at which incubation experiments were conducted. These sites were selected to be within the OMZ (500 m), at the lower OMZ boundary (814 m) and on the continental slope (1156 m).

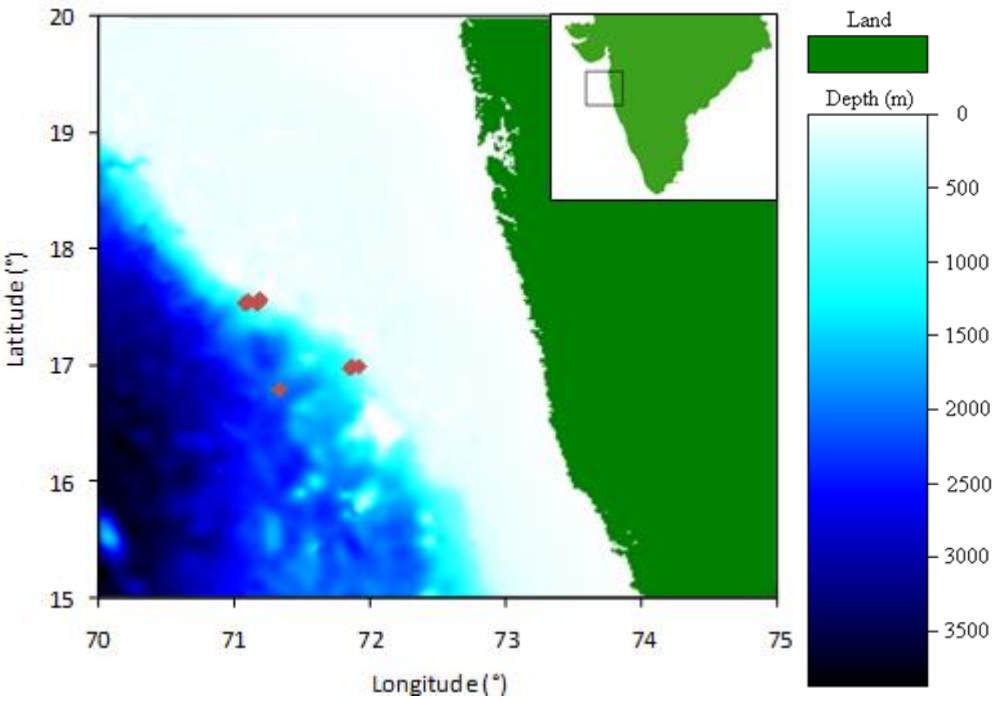


Figure 12. A bathymetric map of the Indian margin of the Arabian Sea showing the location of the sample sites as multiple red diamonds. Some depths were sampled with multiple dives, and/or on both transects.

3.2.2. Gotland Basin, Baltic Sea

In August 2010 a cruise was conducted aboard the R/V Skagerrak across the Gotland Basin of the Baltic Sea. The work was led by Professor Per Hall of Gothenburg University, the Principal Investigator on the cruise, and other participants included researchers from Gothenburg University, the University of Leeds, the National Environmental Research Institute (NERI, Aarhus University, Denmark) and the Norwegian Institute of Research (NIVA). Shipboard and in-situ experiments were designed to investigate biogeochemical cycling, focussing on short-term cycling of organic carbon and pigment distribution, in

Baltic Sea sediments. Sites were selected across the Gotland Basin at depths ranging from 30 to 210 m water depth (Table 2, Figure 13). A range of contrasting redox conditions were chosen, from fully oxygenated to anoxic (with free sulphide present), to test the oxygen threshold hypothesis.

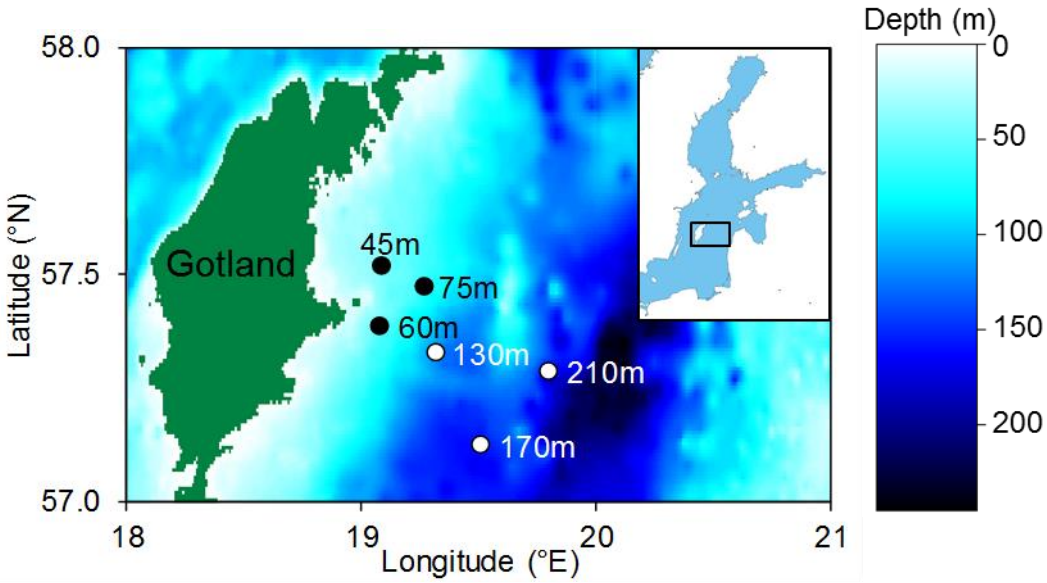


Figure 13.A bathymetric map of the Gotland Basin, showing the location of the six sampling sites: from 45 to 210 m water depth.

3.2.3. Conductivity, Temperature, Depth And Oxygen Measurements

In the Arabian Sea, salinity, temperature, depth, and oxygen measurements were conducted through the water column at each site using sensors mounted on the submersible. In the Baltic Sea, salinity, temperature, depth and oxygen measurements were conducted using a CTD-O fitted with Niskin bottles for sampling bottom waters.

3.2.4. Geochemical Analyses

At each site, replicate cores (8 cm diameter Arabian Sea, 10 cm diameter Baltic Sea) were collected then sectioned. Identical sectioning was conducted on each core at the following intervals: 0–0.5, 0.5–1, 1.0–1.5, 1.5–2.0, 2–3, 3–4, 4–5, 5–6, 6–7, 7–8, 8–9, 9–10, 10–12 cm, then at 2 cm intervals to the core bottom. Pore waters were extracted by centrifugation for the analyses of dissolved carbon, nitrogen and nutrients. Both sediment and pore water samples were frozen at -20 °C to prevent bacterial degradation of compounds.

Table 2. Sampling site details: site conditions and sediment geochemistry. Temperature, salinity and oxygen data are from CTD casts, as described in Chapter 3: Materials and Methods. Sediment geochemistry data are averaged over the surface 2 cm. Arabian Sea data is from Cowie et al. (2016) and White (unpubl. Dissertation). Baltic Sea data collected in this study: sediment geochemistry and texture analysed at Edinburgh University. In all cases, error bars are ± 1 S.D and with n>2.

Site						***Site conditions***			***Sediment geochemistry***						***Sediment texture***			
Site	**Depth**	**Latitude**		**Longitude**		**Temp**	**Salinity**	**O_2**	**$\delta^{13}C$**	**$\delta^{15}N$**	**OC**	**TN**	**C:N**	**OM quality**	**Clay**	**Silt**	**Sand**	**Porosity**
	m	*deg*	*min*	*deg*	*min*	*°C*	*PSU*	*µM*	*‰*	*‰*	*%*	*%*		*DI*	*%*	*%*	*%*	
Arabian Sea	500	17	33.4962	71	11.3439	12.30	35.21	0.5	-20.95	-	6.9	0.8	10.2	0.28	18.5	71.1	10.4	-
	814	17	31.5137	71	10.3246	9.82	35.08	1.8	-20.22	-	4.7	0.5	10.0	0.05	16.8	55.8	27.4	-
	1156	17	31.5236	71	4.9317	7.12	34.83	22.4	-20.32	-	4.6	0.6	9.6	0.02	28.6	60.5	10.9	-
Baltic Sea	45	57	31.059	19	5.428	2.8	7.8	260	-22.24 ± 0.30	2.99 ± 0.48	0.5 ± 0.1	0.06 ± 0.01	8.67 ± 1.12	0.22 ± 0.09	9.6	70.5	19.9	0.24 ± 0.01
	60	57	23.120	19	4.940	4.2	8.7	100	-	-	-	-	-	-	-	-	-	-
	75	57	28.330	19	16.240	5.5	9.9	12	-23.78 ± 0.16	2.62 ± 0.25	7.0 ± 1.4	0.83 ± 0.19	10.02 ± 0.63	0.65 ± 0.19	15.9	76.3	7.8	0.82 ± 0.02
	130	57	19.649	19	19.294	6.9	12.1	0	-24.29 ± 0.16	2.52 ± 0.06	11.8 ± 2.8	1.42 ± 0.32	9.64 ± 0.21	0.86 ± 0.10	16.2	77.5	6.3	0.85 ± 0.02
	170	57	7.432	19	30.596	6.6	12.3	0	-24.38 ± 0.94	3.16 ± 0.77	13.6 ± 1.4	1.51 ± 0.25	10.61 ± 0.56	0.83 ± 0.19	15.8	75	9.2	0.87 ± 0.01
	210	57	17.230	19	48.018	6.4	12.5	0	-24.14 ± 0.22	2.67 ± 0.22	15.2 ± 1.9	1.85 ± 0.24	9.56 ± 0.08	0.94 ± 0.03	4.66	26.4	68.9	0.88 ± 0.01

3.2.5. Pigment Decay Experiments

In order to assess the current degradation state of pigments and potential for further decay, decay experiments were conducted both downcore and at multiple sites. Multiple subsamples were taken from three sites spanning the depth of the Gotland Basin, chosen to represent oxygenated to anoxic bottom waters and faunal to faunal-devoid sediments (60, 130 and 210 m). These included the fluff layer (supra-surface detrital material), 0–1 cm, 1–2 cm, 2–3 cm and 7–8 cm intervals, where available. Sub-samples transferred to centrifuge tubes and fully submerged in collected seafloor sediment at 5 °C, sealed but at atmospheric oxygen concentrations. Replicates were selected for extraction at regular intervals of 1–2 days to build a time-series of 6–10 days. 1 ml of sediment sample was extracted with 10 ml of ethanol, shaken and stored at -20 °C.

3.2.6. Isotope Labelling Experiments

Whole-Community Pulse-Chase Experiments

Whole-community pulse-chase experiments were set up to mimic these seasonal pulses of OM by adding isotopically labelled organic substrate to intact sediments with complete benthic faunal communities, both in-situ and ex-situ. In all experiments a ^{13}C-labelled substrate was added in the form of either algae (^{13}C-enriched diatoms) or lysine sorbed to clay particles.

3.2.6.1. In-Situ Incubations

In-situ processes were studied using the Gothenburg autonomous benthic lander (Figure 14) deployed for 2–2.5 days at two sites, 60 m and 210 m depth. At the shallow site (60 m), bottom waters were oxygenated and metazoan fauna were present. At the deep site (210 m), bottom waters were fully anoxic (free sulphide present) and only bacteria were present. The benthic lander consisted of an external frame carrying buoyancy aids, ballast weights and water samplers, and an internal frame carrying four incubation chambers with electronic stirring, sampling and data-logging. Each chamber was fitted with an electronic paddle stirrer, 10 syringes for sampling or injecting solutes (Figure 15) and microelectrodes to measure dissolved oxygen, CO_2,

temperature and salinity both externally and internally. After deployment, the lander acted as a closed incubation chamber containing intact sediments with a complete benthic community and ambient overlying waters. An injection of pure freshwater (MilliQ) followed by a measurement of the corresponding change in salinity was used to calculate chamber water volumes and assess whether chambers were leaking. Upon experiment initiation a ^{13}C enriched substrate (algae) slurry (approx. 650 mg C m^{-2} of chlorella algae) was injected into the overlying waters of two out of the four chambers, and allowed to settle. Throughout the duration of the experiment, bottom water within the chamber was continuously stirred and internal and external dissolved oxygen concentrations were measured. Overlying waters were sampled into the unused syringes at pre-programmed 9 time points during the experiment to monitor fluxes of dissolved inorganic and organic ^{13}C. Upon experiment completion a shutter attached to the lander was used to recover sediments to be sectioned for sediment geochemistry, pore water and faunal analyses. Faunal sediments were taken in order to measure: isotopes in the faunal individuals and bacterial phospholipid fatty acids; carbon isotopes of dissolved inorganic and dissolved organic carbon.

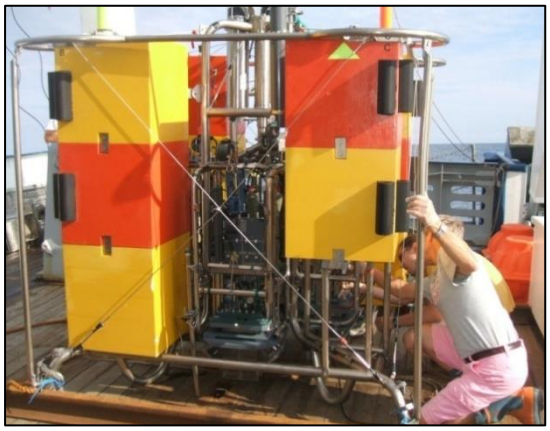


Figure 14. The fully autonomous Gothenburg benthic lander used in the Baltic Sea cruise aboard R/V Skagerrak in 2010.

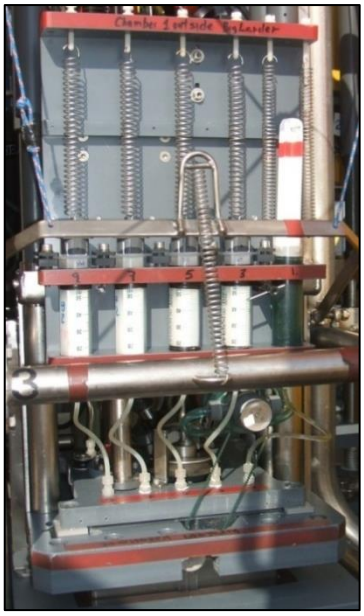


Figure 15. The syringe set up in one of four chambers in the Gothenburg benthic lander used in the Baltic Sea cruise aboard R/V Skagerrak in 2010.

3.2.6.2. Shipboard Incubations

Shipboard experiments were performed on whole sediment cores retrieved by either a submersible (Arabian Sea) or a megacorer (Baltic Sea). Ex-situ experiments afforded the ability to manipulate both the oxygen conditions and the substrate type added to incubated sediments. Experiments were initiated by the addition of ^{13}C and ^{15}N enriched substrate (650 mg C m^{-2} of labelled chlorella) slurries to cores, which was then allowed to settle. Cores were incubated at ambient seafloor temperatures in the dark, submerged in tanks of filtered seawater (Figure 16). Overlying waters in the cores were ambient bottom waters collected by the submersible, while the tanks were filled with filtered surface waters as there was no mechanism for collecting large volumes of bottom water. These small changes from the ambient O_2 conditions were chosen in order to test the hypothesis that oxygen exerts a threshold type effect on benthic faunal processing of OM, and that small changes in O_2 may have large impacts on these OM processing patterns. Following incubation termination after five days, cores were sectioned at intervals of 0–1, 1–2, 2–3, 3–5, 5–7 and 7–10 cm. Core slices were halved and either centrifuged for porewater extraction followed by freeze-drying

for further geochemical studies, or preserved in diluted formalin for later faunal extraction.

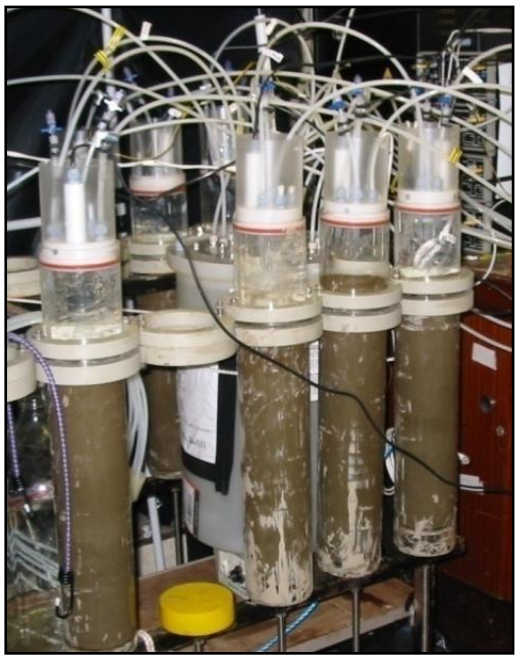


Figure 16. A typical incubation set up during the shipboard experiments conducted during the Arabian Sea cruise.

3.3. Laboratory Analytical Methods

3.3.1. Elemental And Stable Isotopic Analyses

3.3.1.1. Sediments

Elemental and stable isotopic analyses were conducted on homogenised freeze-dried sediments. 10–30 mg of sediment was weighed into silver capsules and carbonates were removed by HCl vapour-phase acidification (Hedges and Stern, 1984). Sediments were further acidified with HCl at ~60˚C, dried overnight and folded into pellets before analysis by an elemental analyser fitted with a mass spectrometer. Acidified blanks did not yield measurable C, so it is assumed that there is negligible contribution by HCl. Results are reported in the standard δ notation, relative to Pee Dee Belemnite (Degens, 1969).

3.3.1.2. Fauna

Sediments from the ^{13}C tracer incubation experiments were washed and sieved at 300 µm before microscopic inspection. Remaining sample material within the 150 to 300 µm fraction were retained and frozen as archive samples. At each depth interval (0–1, 1–2 and 2–3 cm) fauna, in the >300 µm fraction, were picked, photographed and placed in silver capsules in groups based on identification. Faunal samples were acidified with 90 % HCl and analysed for their ^{13}C content by mass spectrometry.

3.3.2. Faunal Uptake Of Isotopic Label

The amount of ^{13}C incorporated by fauna (I_{FAUNA}) in the experiments was calculated as the product of excess ^{13}C *(E)* and faunal carbon biomass (C_{FAUNA}):

$$I_{FAUNA} = E_{13C} \times C_{FAUNA}$$

Excess ^{13}C (E_{13C}) is defined as the difference between the ^{13}C signature *(F)* of the control and the sample:

$$E_{13C} = F_{SAMPLE} - F_{CONTROL}$$

$$F = \frac{^{13}C}{^{13}C + ^{12}C} = \frac{R}{R + 1}$$

$$R = \frac{^{13}C}{1000 + 1} \times R_{VPDB}$$

R_{VPDB} is the $^{13}C/^{12}C$ ratio of the reference material (Vienna PDB; 0.0112372). The amount of ^{15}N incorporated by fauna in the experiments was calculated in the same manner, but. R_{AIR} is the $^{15}N/^{14}N$ ratio of the reference material (atmospheric air; 0.0036765). Due to limited sampling time and financial constraints, natural faunal isotopic signatures were not available in this study and so $F_{CONTROL}$ was calculated using the literature of previously published studies (Table 3). Studies from nearby or similar margins, with similar fauna, were chosen. Small uncertainties in the background signatures will not have affected data processing to a measurable extent, due to the high levels or isotopic enrichment.

Table 3. Average natural faunal isotopic signatures as reported in previous literature from similar environments (i.e. OM rich, O_2 poor).

Group	Taxon	$\delta^{13}C$	$\delta^{15}N$	$C:N_{(SOMATIC)}$	Location	Reference
Foraminifera	*(all)*	-23.0	11.7		Arabian Sea (Pakistan margin)	*(Jeffreys et al., 2015)*
		-19.2	-	5.3	Sagami Bay, Japan	*(Nomaki et al., 2008)*
		-21.9	7.6		Porcupine Abyssal Plain	*(Iken et al., 2001)*
	Pelosina sp.	-21.0	9.2		Arabian Sea (Pakistan margin)	*(Jeffreys et al., 2015)*
	Globobulimina sp.	-22.0	11.4		Arabian Sea (Pakistan margin)	*(Jeffreys et al., 2015)*
		-20.0	7.4		Sagami Bay, Japan	*(Nomaki et al., 2008)*
	Chilostomella sp.	-21.2	11.2		Arabian Sea (Pakistan margin)	*(Jeffreys et al., 2015)*
		-18.8	7.3	3.7	Sagami Bay, Japan	*(Nomaki et al., 2008)*
	Uvigerina sp.	-19.3	8.4		Sagami Bay, Japan	*(Nomaki et al., 2008)*
	Bolivina sp.	-19.5	10.1		Sagami Bay, Japan	*(Nomaki et al., 2008)*
	Nonionella sp.	-22.0	3.6		Arabian Sea(Indian margin)	(Levin et al., 2013)
	Komoki sp.	-21.1	2.7		Arabian Sea (Pakistan margin)	*(Jeffreys et al., 2015)*
Polychaetes	*(all)*		1.6	5.1	Sagami Bay, Japan	*(Nomaki et al., 2008)*
	Linopherus sp.	-13.8	12.1		Arabian Sea(Pakistan margin)	*(Jeffreys et al., 2015)*
	Spionidae	-17.0	10.0	26.0	Arabian Sea(Indian margin)	*(Hunter et al., 2012)*
		-24.3	9.0		Arabian Sea(Indian margin)	*(Levin et al., 2013)*
Macrofauna	*(all)*	-19.0	10.0		Norwegian fjord	*(Sweetman and Witte, 2008)*

3.3.3. Water

3.3.3.1. Dissolved Inorganic Carbon

10 ml samples were collected in acidified pre-evacuated 12 ml Labco exetainers containing 150 µl de-gassed H_3PO_4 (to inhibit further biological activity). Samples were stored upside down at 4 °C until analysis, so that the 2 ml headspace was not in contact with the septa and thus retaining sample integrity. Total DIC and DI^{13}C concentrations were determined from the CO_2 and $\delta^{13}CO_2$ measured in the headspace of the vials, by use of a gas chromatograph, and an isotope ratio mass spectrometer (IRMS), respectively.

3.3.4. Bacterial Phospholipid Fatty Acids

^{13}C tracer experiment sediments were also analysed for bacterial phospholipid fatty acids (PLFAs) by gas chromatography-combustion-isotope ratio mass spectrometry (GC-c-IRMS) (Boschker and Middelburg, 2002).

3.3.4.1. Extraction

PLFAs were extracted from sediments by an adaptation of the Bligh and Dyer method (Bligh and Dyer, 1959; White et al., 1979).

Phosphate buffer water was prepared by addition of $KH_2PO_4$to bi-distilled water to create a 7.2 pH 0.05M solution, before extraction with DCM (dichloromethane). A single-phase Bligh-Dyer solvent was made up of chloroform, methanol, and phosphate buffer (1:2:0.8, v/v/v).

Subsamples (1–2 g) of freeze-dried sediment were sonicated (15 minutes) with 3 ml Bligh-Dyer solvent and centrifuged (~3000 rpm, 5 minutes) before the resulting supernatant was transferred. This step was conducted 3 times to collect all supernatant. The organic and aqueous phases were separated by addition of chloroform:phosphate buffer, (1:1 v/v) to the removed supernatant before centrifuging (~3000rpm, 5 minutes) and removal of the organic layer (bottom layer). The remaining aqueous layer was washed 3 times with chloroform and the organic layers were removed and combined. The organic extracts dried under N_2 and weighed to determine total lipid extract (TLE) before storage at -20 °C.

3.3.4.2. Fractionation

Lipids were fractionated using a solid phase extraction method. Silica gel (particle size, 60Å) was activated by baking at 450 °C for at least 4 hours and then stored at 125 °C before use. Silica columns were made by weighing heat-activated silica gel into glass pipettes plugged with DCM-extracted glass wool.

Before lipid fractionation, silica columns were conditioned with chloroform which was discarded. Dried TLEs were reconstituted in chloroform and brought to room temperature before loading onto prepared silica columns. The sample vial was rinsed twice with chloroform and added to the silica column to ensure all lipids were removed from the vial.

First the neutral lipids were eluted with chloroform:acetic acid (100:1 v/v), collected separately and dried down under N_2. Second, glycolipids were eluted with acetone, again collected and dried down under N_2. Both neutral and glycolipids were stored at -20 °C, for potential future research. Polar lipids (containing the phospholipids) were eluted in methanol, collected in glass centrifuge tubes, and dried down under N_2.

3.3.4.3. Alkaline Methanolysis

The phospholipid-containing polar lipid fraction underwent mild alkaline methanolysis, transesterifying the fatty acids into methyl esters (FAMEs). An internal standard (10 µl methyl nonadecanoate, C19:0 fatty acid methyl esters)was added to the N_2-dried polar lipid fraction, before addition of 5 % hydrochloric acid in methanol. The mixture was tightly sealed and heated at 100 °C for 3 hours. Double-distilled DCM-extracted water and chloroform were added to the cooled acidified fraction to separate the aqueous and organic phases, before the organic layer (bottom layer) was removed. The remaining aqueous layer was washed two more times with chloroform and the organic layers were removed and combined. The organic extracts dried under N_2.

3.3.5. Pigments

3.3.5.1. Extraction

Sediments were analysed from all intervals sampled in each core. Using a syringe, 1 ml of homogenised wet sediment was transferred into 20 ml glass vials containing 10 ml of 100 % ethanol and shaken vigorously (resultant extraction: approx. 90 % ethanol in water). Samples were stored on board the ship at -20 °C and then at -80 °C upon transfer

to the laboratory. Immediately before HPLC analysis in the laboratory, 1.5-ml subsamples of ethanol extract were decanted then centrifuged (2500 rpm for 5 minutes) to remove sediment particles. During extraction, samples were protected from light and stored at <4 °C to prevent pigment alteration where possible.

3.3.5.2. Method Comparison

Aboard ship, ethanol was the only solvent available for pigment extraction. However, it has been shown that different extraction and analytical methodologies can yield varying results (e.g. Jeffrey et al., 1997; Buffan-Dubau and Carman, 2000). To compare extraction solvents, archived frozen sediments from the 45 m site were also extracted with acetone in the laboratory (Table 4) following common extraction use in the literature (e.g. Bianchi et al., 1997a; Łotocka et al., 2004; Poutanen and Nikkila, 2001).

Using a syringe, 3 ml (i.e. 3 cm^3) of homogenised wet sediment was transferred into centrifuge tubes and freeze-dried at -50 °C for 48 hours in darkness. 9 ml of acetone was added to the lyophilized sediments, mixed with a vortex mixer, and placed in a sonic bath at 3 °C for 20 minutes in the dark. Samples were left overnight in a fridge before 1 ml of MilliQ water was added to each sample to make up an extraction solvent of 90 % acetone. Immediately before HPLC analysis, 1.5 ml subsamples of 90 % acetone extract were decanted and filtered with acetone-cleaned glass fibre filters. During extraction, samples were protected from light and stored at <4 °C to prevent pigment alteration where possible.

Table 4. Differences between the two methods used to extract pigments from sediments at the 45 m site, Baltic Sea.

Step	Method 1	Method 2
Volume	1 ml (wet sediment)	3 ml (wet sediment)
Dehydration	none	freeze-dried
Extraction solvent	100 % ethanol	90 % acetone
Particle removal	centrifuged	filtered

3.3.5.3. Analysis

Analysis by high performance liquid chromatography (HPLC) was conducted using an Agilent 1100 series HPLC system with a photodiode array and a fluorescence detector. The HPLC was fitted with a Nova-Pak C18 4 µm, 3.9 x 150 mm reverse phase column (Part No. WAT086344) and a Nova-Pak C18 5 µm guard column. Separation of pigments was achieved in a gradient mixture of methanol, acetonitrile and water, with the gradients described in Table 5: 0.5M ammonium acetate in 85:15 methanol:Milli-Q, 90:10 acetonitrile:Milli-Q and ethlyacetate (modified from Airs et al., 2001). The flow rate was 0.8 ml min^{-1} and the sample injection volume was 60 µl. Absorption chromatograms were obtained for all samples at three wavelengths on the HPLC diode-array (410nm, 430nm and 450nm) and one from the fluorescence detector (Ex/Em: 440/665nm) (Table 6). The wavelengths used for either quantification or identification for each individual pigment are presented. Pigment identification was confirmed by comparing spectra and retention times with those of standards. The 430 and 450 nm chromatograms were used to quantify the accessory pigments, and the 410 nm absorption chromatograph was used as an additional aid Figure 17 and Figure 18.. The fluorescence detector chromatogram was used to quantify the chlorophylls and pheopigments. Choices for chromatograph use were made according to the extensive literature review presented by Jeffrey (1997). Example chromatographs for a sample (0–1 cm, 45 m site) are shown in Figure 19 and Figure 20. While many compounds were spectrally observed in the samples, only some could be identified with confidence using standards for reference. In total, 15 pigments were selected for quantification in this study. Individual pigment concentrations in samples were quantified using peak area-concentration calibration curves constructed for each standard (e.g. Figure 22). No systematic differences in concentration were found for pigments measured on two diode array detectors, or between the diode array detectors and fluorescence detector. The overall elution order and expected retention times of specific pigments were corrected systematically using a mixed pigment standard (DHI Group, Denmark) which was analysed at regular intervals to track retention shifts and peak quality.

Table 5. Solvent gradients during the HPLC analysis: all gradients are linear. Solvent A: 0.5 m ammonium acetate in 85:15 methanol:Milli-Q. Solvent B: 90:10 acetonitrile:Milli-Q. Solvent C: ethlyacetate.

Time (minutes)	Solvent		
	% A	% B	% C
0	60	40	0
2	0	100	0
7	0	80	20
17	0	50	50
21	0	30	70
28.5	0	30	70
29.5	0	100	0
30	60	40	0
35	60	40	0

Table 6. Identification of pigments from HPLC-produced chromatographs. I: that the signal was used to aid pigment identification. Q: indicates use for absolute quantification. Q : if two concentration values were available, the maximum value was used.*

Pigment	Retention time (min)	Diode array detector (DAD) wavelength			Fluorescence detector (FLD) Ex = 430 nm Em = 655 nm
		410 nm	430 nm	450 nm	
Chlorophyll-c_3	2.868		Q*	I	Q*
Chlorophyllide-a	3.041	Q*			Q*
Chlorophyll-c_2	3.525		Q*	I	Q*
Fucoxanthin	5.573		Q	I	
Pheophorbide-a	7.241	Q*			Q*
Alloxanthin	9.355		Q	I	
Diatoxanthin	10.093		Q	I	
Lutein	10.560		Q	I	
Zeaxanthin	10.858		Q	I	
Canthaxanthin	11.863		Q	I	
Chlorophyll-b	14.354		I		Q
Chlorophyll-a	16.117	Q*	I		Q*
Echinenone	16.718		Q	I	
Pheophytin-a	20.102	Q*			Q*
Beta-carotene	21.416		Q*	Q*	

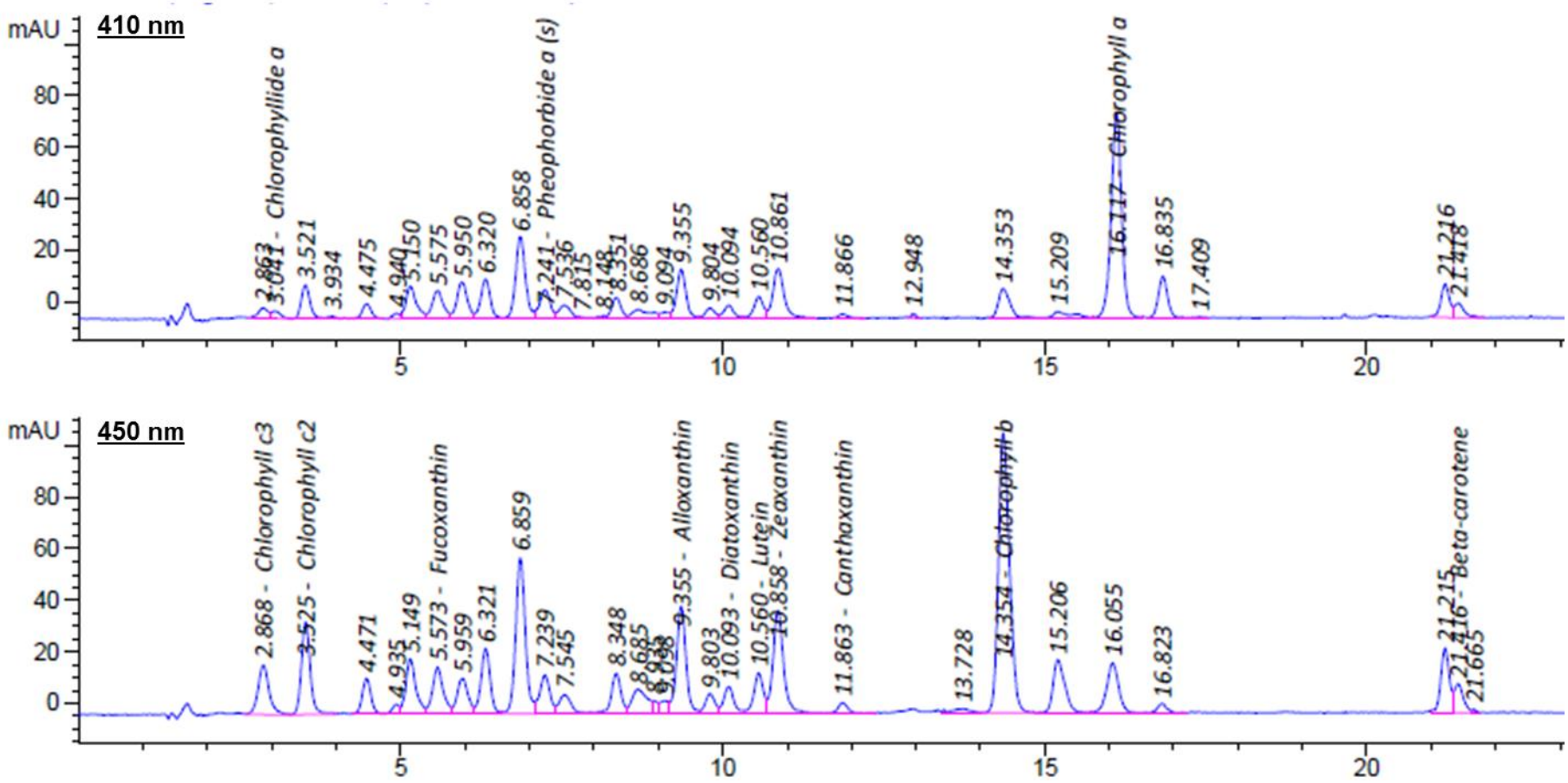


Figure 17. Chromatogram for standard mix (DHI Group, Denmark) - used to establish expected retention times of compounds, pigment elution order and identify co-eluting peaks. Only the pigments with standards are shown. Other peaks are unidentified.

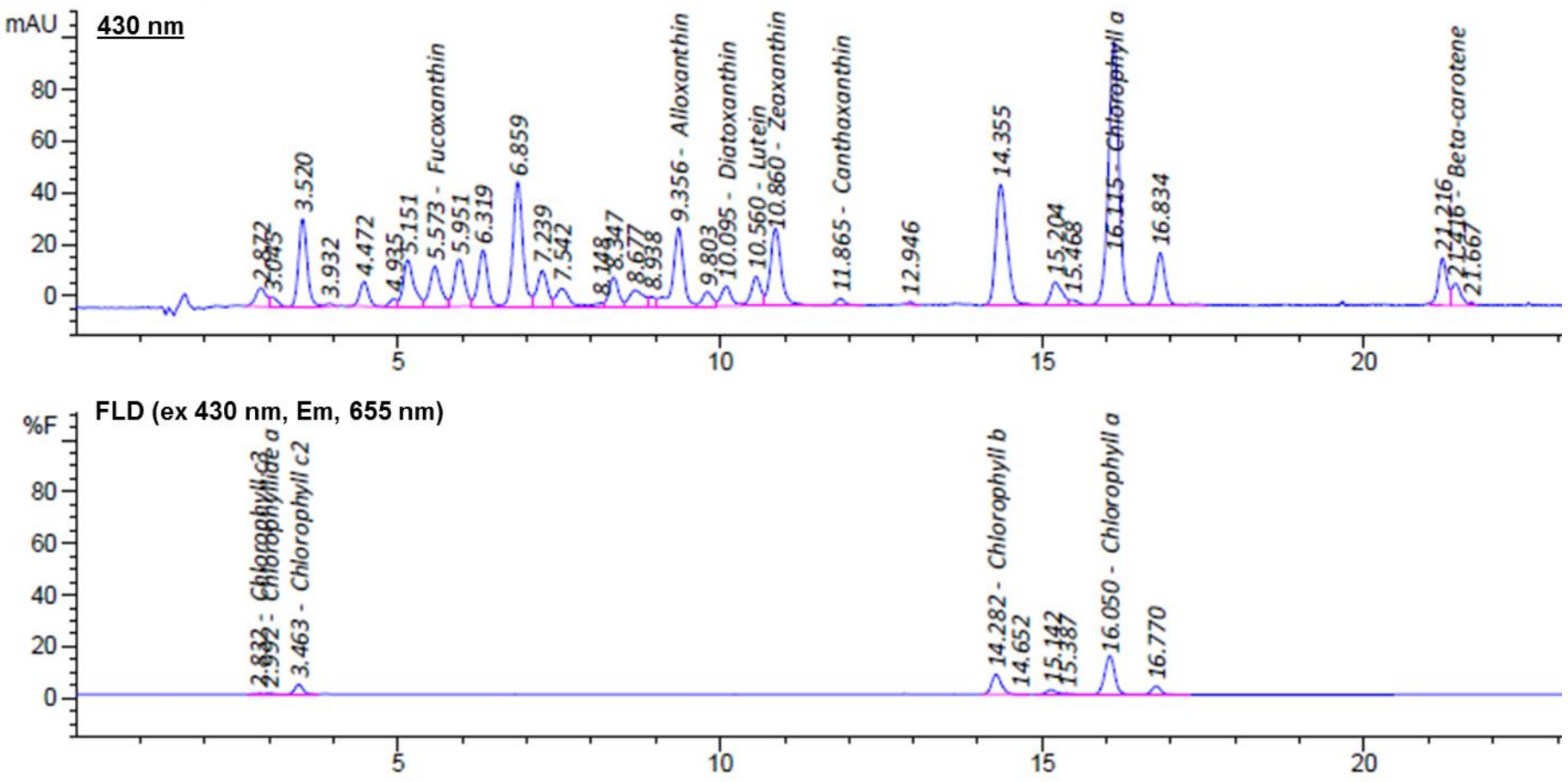


Figure 18. Chromatogram for standard mix (DHI Group, Denmark) - used to establish expected retention times of compounds, pigment elution order and identify co-eluting peaks. Only the pigments with standards are shown. Other peaks are unidentified.

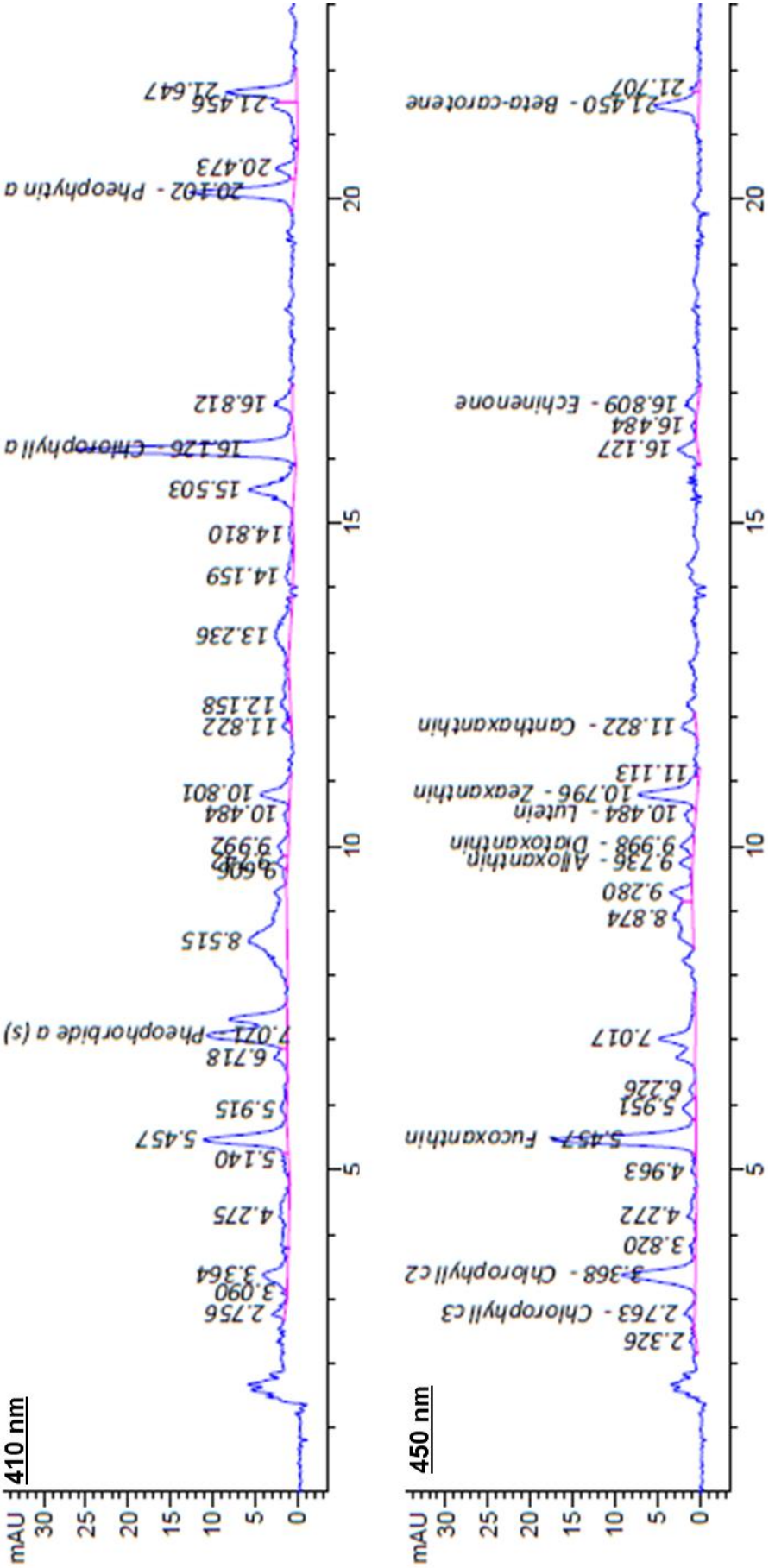


Figure 19. Example chromatographs for a sample (0–1cm, 45 m site). Only the pigments with standards are shown. Other peaks are unidentified.

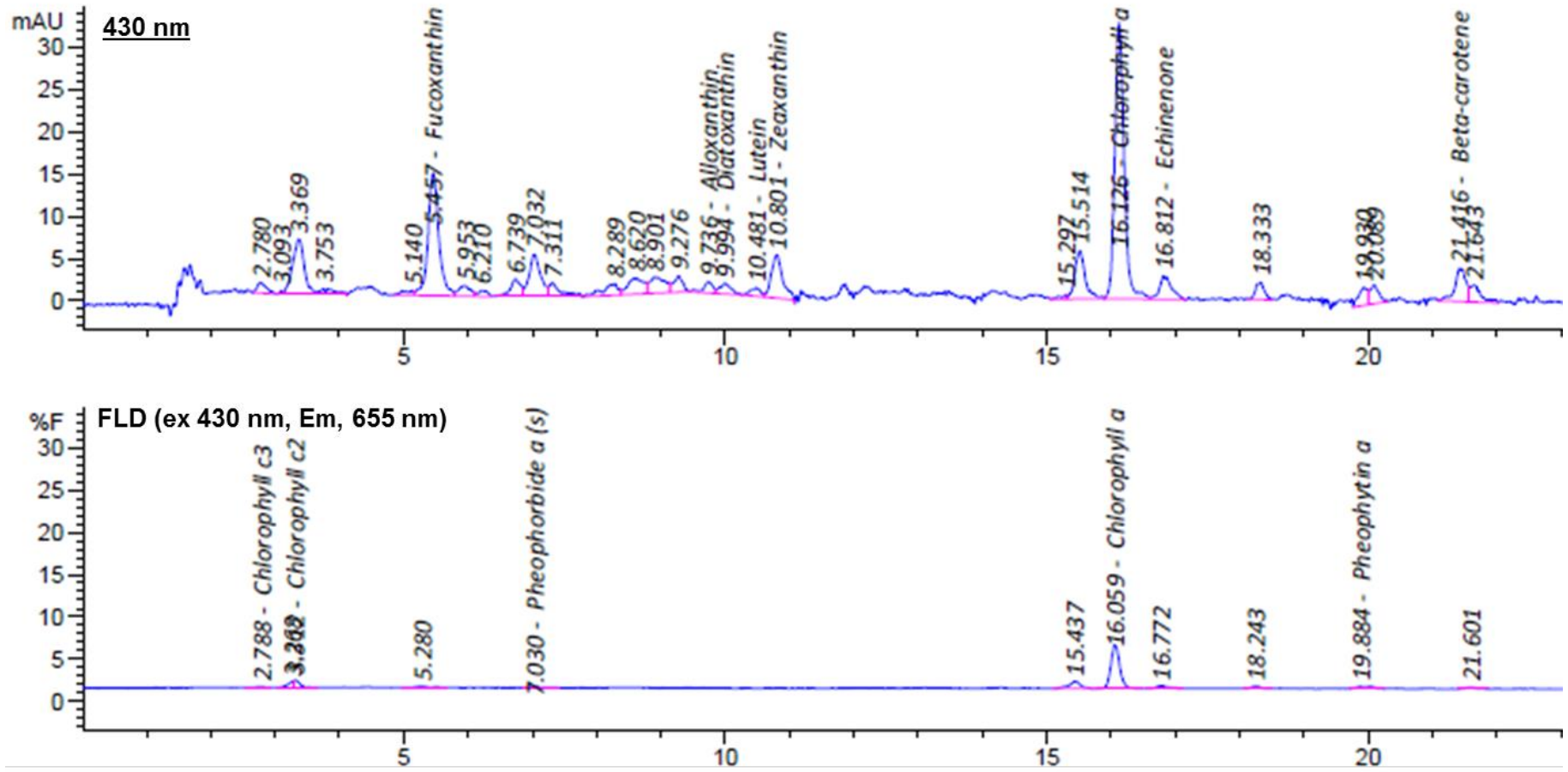


Figure 20. Example chromatographs for a sample (0–1cm, 45 m site). Only the pigments with standards are shown. Other peaks are unidentified.

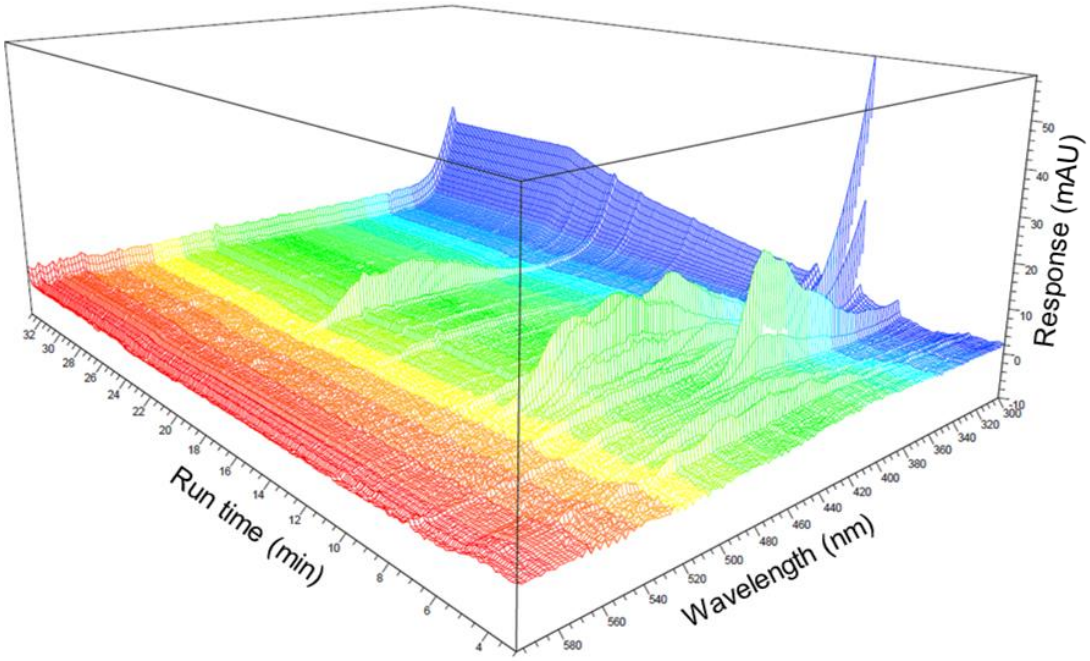


Figure 21. 3D representation of all compounds identified in a sample HPLC analysis. This example: 0–1 cm sediment interval at 210 m water depth, following decay incubation treatment.

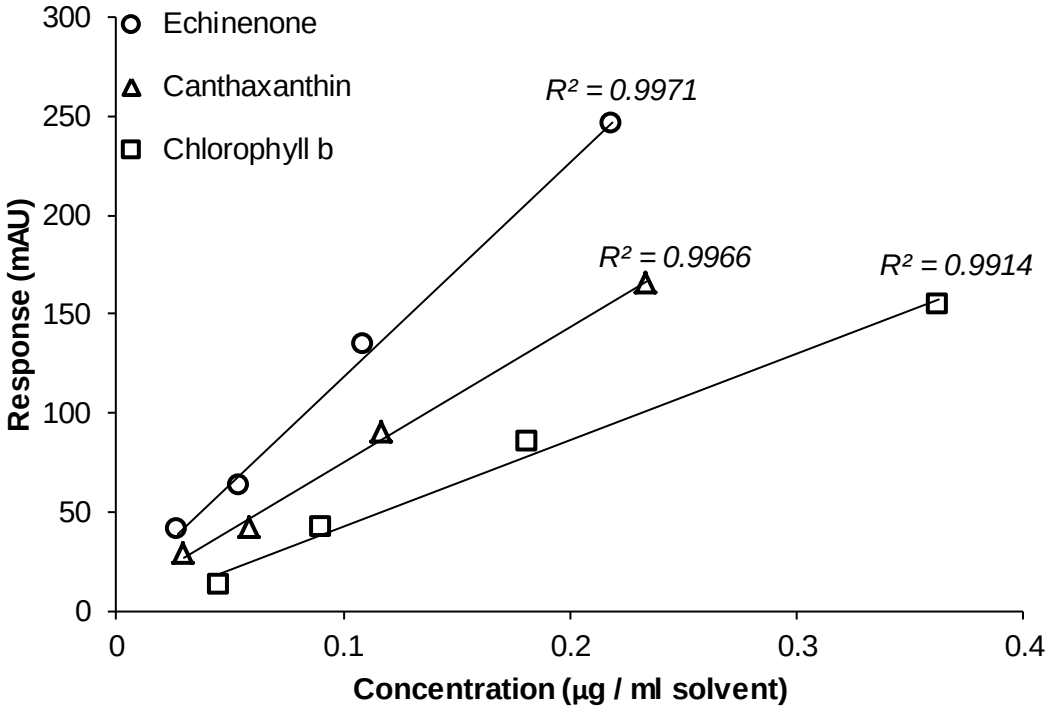


Figure 22. Example calibration graph used to quantify pigment concentrations from chromatographs. This example: calibration of canthaxanthin, chlorophyll-b and echinenone standards at 450 nm.

3.4. Data Processing

3.4.1. Respiration Rates

Respiration of the added ^{13}C-labelled material was calculated from the production of $DI^{13}C$in either the overlying waters during the incubations, or where not available, the porewater of downcore sediments.

3.4.1.1. Overlying Waters

Linear regressions were applied to the time-series of $DI^{13}C$ produced in overlying waters, to obtain average respiration rates. Total respired carbon in each experiment was calculated from the product of average respiration rate and experiment length.

3.4.1.2. Modelling Of Porewater Fluxes

While the fluxes of DIC, DOC and other nutrients are often quantified using benthic flux chambers, as in the Baltic Sea experiments, it is also possible to estimate benthic fluxes from porewater profiles of the selected compound (e.g. Emerson et al., 1984; Jahnke et al., 2005; Lettmann et al., 2012). This approach requires applying models to the gradient of porewater profiles, and can be refined through greater understanding of several sediment characteristics (e.g. porosity, density, bioturbation) and modelling software is available, e.g. PROFILE (Berg et al., 1998). However, in this study not all sediment characteristics are known and so a basic flux model was used with the understanding that the resulting fluxes are estimates.

Assuming steady state, diffusive benthic DIC fluxes, Fick's First Law was applied to estimate the porewater fluxes (Q) from the sediments into the overlying water column (Berner, 1980):

$$Q_{DIC} = -\phi D_{sed} \left[\frac{\Delta C}{\Delta x}\right]$$

Where ϕ is the porosity of the sediments, $D_{sed}$is the sediment diffusion coefficient, and $\left[\frac{\Delta C}{\Delta x}\right]$ is the concentration gradient of the porewater profile in the surface sediments. Ideally $\left[\frac{\Delta C}{\Delta x}\right]$ would take into account the sediment-water interface concentration of DIC but it was not measured, the 0–1 cm interval was used. The whole sediment diffusion coefficientD_{sed} was given by:

$$D_{sed} = \frac{D_{sw}}{\theta^2}$$

whereD_{sw} is the diffusion coefficient of the solute in seawater ,and θ the tortuosity. D_{sw} was corrected for bottom water temperature to produce a D_{sw} of 1 x 10^{-5} cm^2 s^{-1} (Broecker and Peng, 1974; Li and Gregory, 1974). The tortuosity of the sediment was estimated from its porosity (Boudreau, 1997):

$$\theta^2 = 1 - \ln(\phi^2)$$

3.4.2. Degradation Index

Total hydrolysable amino acid distributions were used to calculate a degradation index (DI) as devised by Dauwe et al. (1998) and revised later by Dauwe et al. (1999a):

$$DI = \sum_i \left[\frac{var_i - AVGvar_i}{STDvar_i}\right] \times fac.coef_i$$

where var_i, AVG var_i, STD var_i and face.coef.$_i$ represent the molar percentage, mean, standard deviation and factor score coefficient of a sample amino acid *i*. The DI is based on a principal components analysis (PCA) of the molecular composition of protein amino acids extracted from the sediments. The quantifies the degradation state of a sample, where a value of +1 represents fresh algal material and -2 denotes extensively degraded material (Dauwe and Middelburg, 1998; Dauwe et al., 1999). It is often used in conjunction with other diagenetic indicators to examine differences in OM degradation states (Gelinas et al., 2001; Meckler et al., 2004; Unger et al., 2005). However, the DI should be used cautiously since differences in OM sources and solid-solute partitioning processes can lead to ambiguous interpretations (Dauwe and Middelburg, 1998; Ingalls et al., 2003).

14 protein amino acids were extracted and analysed at the University of Edinburgh in 2009 (Cowie et al., 2014; Cowie et al., 2016.; White et al., unpub. dissertation). Ornithine and the two non-protein amino acids β-alanine and γ-amino butyric acid are not included in the calculation. The data set comprises a range of samples with very different OM sources and degradation states from a range of settings. Averages, standard deviations and factor coefficients of the PCA are detailed in Dauwe et al. (1999a). Vandewiele et al. (2009) revised the DI following problems in separating histidine from glycine peaks. The revised index (DI') was found to be comparable to the original DI, with an R^2= 0.95, where

p<0.001. This study uses the revised factor coefficients from Vandewiele et al. (2009) to determine degradation indices.

3.4.3. Phospholipid Fatty Acids

Once bacteria-specific (PLFAs) were identified by GC-c-IRMS, the concentrations were converted to determined bacterial biomass, total bacterial ^{13}C incorporation and individual PLFA ^{13}C incorporation (Boschker and Middelburg, 2002).

3.4.4. PLFA Nomenclature

There are several different forms of fatty acid terminology in the literature, and for clarification the nomenclature used in this thesis is described as follows. Fatty acids are designated as:

$$C{:}\,D\omega P\ (e.g.\,16{:}\,1\omega 7)$$

Where C denotes the total number of carbon atoms, D represents the number of double bonds present in the fatty acid molecule, and P gives the position of the first double bond, relative to the aliphatic end of the molecule. Prefixes may also be used to show the location of a methyl branch one ("i") or two ("ai") carbons from the aliphatic end. The prefix "br" indicated an unknown branching position, and "cy" refers to a cylopropane-structured fatty acid. Where relevant, the suffixes "c" or "t" indicate the cis- or trans-orientation of double bonds (Zelles, 1999). Saturated fatty acids take the form C:D (D= 0), whereas unsaturated fatty acids will be designated as described above.

3.4.5. Data Treatment

There are several PLFAs that have been identified and routinely used as bacterial biomarkers in the literature. The branched fatty acids i14:0, i15:0 and ai15:0 are exclusively found in bacteria and i16:0 is a common bacterial biomarker (Dijkman et al., 2009; Kaneda, 1991). A fifth biomarker PLFA, 18:1ω7c,is also commonly used (e.g. Middelburg et al., 2000; Moodley et al., 2000) as it has been found in large amounts in purple sulphur bacteria (Grimalt et al., 1992). However, caution is required as it may also represent cyanobacteria and diatoms (Dijkman et al., 2010) .

While the background ^{13}C signatures for individual PLFAs were not available in this study, they are relatively easy to estimate. Bacterial PLFA ^{13}C signatures are depleted by 3–6‰ relative to the substrate due to fractionation effects during fatty acid synthesis (Hayes,

2001). Similar depletion levels have been observed in-situ, e.g. 4–6 ‰ (Boschker et al., 1999), and 1.2‰ in the Scheldt Estuary (Boschker et al., 2005) and others (Cifuentes and Salata, 2001; Abraham et al., 1998; Blair et al., 1985). Additionally, it has been shown that PLFA ^{13}C signatures closely track those of POC in the sediment and a correction factor can be applied to sediment POC signatures.(Boschker et al., 2005) (Table 7).

It is important to note that PLFAS were not used here to elucidate source carbon, and so the effect of isotopic fractionation is of limited concern. However, PLFA isotopic signatures were corrected for the $\delta^{13}C$ values of sedimentary OC, and depleted by further by 5 %, following the correction factor of (Boschker et al., 1999).

Site	Depth *m*	Sedimentary OC $\delta^{13}C$
Arabian Sea	500	-20.91
	814	-20.22
	1156	-20.32
Baltic Sea	60	-23.04
	210	-24.29

Table 7. Sedimentary organic carbon ^{13}C signatures at all sites in both study areas.

In this study, the concentration and ^{13}C-labelling of selected bacteria-specific compounds (i14:0, i15:0, ai15:0, i16:0 and 18:1ω7) were used to quantify both bacterial biomass and bacterial carbon uptake. The carbon biomass of the bacterial community (C_b) is quantified using the summed carbon concentrations of the chosen bacteria-specific PLFAs ($\sum C_{PLFA-b}$: i14:0, i15:0, ai15:0, i16:0, 18:1ω7) and applying the correction detailed by (Middelburg et al., 2000):

$$C_b = \sum C_{PLFA-b} / (A \times B)$$

A is the average PLFA concentration in bacteria: 0.056 g of carbon PLFA per gram of carbon biomass (Brinch-Iversen and King, 1990). B represents the fraction of total bacterial PLFAs represented by the sub-set used here: 0.28 ± 0.04 as used by (Middelburg et al., 2000). Similarly, label incorporation (I_b) into bacterial biomass was calculated from the sum of incorporated label in these bacteria-specific PLFAs ($\sum I_{PLFA-b}$), and corrected for A and B as described above:

$$I_b = \sum I_{PLFA-b} / (A \times B)$$

4. DISTRIBUTION AND DEGRADATION STATE OF SEDIMENTARY PIGMENTS IN THE GOTLAND BASIN, BALTIC SEA

4.1. Introduction

Pigments are a reactive component of natural organic matter found in seafloor sediments worldwide and are produced by marine autotrophs, including phytoplankton and photosynthetic bacteria. In coastal environments, pigments may also derive from terrestrial organic matter. The major phytoplankton pigments participate in the photosynthesis of organic matter by mediating the conversion of solar energy to chemical energy, playing an important role in primary production and carbon and nutrient cycles in the biosphere (Millie et al., 1993).

In contrast to higher plants, many phytoplankton pigments are group-specific, and have been used as taxonomic biomarkers to indicate phytoplankton community structure (Barlow et al., 2004; Claustre and Marty, 1995; Gieskes et al., 1988; Vidussi et al., 2001) and source of organic matter to a range of aquatic systems (Bianchi and Findlay, 1990; Goericke and Repeta, 1992; Jeffrey, 1997; Mantoura and Llewellyn, 1983; Millie et al., 1993; Wright and Jeffrey, 1987; Wright et al., 1991). Distinct phytoplankton groups have specific environmental requirements (e.g. light, nutrient, temperature) which in turn allow group-specific pigments to be used as markers for environmental change. As a result, phytoplankton pigment compositions are often used to measure the response of phytoplankton to environmental changes in various marine and freshwater systems. For example, marker pigments have been used to describe phytoplankton responses to monsoons (Indonesian Sea, Gieskes et al., 1988), assess environmental controls on phytoplankton blooms (Barlow et al., 1993a, b) monitor El Niño conditions (Bidigare and Ondrusek, 1996; Latasa et al., 1996) assess phytoplankton communities across lakes, coasts and the open sea (Barlow et al., 1997; Vinebrooke and Leavitt, 1999; Wilhelm et al., 1995) and as indicators of organic matter decay and diagenesis (e.g. Abele-Oeschger, 1991; Mantoura and Llewellyn, 1983; Villanueva and Hastings, 2000).

Cyanobacteria are thought to have existed in the Baltic Sea for 7000 years and are regarded as the main nitrogen-fixing organisms in the region (Bianchi et al., 2000a; Degerholm et al., 2008; Ploug et al., 2011; Poutanen and Nikkila, 2001). Increasingly extensive blooms have been observed in the Baltic Sea since the 1960s and the trend is thought to be due to human-induced eutrophication (Conley et al., 2009a; Finni et al., 2001; Larsson et al., 1985; Zillen et al., 2008). Large blooms of diazotrophic cyanobacteria accumulate in the late summer (July–August) in the surface waters of the central parts of the Baltic Sea, , the Gulf of Finland, and the Gulf of Riga (Figure 23)(Kahru et al., 1994; Kahru et al., 2000; Wasmund et al., 2005). The cyanobacterial community is typically dominated by *Nodularia spumigena*, *Aphanizomenon* sp. and *Anabeana* sp. (Finni et al., 2001; Ploug et al., 2011; Rolff et al., 2007; Wasmund, 1997). While most phytoplankton blooms require an enhanced supply of both nitrogen and phosphorus, nitrogen-fixing cyanobacteria can maintain their own nitrogen supply by biological fixation of dissolved atmospheric nitrogen gas (Graneli et al., 1990). These conditions are readily available in the Baltic Sea as widespread hypoxia maintains re-supply of phosphorus from the sediments to the water column and cyanobacteria can flourish after the spring bloom which exhausts dissolved nitrogen availability (Jilbert et al., 2011; Stal et al., 2003; Vahtera et al., 2007; Wasmund et al., 2005; Westman et al., 2003). The increased supply biological available nitrogen by nitrogen-fixing cyanobacteria, combined with an increased flux of organic matter to the water column leads to increased oxygen consumption and further phosphorous regeneration (Larsson et al., 2001; Vahtera et al., 2007). Kahru and Elmgren (2014) studied satellite images of surface water cyanobacteria accumulations in the Baltic Sea (1979–2013) and found that the bloom onset now occurs in mid-July, three weeks earlier than 35 years ago.

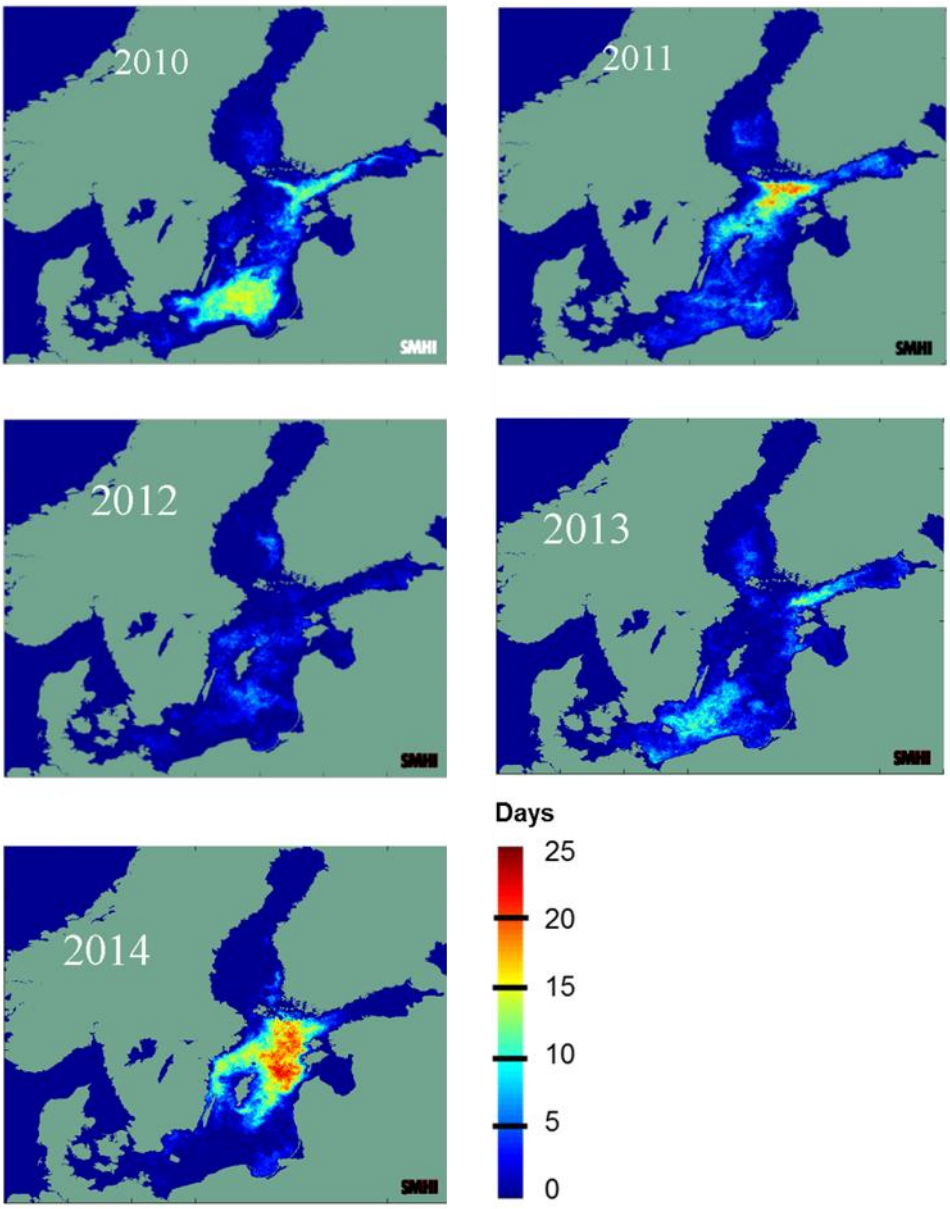


Figure 23. Annual cyanobacterial blooms in the Baltic Sea, during the period 2010–2014. Comparisons cannot be made between these results and those from the period 1997–2009 as the detection method has changed (adapted from HELCOM, 2016).

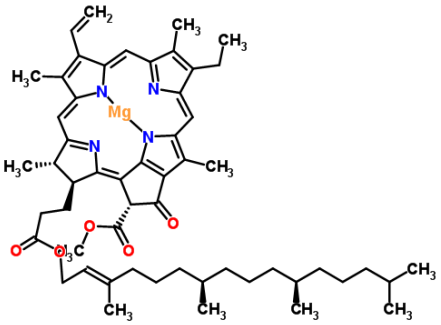
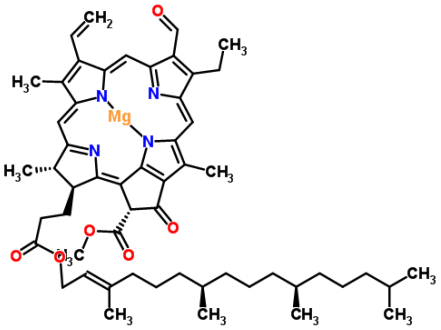
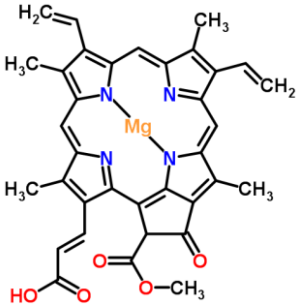
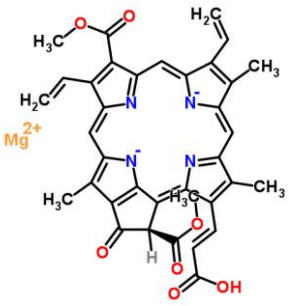
4.1.1. Pigments And Their Sub-Groups

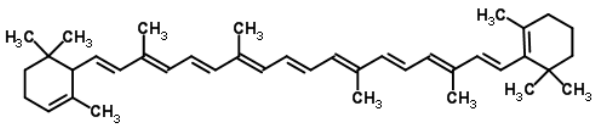
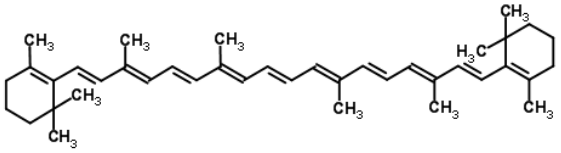
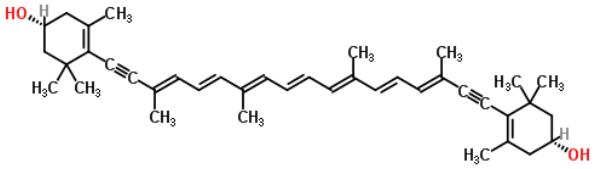
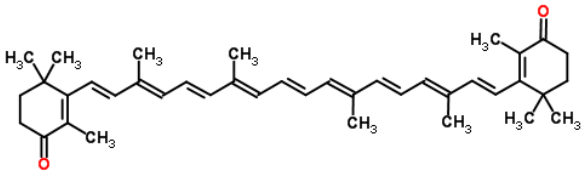
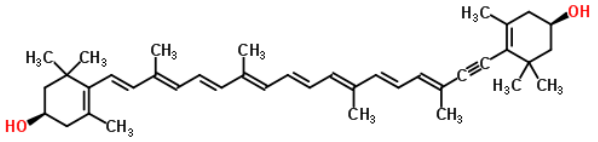
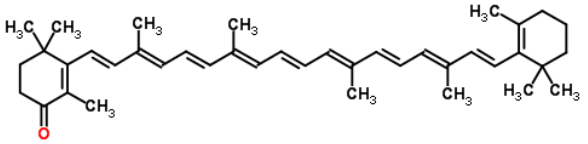
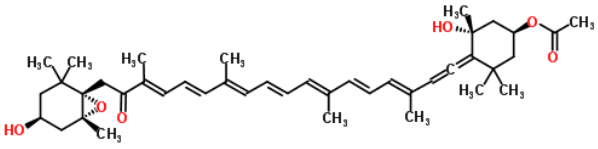
Pigments are present in all photosynthetic organisms, responsible for harvesting light energy and thus providing energy for photosynthesis. Marine pigments can be divided into two main groups: chlorophylls and carotenoids (carotenes and their oxygenated derivatives, the xanthophylls) (Table 8). Pigments do not exist "freely" but are bound within pigment-protein complexes where chlorophylls and carotenoids are close together, allowing the latter to provide photo-protection and accessory roles to the chlorophyll molecules. Chlorophyll-a, the primary pigment, is the only pigment that directly participates in in the light-dependent reactions in photosynthesis. Other pigments, such as chlorophyll-b and carotenes, serve as accessory pigments in two main ways:

- by producing energy from light wavelengths which chlorophyll-a cannot, transferring it to chlorophyll-a molecules, and thus extending the light-harvesting spectrum from which energy can be produced;
- by absorbing excess photo-radiation and thus protecting the chlorophyll-a molecule from photo-damage.

The chlorophylls are composed of cyclic complexes with a Mg^{2+} ion at the centre (the Mg-phorbin ring) and a long-chain isoprenoid alcohol ester group (the phytol chain, but usually absent from chlorophyll-c pigments). The carotenoids are made up of two ring structures connected by hydrocarbon chains, and may be oxygenated (xanthophylls) or oxygen-free (carotenes). In comparison to other marine organic matter, pigments are thought to be most labile, followed by lipids, amino acids and carbohydrates (Wakeham et al., 1997). While pigments in general are labile compounds, stability varies between individual compounds (Table 9, Table 10). Pigments can be degraded by chemical, photochemical and biological activity, and the breakdown products are commonly detected in pigment analysis and may serve as useful biomarkers (see section 4.1.3 for further discussion).

Table 8. Chemical structures of pigments in this study (ChemSpider, Royal Society of Chemistry, 2015).

Group	Pigment	Chemical structure
Chlorophylls	Chlorophyll-a	
	Chlorophyll-b	
	Chlorophyll-c_2	
	Chlorophyll-c_3	

Group	Pigment	Chemical structure
Carotenes	α-carotene	
	β-carotene	
Xanthophylls	Alloxanthin	
	Canthaxanthin	
	Diatoxanthin	
	Echinenone	
	Fucoxanthin	

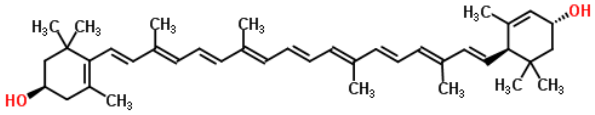
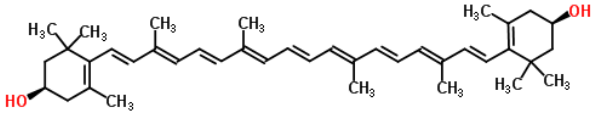
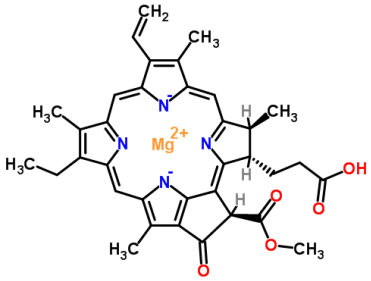
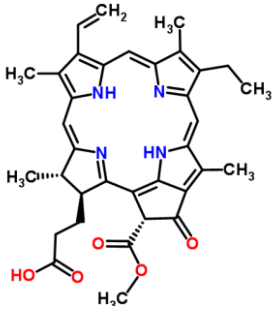
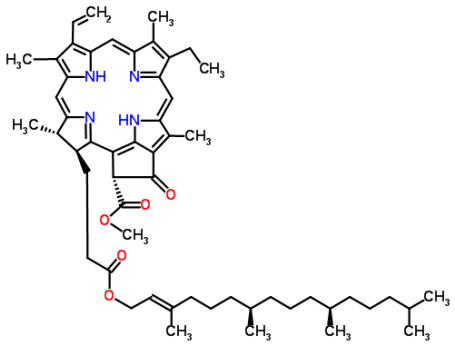
Group	Pigment	Chemical structure
Xanthophylls *(continued)*	Lutein	
	Zeaxanthin	
Chlorophyll derivatives	Chlorophyllide-a	
	Pheophorbide-a	
	Pheophytin-a	

Table 9. Pigments identified in this study: stabilities and uses as diagnostic biomarkers of algal groups (compiled from Jeffrey, 1997). Relative chemical stability is ranked from most (1) to least (4) stable.

Group	Name	Stability	Diagnostic algal group / biomarkers (s)
Chlorophylls	Chlorophyll-a	3	All photosynthetic algae
	Chlorophyll-b	2	Macrophytes
	Chlorophyll-c_2	4	Cryptomonads, diatoms, dinoflagellates, coccolithophorids, raphidophytes, chrysophytes, silicoflagellates,
	Chlorophyll-c_3	4	Coccolithophorids, chrysophytes, silicoflagellates
Carotenes	Alpha-carotene	2	Cryptomonads, prochlorophytes
	Beta-carotene	1	Accompanies chlorophyll-a in most groups
Xanthophylls	Alloxanthin	1	Cryptomonads
	Canthaxanthin	1	Cyanobacteria
	Diatoxanthin	2	Euglenoids, diatoms, dinoflagellates, coccolithophorids, raphidophytes, chrysophytes, silicoflagellates
	Echinenone	1	Cyanobacteria
	Fucoxanthin	2	Diatoms, coccolithophorids, raphidophytes, chrysophytes, silicoflagellates
	Lutein	1	Green algae, green flagellates
	Zeaxanthin	1	Cyanobacteria, prochlorophytes, red algae, chrysophytes, silicoflagellates
Chlorophyll derivatives	Chlorophyllide-a	2	Chlorophyll-a derivative
	Pheophorbide-a	3	Chlorophyll-a derivative
	Pheophytin-a	1	Chlorophyll-a derivative

4.1.1.1. Chlorophylls

The most common pigments, chlorophylls, have a primary function as light-harvesting agents and the different chlorophylls (a, b and c) are produced by variations in the attached functional groups (Table 8). Chlorophyll-c pigments are different from chlorophyll-a and –b in that they are Mg-phytoporphyrins rather than Mg-chlorins (Jeffrey, 1997). Due to its ubiquitous nature, chlorophyll-a is used as an indicator of total marine phytoplankton biomass living in the euphotic zone. As a result, sedimentary chlorophyll-a is a common marker of the "freshness" of the algal matter inputs to the sediment (Boon and Duineveld, 1998). Chlorophyll-b is predominantly found in green algae while chlorophyll-c occurs in diatoms, dinoflagellates and brown microalgae (Bianchi et al., 1997; Jeffrey and Vesk, 1997). Chlorophyll-c has been found in near-equal amounts to chlorophyll-a in diatoms, dinoflagellates and brown algae (Jeffrey and Vesk, 1997). Chlorophyll-c can be further sub-divided into chlorophyll-c_1, -c_2 (the most common form) and –c_3, and further chlorophyll-c-like pigments have been isolated and characterised (e.g. Goericke and Repeta, 1993).

4.1.1.2. Carotenoids

The second group, the carotenoids, can be split into the carotenes (e.g. alpha- and beta-carotene) and their oxygenated derivatives, the xanthophylls (e.g. alloxanthin, diatoxanthin, fucoxanthin, zeaxanthin).

Carotenoids are often termed 'accessory pigments' and play a role in light-harvesting or in protecting chlorophyll-a from photo-damage. Photosynthetic carotenoids (PSCs) have a significant function in extending the light-harvesting spectrum in the phytoplankton and supplement photosynthesis by transferring absorbed energy to chlorophyll molecules thus ensuring optimal absorption efficiencies (Kirk, 1994). Other carotenoids serve as photo-protecting carotenoids (PPCs) and act to protect the chlorophyll molecule from harmful radiation (Kirk, 1994; Louda et al., 2002; Ston and Kosakowska, 2000). While some carotenoids exist in both groups, Table 10 gives examples of each functional classification.

Differences in the molecular structures of individual carotenoids are changes in the functional groups attached to the ring structures. Xanthophylls may transform from one to another as the result of photochemical reactions under light-stress, in a process called the 'xanthophyll cycle'. Carotenoids are often found in only certain taxonomic groups, and

thus make good biomarkers. For example, zeaxanthin is a common indicator pigment for cyanobacteria, and lutein is often used as a marker for Chlorophyta (green algae) (Table 9). The biomarker potential of individual pigments is discussed in section 4.1.3.

Table 10. Functional classification of carotenoids, and selected examples (Ston and Kosakowska, 2000).

Functional classification	Example pigments
photosynthetic carotenoids (PSCs)	alpha-carotene, fucoxanthin, peridinin
photo-protective carotenoids (PPCs)	alloxanthin, beta-carotene, diadinoxanthin, diatoxanthin, lutein, violaxanthin, zeaxanthin

4.1.2. Degradation Of Pigments

Pigments are subject to both biotic and abiotic degradation in the aquatic environment, in the water column and at the seafloor. Chlorophyll degradation occurs through the loss of the Mg^{2+} ion and/or the phytol chain, to form pheopigments. Decay occurs rapidly in the water column, within hours to weeks, and chlorophyll has a half-life of several weeks in the sedimentary environment (Abele-Oeschger, 1991). Pheophytin is formed when only the Mg^{2+} ion is lost, chlorophyllide when the phytol chain is lost, and pheophorbide when both are lost (Figure 24) (Yentsch, 1967). While chlorophyll-a degradation pathways are often given as examples of general chlorophyll decay, chlorophyll-b degradation follows the same pathway, forming pheophytin-b, pheophorbide-b and chlorophyllide-b. Other pheopigments, such as pyropheophorbide, may also be formed during chlorophyll degradation but it was not possible to identify them in this study.

Pheopigments may decay further to produce porphyrins: organic compounds that remain in the sediments for geological timescales (Eckardt et al., 1991). Pheopigments may be produced under abiotic influences such as temperature, light and oxidation (Sun et al., 1993, Bianchi et al., 2000; Louda et al., 2002), or due to biotic factors including cell senescence and the metabolic activities of organisms both in the water column and in sediments (Shuman and Lorenzen, 1975; Villanueva and Hastings, 2000; Louda et al., 2002; Bianchi et al., 2000). Thus the distribution of chlorophyll and its degradation products can be useful biomarkers to indicate biotic and abiotic processes in the water column and/or the sediments (Mantoura and Llewellyn, 1983; Villanueva and Hastings, 2000).

Abiotic degradation of chlorophylls has been shown to be dependent on oxygen availability, temperature and light. While the roles of oxygen and organic matter supply in sedimentary organic matter preservation has been widely debated, there is yet no consensus (e.g. Henrichs and Reeburgh, 1987; Canfield, 1989). However, increased preservation of sedimentary organic matter during anoxic periods has been documented in the Baltic Sea (Jonsson et al., 1990). Chlorophyll has been seen to degrade fully to colourless organic compounds under oxic conditions, but decay is incomplete under anoxic conditions, resulting in the accumulation of pheopigments (Bianchi et al., 2000b; Sun et al., 1993). This supports the idea that organic matter preservation is enhanced under short- to mid-term anoxia (months to years), which is important in attempts to use pigments in sediment cores to reconstruct cyanobacterial blooms in the Baltic Sea (Bianchi et al., 2000a). Low temperatures have been shown to reduce chlorophyll decay, however this influence was only found in oxygenated incubations and not in anoxic conditions (Louda et al., 2002; Sun et al., 1993).

The digestive processes of marine herbivores are known to result in chlorophyll degradation, and thus production of pheopigments (Shuman and Lorenzen, 1975; Bianchi et al., 2000). Pigment decay is enhanced by faunal activity in both the water column and within the underlying sediments. Chromatographic pigment separations have shown pheophorbide to be the dominant chlorophyll degradation product of herbivory. (Shuman and Lorenzen, 1975) conducted laboratory zooplankton grazing experiments to quantify pheopigment production from chlorophyll-a; they observed that for each mole of chlorophyll-a ingested by the grazers, a corresponding mole of pheophorbide was found in egested faecal zooplankton material. In general, the formation of pheophorbide is mainly due to herbivore activity, chlorophylls are degraded to chlorophyllide during cell senescence, and pheophytin is formed during herbivory, cell senescence, and microbial degradation. However, some studies have observed different patterns of pigment alteration by different grazers and thus, the use of chlorophyll degradation products to indicate the presence of herbivory is limited (e.g. Pandolfini et al., 2000; Strom et al., 1998). The role of fauna in pigment degradation is interlinked with oxygen availability. For example, Bianchi et al. (2000b) conducted sediment microcosms to show that faunal effect on pigment breakdown was absent under anoxic conditions, and that the fastest decay of chlorophyll and fucoxanthin occurred under oxic conditions in the presence of macrobenthos.

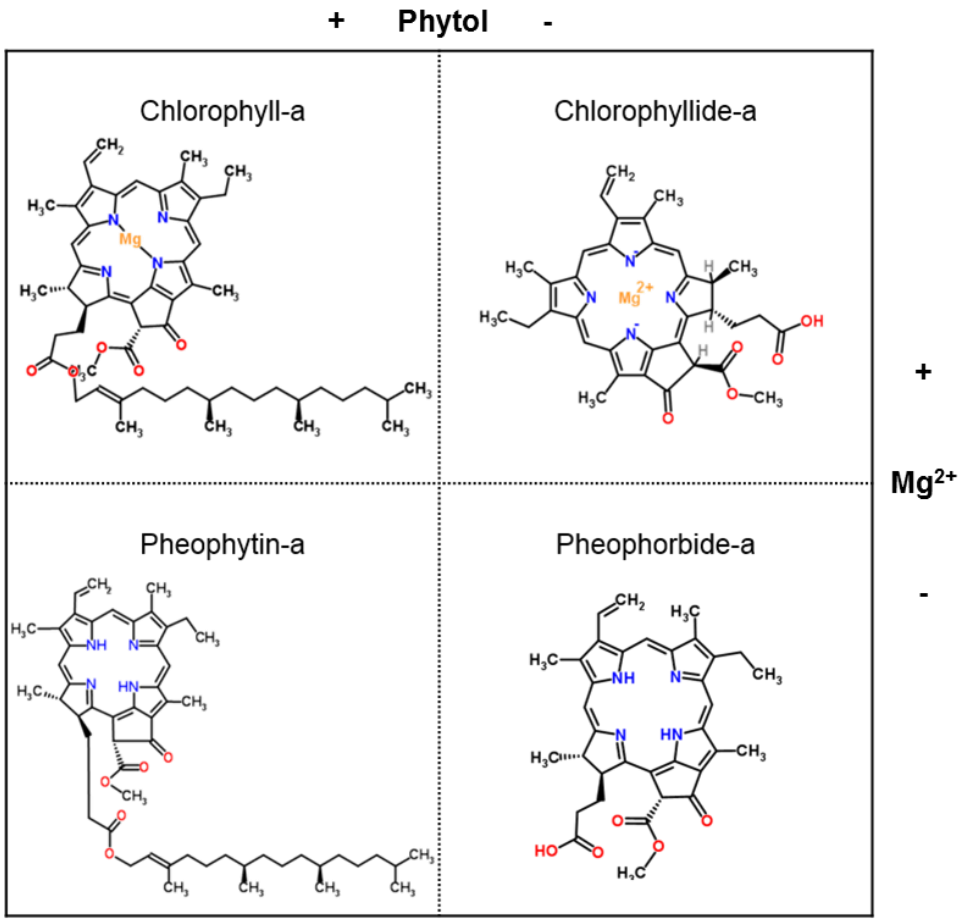


Figure 24. Structural changes during pheopigment production from chlorophyll-a (Yentsch, 1967; Shuman and Lorenzen, 1975).

Like chlorophylls, carotenoids also undergo chemical alteration, despite generally more stable (e.g. Abele-Oeschger, 1991). During decay, carotenoids are transformed into mostly colourless low molecular weight products (e.g. loliolide) following processes including the breakdown of double bonds in the hydrocarbon chains and hydrolysis of esters attached to the ring structures (Repeta, 1989). For example, hydrolysis of fucoxanthin forms two decay successive products (fucoxanthinol, then fucoxanthinol 5'-dehydrate) and may occur as the result of faunal grazing (Repeta and Gagosian, 1984). Unfortunately, many of these decay products are not detectable using standard pigment analysis approaches, and require the use of mass spectrometry (e.g. Abele-Oeschger, 1991). Carotenoids are easily oxidised and thus, oxygen availability plays a key role in sedimentary carotenoid preservation and distribution (Sanger, 1988). Where oxygen is depleted, light is not thought to enhance carotenoid decay further highlighting the importance of oxygen in pigment preservation dynamics (Leavitt, 1988). Previous studies have found beta-carotene and lutein to be relatively stable in anoxic sediments while fucoxanthin however,

has low stability and has been shown to be significantly reduced (50 %) following hydrolysis in zooplankton guts (Repeta and Gagosian, 1982; Abele-Oeschger, 1991). Strom et al. (1998) observed variable carotenoid degradation rates in laboratory incubation experiments. Both chlorophylls and carotenoids were degraded by zooplankton feeding, but small planktonic protozoa (<25 pm) grazed more heavily on water column pigments than large protozoa (>80 pm) (Strom et al., 1998).

4.1.3. Pigments As Biomarkers

Similar to other forms of organic material, the sedimentary preservation of pigments is generally favoured by high primary production, high sedimentation rates, and low oxygen conditions (Schulte et al. 1999, Kowalewska et al. 2004). Thus, sedimentary pigments and their decay products have been used in both short-term and long-term studies of marine ecosystems; including changes in organic matter dynamics, eutrophication, cyanobacterial blooms and hydrodynamics (e.g. Harris et al., 1996; Chmura et al., 2004; Kowalewska et al,. 2004; Zhao et al., 2000; Kowalewska, 2001; Bianchi et al., 2000; Poutanen and Nikkilä, 2001).

In combination with pheopigments, chlorophyll-a can be used as a proxy both past and present-day algal productivity (e.g. Summerhayes et al., 1995; Harris et al., 1996; Schubert et al., 1998) and to assess the freshness and/or degradation state of algal matter in marine sediments (Boon and Duineveld, 1996; Mantoura and Llewellyn, 1983; Villanueva and Hastings, 2000). The Chlorin Index (Schubert et al., 2002) is one such proxy that can be used to estimate organic matter freshness, placing samples on a scale of 0 (fresh) to 1 (degraded):

$$\text{Chlorin Index (CI)} = \frac{\mathrm{F}_{acidified\ extract}}{\mathrm{F}_{original\ extract}}$$

Where F is the fluorescence (at 665 nm) measured either before (original extract) and after (acidified extract) acidification of a sample with 25 % hydrochloric acid. The effect of acidification is to transform any chemically labile chlorophyll-a into pheophorbide-a and thus change their optical properties, leading to a lower fluorescence. Thus, an extract of fresh material will display larger changes in fluorescence due to acidification than an already-degraded sample (Schubert et al., 2002). However, a purely fluorometric measurement and acidification of chlorophyll-a is now known to be compromised when

chlorophyll-b is present, leading to overestimation of the pheopigments (Gibbs, 1979; Lorenzen, 1981; Gieskes, 1991).

Both chlorophylls and carotenoids have been used as biomarkers of phytoplankton source, herbivory and organic matter cycling in marine sediments and the water column (e.g. Bianchi et al., 1996; Jeffrey and Vesk, 1997; Boon and Duineveld, 1998; Josefson et al., 2002; Bianchi et al., 2002; Woulds and Cowie, 2009; Josefson et al., 2012). Many of the accessory pigments (i.e. carotenoids and xanthophylls) display taxonomic specificity, which allows them to be used as biomarkers for specific algal groups (Gieskes and Kraay, 1984; Jeffrey et al., 1997). Due to this specificity, carotenoids can therefore be diagnostic of phytoplankton organic matter source (Table 1), and ratios between pigments may also yield useful information (e.g. Liaaen-Jensen, 1978; Rowan, 1989; Everitt et al., 1990, Bianchi et al., 1996; Jeffrey and Vesk, 1997). For example, fucoxanthin is widely considered to indicate diatom presence (Wright and Jeffrey, 1987) and the chlorophyll-b/lutein ratio has been found to be higher in emergent than in submergent lake macrophytes (Bianchi and Findlay, 1990). Zeaxanthin, echinenone, and myxoxanthophyll are known markers for cyanobacterial populations (Hertzberg & Liaaen-Jensen, 1969; Leavitt & Carpenter 1990; Bianchi et al., 1996; 1997, 2002). While echinenone is almost exclusive to cyanobacteria, high zeaxanthin concentrations have been interpreted to indicate dominance of cyanobacterial blooms in the southern Bothnian Sea and Baltic Proper, as zeaxanthin is more stable than echinenone (Bianchi et al., 1997b; Bianchi et al., 2002). However, although zeaxanthin was found to be present in the cyanobacteria *Aphanizomenon* sp. , it was not found in *Nodulari*a sp. (Bianchi et al., 2000a; Poutanen and Nikkila, 2001). Additionally, if organic matter is already degraded, care must be taken when using individual pigments as indicators in this way, as selective pigment alteration occurs in the early stages of diagenesis.

Pigments can also be valuable indicators of sedimentary organic matter dynamics. It is generally understood that organic matter (including pigments) degradation is slower in anoxic environments than in oxic sediments (Bianchi et al., 2000b; Sun et al., 1993). Using sediments from the Kiel Bight, Germany, Abele-Oeschger (1991) conducted laboratory and incubation experiments to assess both the short-term degradation and the long-term fate of pigments. The study showed that fucoxanthin, chlorophyll-a and chlorophyll-b typically reflected recent sedimentation of organic matter and were rapidly degraded after deposition. However, lutein and beta-carotene were found to be relatively stable, irrespective of oxygen concentrations, in all sediments (Abele-Oeschger, 1991). Lotocka

(1998) examined the vertical profiles of pigments in organic-rich, anoxic (or near-anoxic) Baltic Sea sediments to measure historical carotenoid contents and investigate organic matter degradation. Whilst being the most abundant pigments, fucoxanthin and zeaxanthin also decreased steeply down-core. However, lutein and beta-carotene exhibited more stable profiles, indicating slower-breakdown, in agreement with similar work by Abele-Oeschger (1991). Photosynthetic accessory carotenoids (PSCs, Table 10) that play role in light-harvesting tend to covary with chlorophjyll-a (Green & Durnford 1996), while photo-protective carotenoids (PPCs) have been shown to increase under high light intensities (Goericke & Montoya 1998). Chlorophyll-a has a short half-life, making it suitable as a biomarker for short-term (days-months) bioturbation in marine sediments. The downcore profiles of chlorophyll-a can be modelled to estimate bioturbation rates, using the decay rate of chlorophyll-a (specific to each environment) (Boon and Duineveld, 1998; Garcia et al., 2008; Sun et al., 1993; Woulds and Cowie, 2009).

Faunal processes are thought to play an important role in sedimentary pigment dynamics. For example, fauna may enhance burial of organic matter (e.g. Josefson et al., 2002) or increase degradation rates (e.g. Bianchi et al., 2000). Several studies have shown the conversion of chlorophyll to pheophorbide by water column herbivory (e.g. Shuman and Lorenzen, 1975; Billet et al., 1983; Spooner, 1994; Strom, 2001) or benthic sediment consumption (e.g. Josefson et al., 2002; Bianchi et al., 1988; Riaux-Gobin 2000). Josefson et al. (2002) incubated box-cores with ^{14}C-labeled detritus to study chlorophyll-a degradation rates with different benthic faunal communities: suspension feeders vs. subsurface deposit feeders. The authors found that vertical mixing was elevated in the sediments dominated by deposit feeders, and that the added ^{14}C-labeled detritus was rapidly buried, limiting mineralisation, agreeing with previous work by van de Bund et al. (2001). Further work by Josefson et al. (2012) observed an decrease in pigment concentrations in sediments with greater bioturbation, concluding that degradation rates in oxygenated environments are heavily controlled by benthic faunal activities. In contrast, Bianchi et al. (1988) observed increased transformation of chlorophyll-a to pheopigments in microcosms containing macrofauna relative to those without. In agreement with earlier studies, the authors also found that microcosms with combined co-existing species led to lower feeding activity, compared to individual species microcosms (Levinton, 1972; Levinton, 1977). However, it is still uncertain whether zooplankton grazing is the primary mechanism for pheopigments production, or if pheopigments can simply survive unaltered through the guts of zooplankton. For example, (Villanueva and Hastings, 2000)

interpreted the correlation of chlorophyllide-a pheophorbide-a to mean that the production of these pheopigments was due to cell lysis and bacterial degradation. The production of pheophorbide-a and pyropheophorbide-a has been observed in incubation experiments devoid of fauna (Louda et al., 2002). Thus, while pheopigments have been used to trace grazing processes in both the water column and the sediment it has also been argued that it might not always be a relevant indicator of herbivorous activities, as pheopigments may be produced as a result of bacterial activity and cell decay (e.g. Villanueva and Hastings, 2000). While specific grazing biomarkers do exist (e.g. steryl chlorin esters, Goericke et al., 1999) the detection techniques required to resolve these compounds were not available in this project.

In summary, sedimentary chlorophyll-a can indicate the freshness of organic matter inputs to the sediment, taxonomic –specific accessory pigments (such as the xanthophylls) can identify the inputs of different algal groups, and degradation products may yield information on the nature of degradation the organic matter has undergone.

4.1.4. Aims And Hypotheses

Pigments make sensitive indicators of early organic matter degradation, due to their short half-lives. The degradation and burial of organic matter in marine sediments play a large role in oxygen dynamics in the associated bottom waters. On the one hand, degradation increases oxygen demand, while burial can mitigate this by decreasing degradation rates – thus organic matter and oxygen dynamics are intrinsically linked. Therefore in this study, the ability of pigments to elucidate aspects of organic matter sources and cycling will be used to investigate the fate of organic matter in sediments of the Baltic Sea. The same approach was not taken in the Arabian Sea, as samples had been collected before the initiation of this study and not preserved in an appropriate manner for pigment analyses.

This study is centred in the Baltic Sea, a semi-enclosed brackish water body, notable for its large and rapidly increasing bottom water hypoxic zone (Conley et al., 2002). Several of its deep basins are now anoxic, including the Gotland Deep, Baltic Proper, and Gdansk Deep (Figure 25). The presence of a strong halocline separates the surface waters from the bottom waters and thus prevents vertical mixing of the water column and ventilation of the oxygen-depleted bottom waters (Matthaus and Schinke, 1999; Rabalais et al., 2010). Given impact of increasing eutrophication, and the associated hypoxia, on the cyanobacteria populations in the Baltic Sea (Conley et al., 2009a; Finni et al., 2001; Larsson et al., 1985; Zillen et al., 2008), it is important to be able to assess the impact of these

blooms on the sedimentary organic matter dynamics in the region. The Gotland Basin displays a range of natural biogeochemical gradients (e.g. oxygen, grainsize, organic inputs, faunal communities) making it an exceptional area for studying sedimentary organic matter dynamics in the region and how this relates to local sediment geochemistry and benthic communities. Full details of the study area are given in Chapter 2 (Literature Review) and Chapter 3 (Materials and Methods). Sedimentary pigment abundances and compositions were investigated across the natural biogeochemical gradients (e.g. oxygen, grainsize, organic inputs, faunal communities) in the Gotland Basin of the Baltic Sea. Key ancillary information regarding sediment textural properties and geochemistry was made available by Cowie et al. (unpublished), allowing an attempt to deconvolve the range of factors which play a role in organic matter cycling in the area. Fine-grained sediments have been found to have higher concentrations of organic carbon due to the similar hydrodynamic transport properties of both organic and fine particles, and sorption of organic matter onto mineral surfaces (Hedges and Keil, 1995; Mayer, 1994). This study aims to be the first attempt to assess whether this relationship holds for the pigment component of the organic matter pool in the Baltic Sea.

Thus, the following hypotheses were addressed:

- Systematic differences in pigment suites and/or degradation state exist between sites and down core.
- Pigment suites and/or degradation state reflect one or more of the following environmental factors: oxygen availability, faunal activity, sediment texture, organic matter source (i.e. changing phytoplankton communities). Specifically:
    - Absolute pigment concentrations are elevated at sites with anoxic, or oxygen-depleted, bottom waters.
    - Absolute pigment concentrations are reduced at sites with faunal communities.
    - Fine-grained sediments will have higher concentrations of intact pigments (fresher organic matter).
    - Pigment compositions reflect organic matter source and can be used as indicators of phytoplankton species.

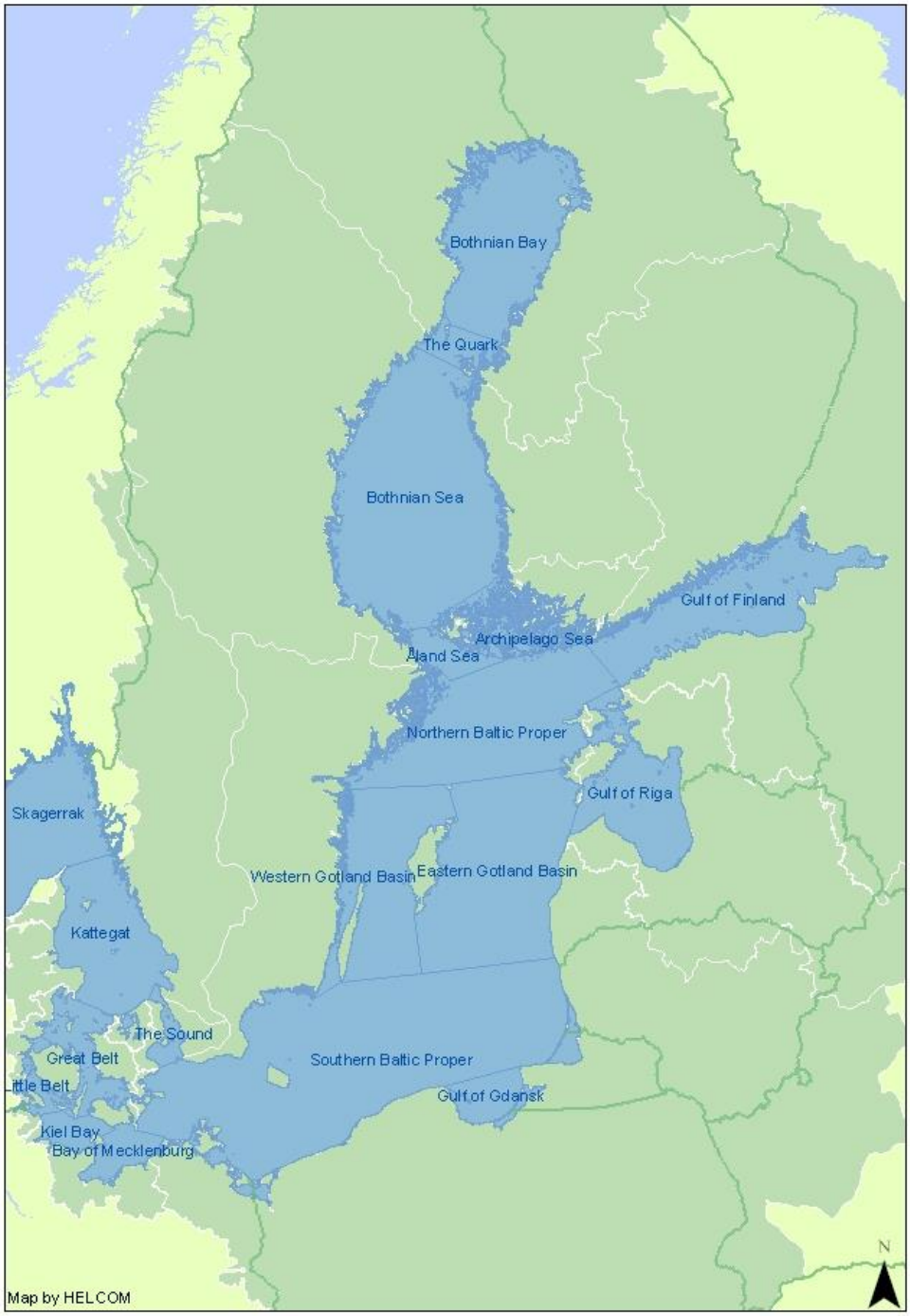


Figure 25. A map to show the sub-regions of the Baltic Sea, including the Eastern Gotland Basin as studied here (HELCOM, 2016).

4.2. Methodology

4.2.1. Sediment Sampling

Samples were collected from six sites across the Gotland Basin, at water depths of 45 m, 60 m, 75 m, 130 m, 170 m and 210 m (Figure 13, see Chapter 3: Materials and Methodology). Sites were selected due to their broad ranges in local environmental conditions and sediment geochemistry as shown in Table 2 (see Chapter 3: Materials and Methodology). These natural site differences allow assessment of the relationships between sedimentary pigment geochemistry and local environmental factors including organic matter characteristics, quantity, and quality, and also oxygen availability. Megacore samples (10 cm diameter) were taken during a single cruise aboard the R/V Skagerrak (August-September 2010). Upon retrieval, sediment cores were extruded and sectioned at intervals of 0.5 cm to 2 cm depth, then at 1 cm intervals to 10 cm depth, and then at 2 cm intervals to the bottom of the core. In some cores, detrital layers were observed above the sediment surface consisting of not-quite settled sediment particles with high water contents. Where present, these layers were sampled and named “fluff“ layers. Sediments were homogenised before storage in plastic bags at -20 °C aboard the ship.

4.2.1.1. Decay Experiments

In order to assess the current degradation state of pigments and potential for further decay, decay experiments were conducted, as described in Chapter 3: Materials and Methodology.

4.2.2. Pigment Extraction

Sedimentary pigments were from all intervals sampled in each core using 90 % ethanol in water. Samples were stored on board the ship at -20 °C and then at -80 °C upon transfer to the laboratory.

4.2.2.1. Method Comparison

Aboard ship, ethanol was the only solvent available for pigment extraction. To compare extraction solvents, archived frozen sediments from the 45 m site were also extracted with acetone in the laboratory following common extraction use in the literature (e.g. Bianchi et

al., 1997a; Łotocka et al., 2004; Poutanen and Nikkila, 2001) and the method detailed in Chapter 3.

4.2.3. Analysis

Analysis by high performance liquid chromatography (HPLC) was conducted using an Agilent 1100 series HPLC system with a photodiode array and a fluorescence detector. The HPLC was fitted with a Nova-Pak C18 4 µm, 3.9 x 150 mm reverse phase column (Part No. WAT086344) and a Nova-Pak C18 5 µm guard column. Separation of pigments was achieved in a gradient mixture of methanol, acetonitrile and water (modified from Airs et al., 2001). Details of the pigment identification process, sample chromatographs and standard calibration information are fully described in Chapter 3: Materials and Methods.

4.2.4. Statistical Approaches

4.2.4.1. Correlation Analysis

Pearson product-moment correlation coefficients between absolute individual pigments concentrations, total pigment concentrations, and conditions, sediment geochemistry and textural properties were calculated to identify the significance of relationships. A two-tailed test was performed on data from six cores (four degrees of freedom). Significance was reported at the 1 % level ($P \leq 0.01$). Two correlation analyses were conducted:

1. An analysis of downcore pigment concentrations at each site and environmental parameters for which data was available downcore (mid-point sediment depth, $\delta^{13}C$, $\delta^{15}N$, %OC, %N, C:N and DI).
2. A second analysis of surficial (0–3 cm) pigment concentrations and environmental parameters for which data was only available at the surface (water depth, oxygen, salinity, temperature, % clay, % silt and % sand).

4.2.4.2. Principle Component Analysis

Principal component analysis of down-core pigment data was carried out using Minitab 16 software. Data were standardised before use, by converting pigment concentrations to weight percentages (of total pigment yields). Factor coefficients and scores were generated for each sample, on the principle component axes 1 and 2 (PC1 and PC2).

4.3. Results

4.3.1. Spatial Distribution Of Surface Pigments

In order to remove the variability observed in downcore pigment profiles, pigment concentrations observed in duplicate cores at each site were averaged to give surficial values (0–3 cm) for each site. Average surficial pigment concentrations varied across the Gotland Basin (Figure 26). The three anoxic sites (130, 170 and 210 m) showed the highest average pigment concentrations (162–265 µg /g dry sediment) while the fully oxygenated site (45 m) displayed the lowest concentrations (15 ± 5.5 µg /g dry sediment). Most individual pigments showed the same cross-margin pattern as total pigment concentrations (Figure 26). The exceptions were chlorophyll-a, chlorophyll-b, echinenone and pheophytin, which displayed highest concentrations at oxygenated sites or were not present at some sites (Figure 27).

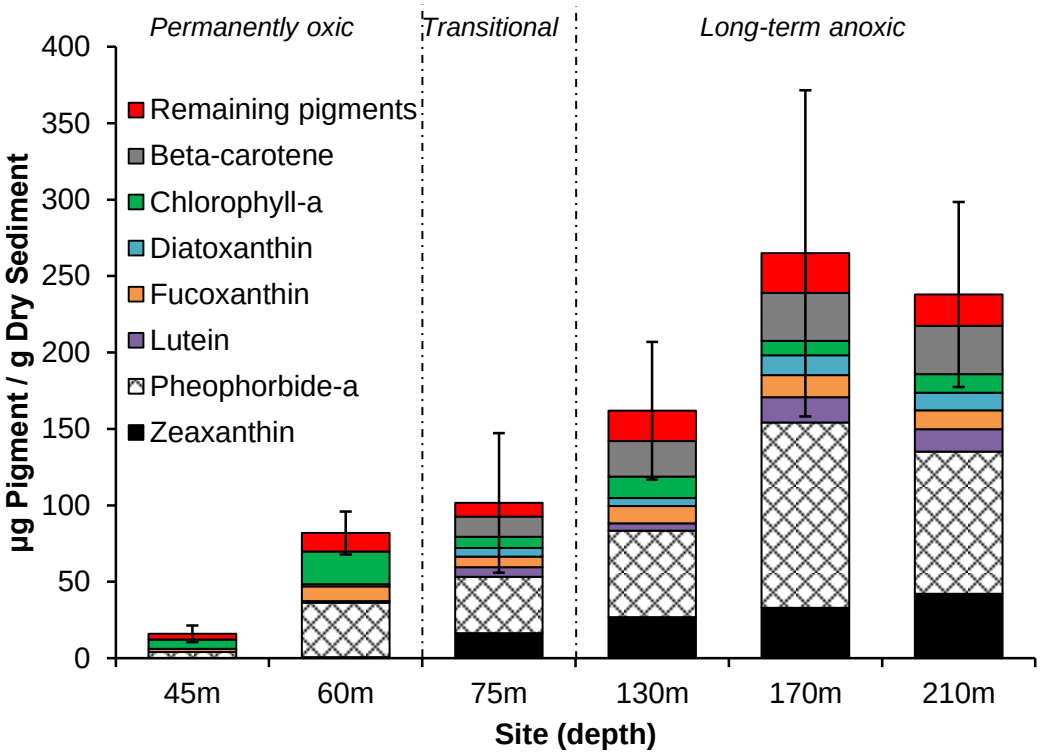
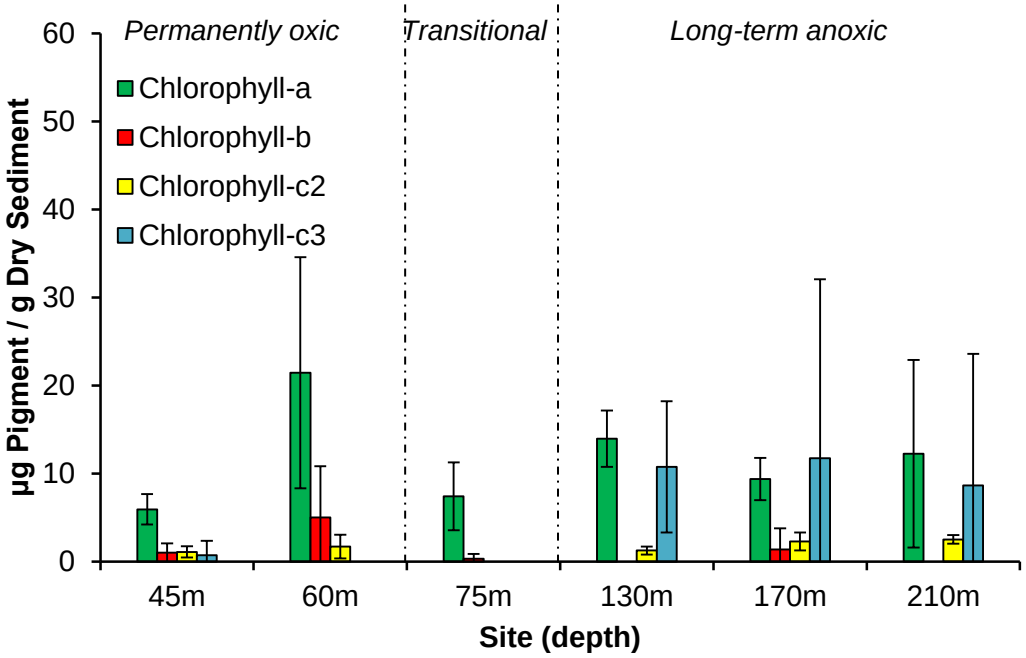
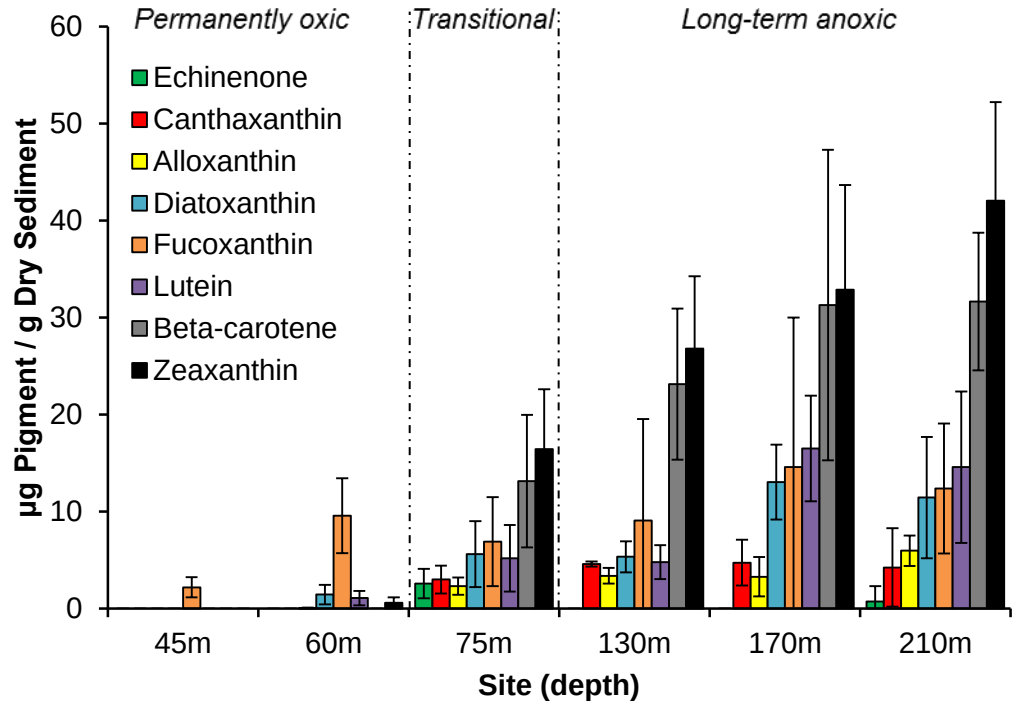


Figure 26. Average pigment concentrations of surficial sediments at all sites in the Gotland Basin of the Baltic Sea (top 3 cm, average). Error bars represent range, n=2.

A:


Permanently oxic
Transitional
Long-term anoxic
Chlorophyll-a
Chlorophyll-b
Chlorophyll-c2
Chlorophyll-c3
µg Pigment / g Dry Sediment
0
10
20
30
40
50
60
45m
60m
75m
130m
170m
210m
Site (depth)

B:


Permanently oxic
Transitional
Long-term anoxic
Echinenone
Canthaxanthin
Alloxanthin
Diatoxanthin
Fucoxanthin
Lutein
Beta-carotene
Zeaxanthin
µg Pigment / g Dry Sediment
0
10
20
30
40
50
60
45m
60m
75m
130m
170m
210m
Site (depth)

C:

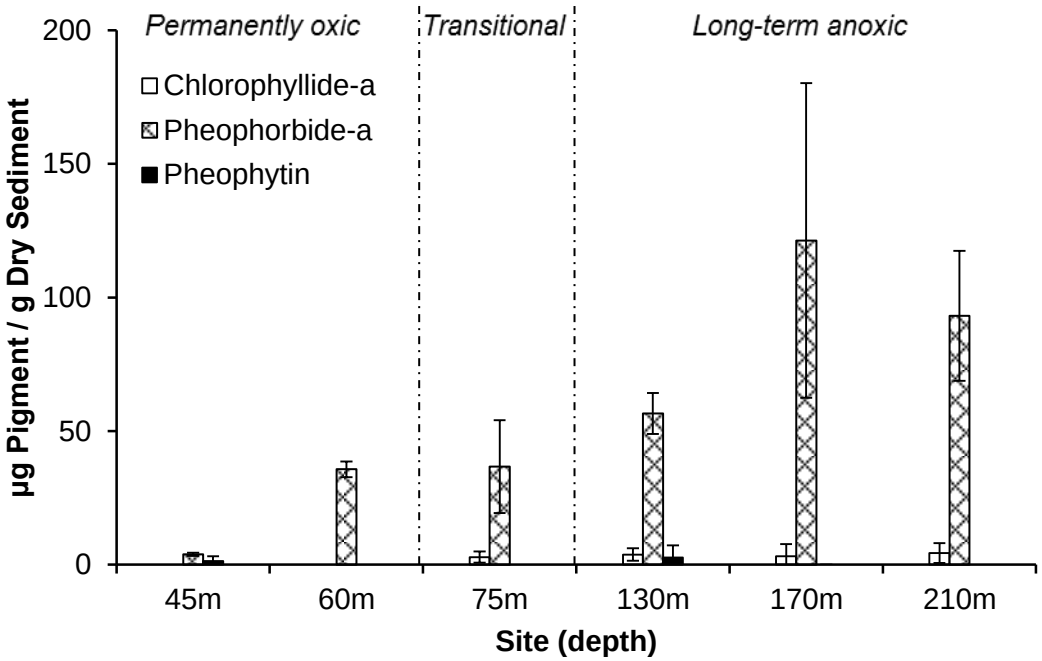
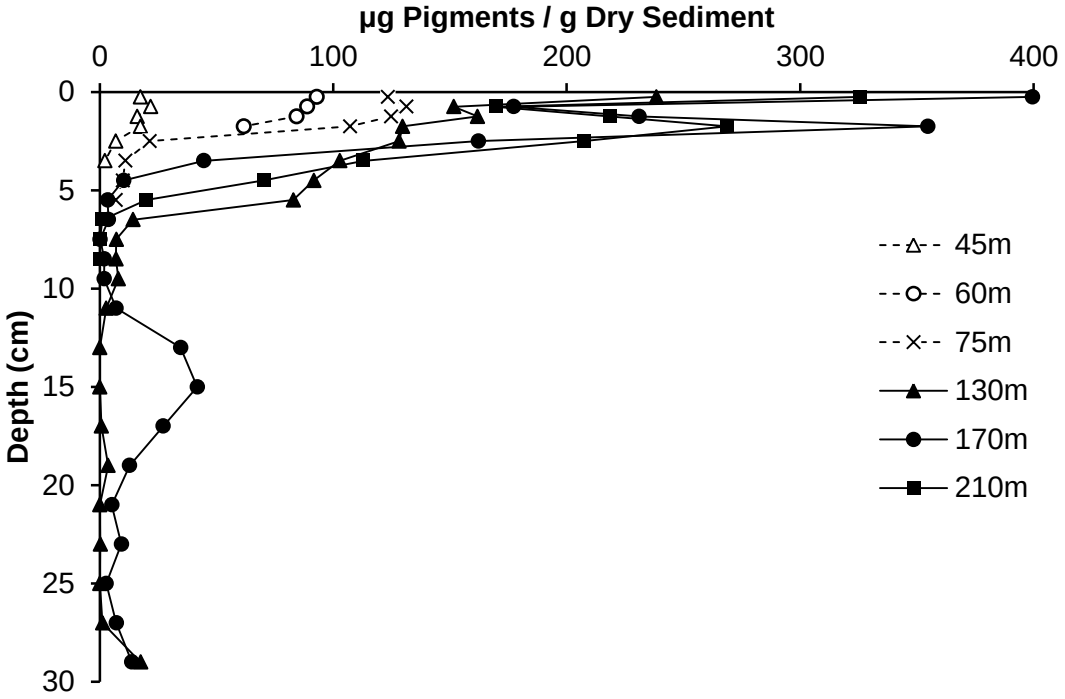


Figure 27. Average surficial concentrations of individual pigments at all sites across the Gotland Basin of the Baltic Sea (top 3 cm, average). Error bars represent range, n=2.

4.3.2. Vertical Distributions

Total pigment concentrations declined with down-core depth at all sites, with notable subsurface peaks at the 170 m site only (Figure 28A). The total concentration of pigments down-core showed the same cross-margin pattern as the concentrations found in surface sediments. The 170 m site contained the highest surface concentrations and displayed a subsurface peak between 10 and 20 cm sediment core depth. The 45 m site showed the smallest concentrations followed by the 60 and 75 m sites. The oxygenated sites (45 and 60 m) displayed the smallest down-core changes as the low surface concentrations (Figure 26) were closer to background values. Down-core profiles of alloxanthin (Figure 29a), canthaxanthin (Figure 29b), diatoxanthin (Figure 30a), lutein (Figure 30b), beta-carotene (Figure 31a), zeaxanthin (Figure 31b) and pheophorbide a (Figure 32) all showed similar cross-margin trend. However, whilst also having a subsurface peak at the 170 m site, chlorophyll down-core concentrations were highest at the oxygenated sites as observed in its cross-margin distribution (Figure 28B).

A



B

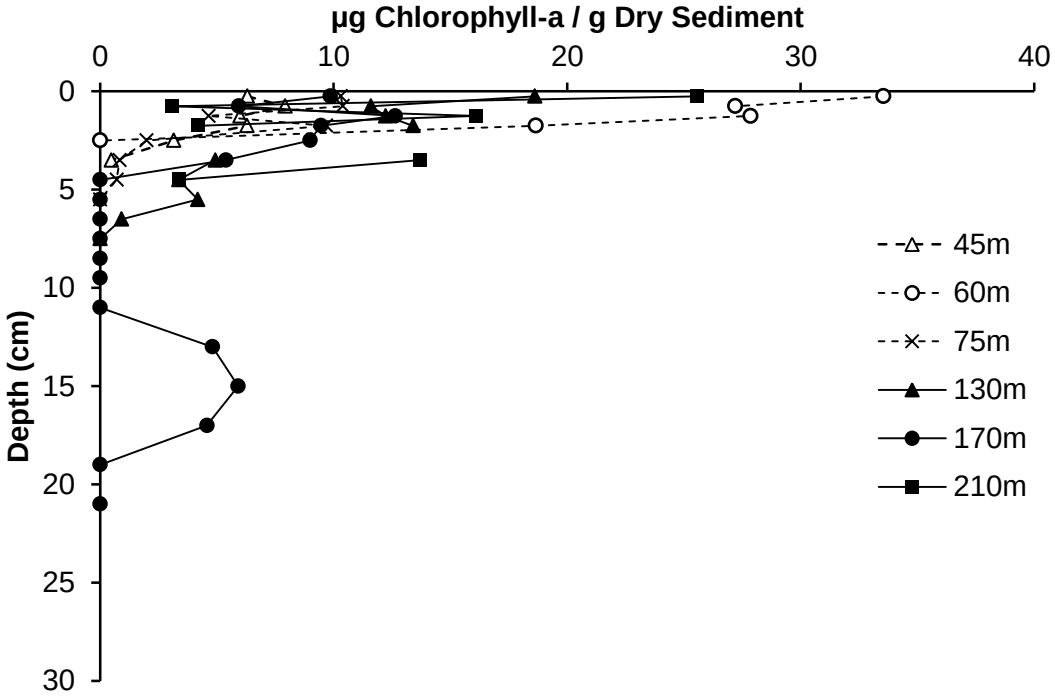
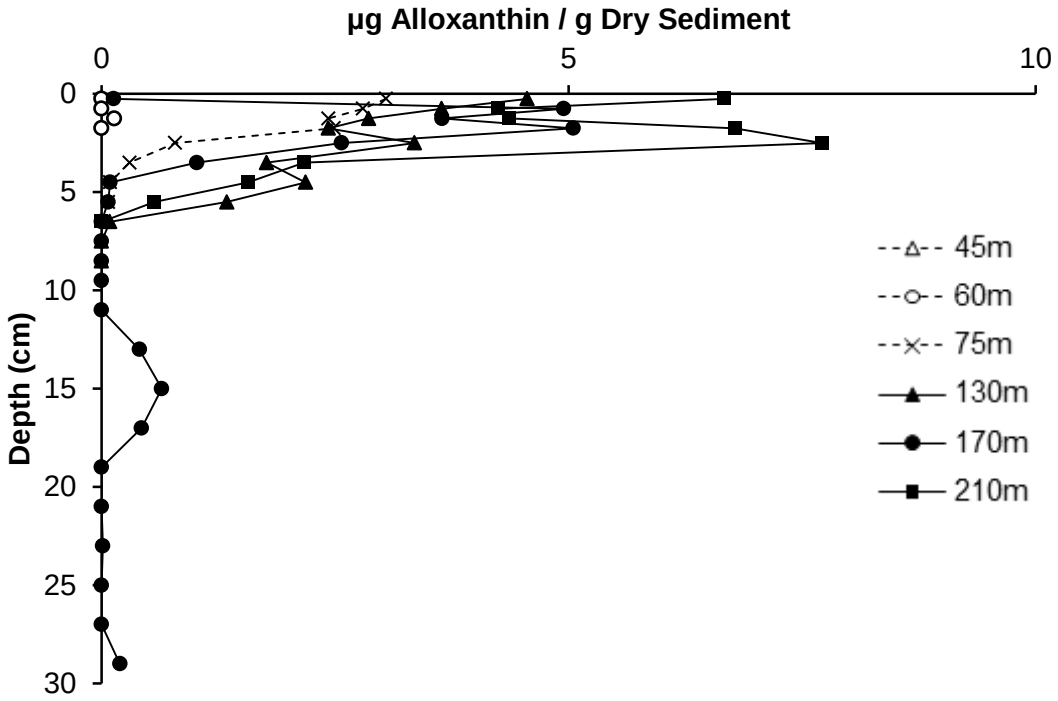


Figure 28. Down-core sediment profiles of A: total pigment concentrations, B: chlorophyll-a.

A



B

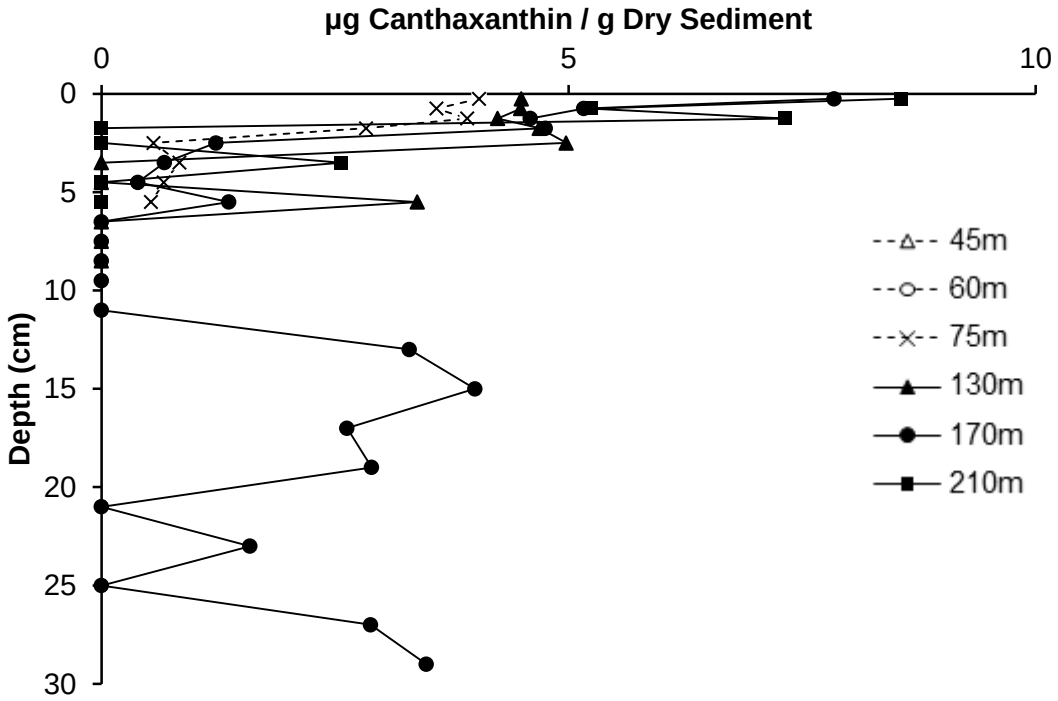
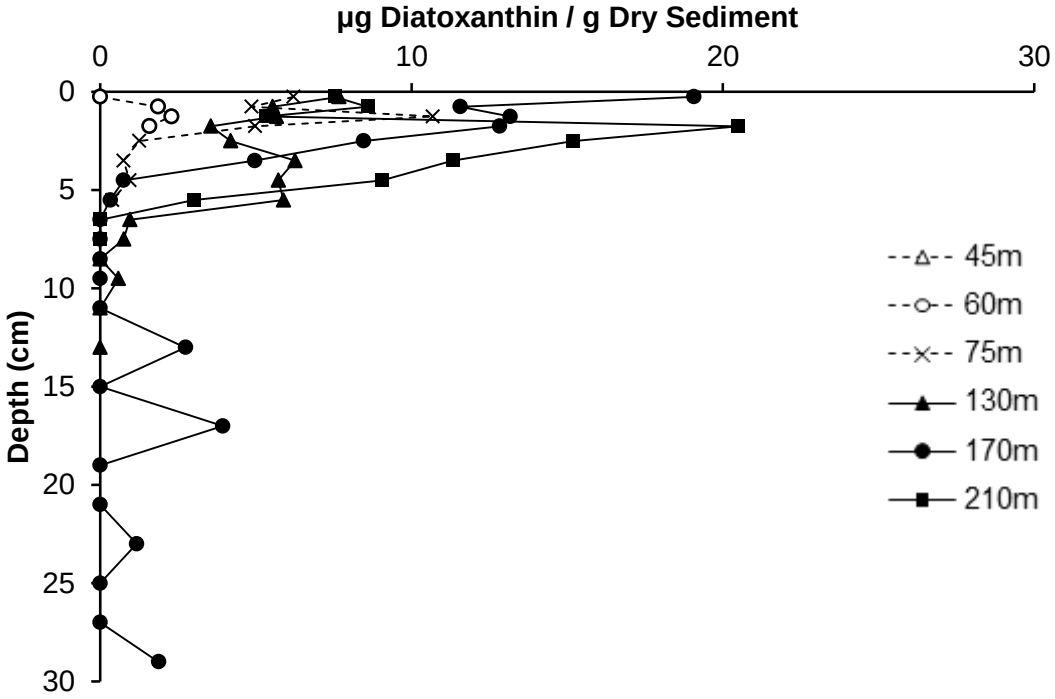


Figure 29. Down-core sediment profiles of A: alloxanthin, B: canthaxanthin concentrations.

A



B

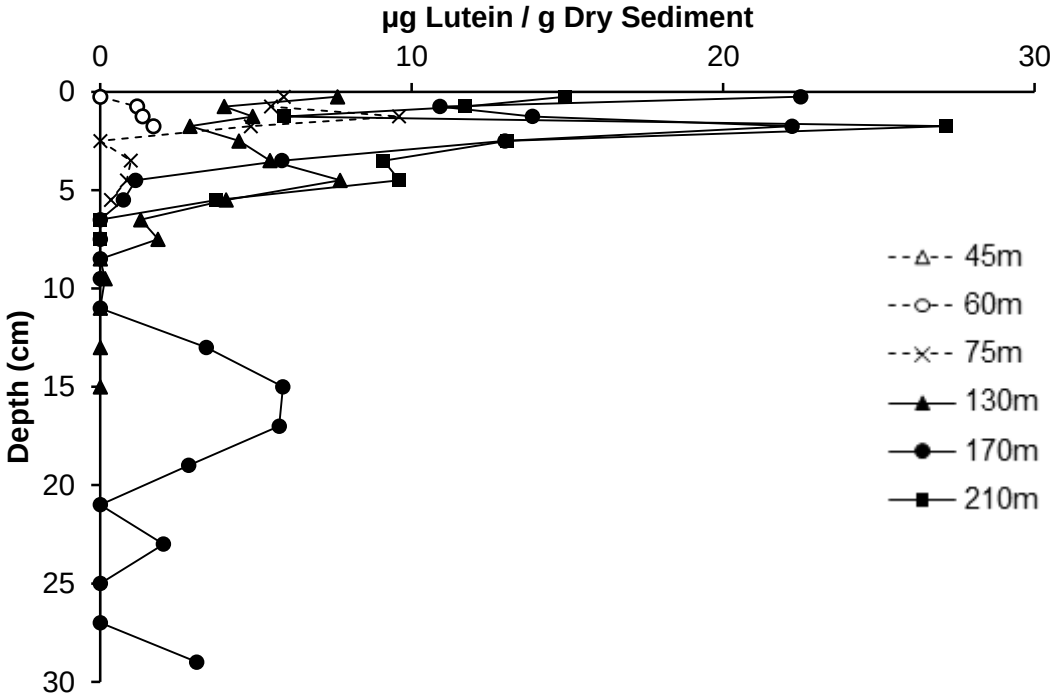
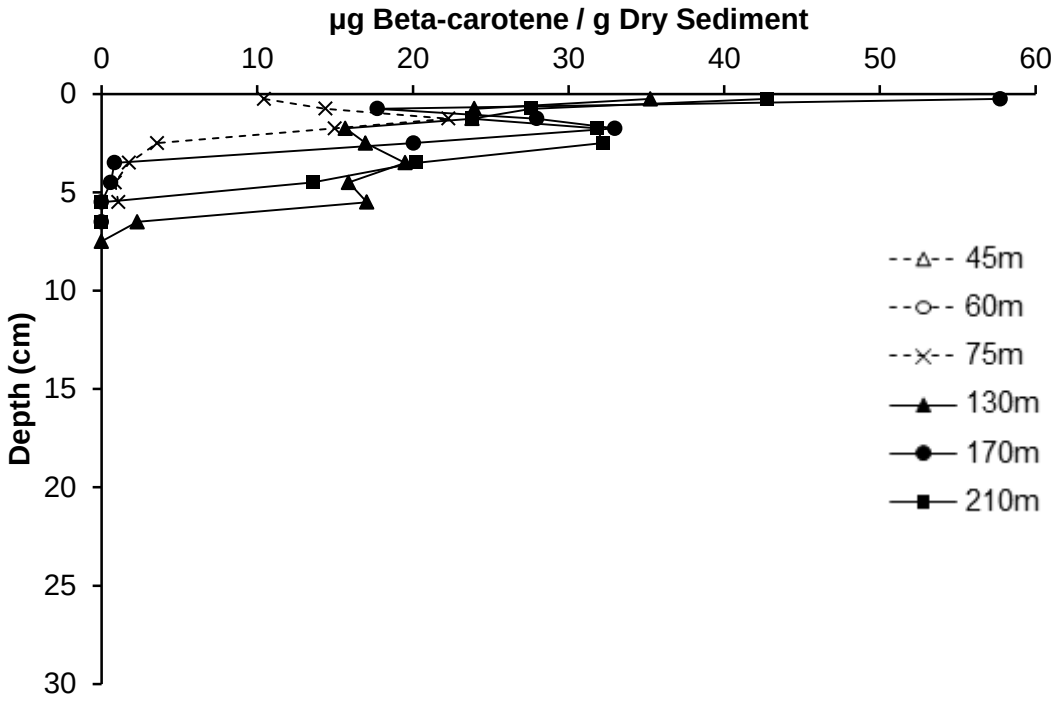


Figure 30. Down-core sediment profiles of A: diatoxanthin, B: lutein concentrations.

A



B

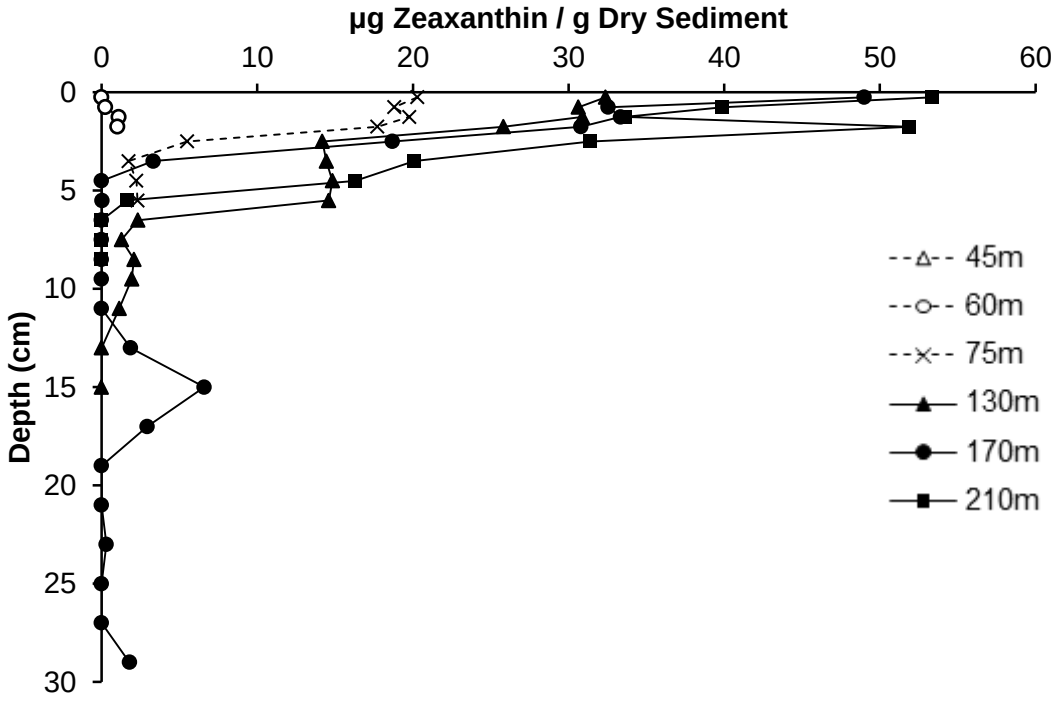


Figure 31. Down-core sediment profiles of A: beta-carotene, B: zeaxanthin concentrations.

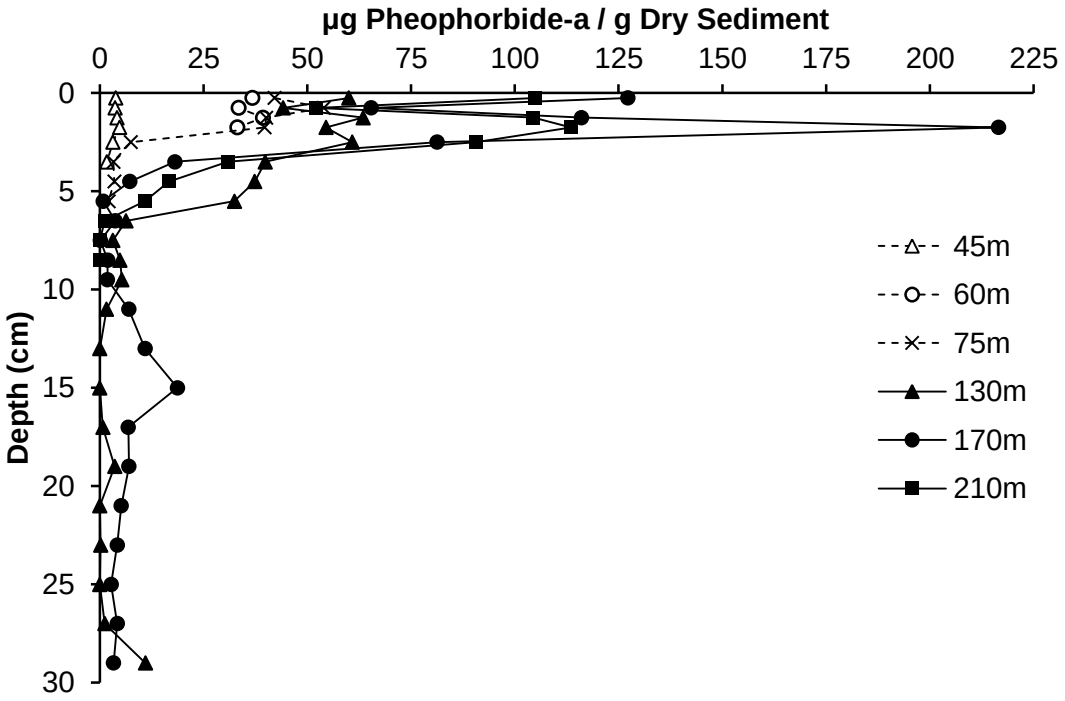


Figure 32. Down-core sediment profile of pheophorbide-a concentrations.

4.3.3. Pigment Suites

All percentages given here are weight percentages of total pigments extracted. At the anoxic sites, the surface pigment suites (Figure 33) were dominated by pheopigments (32–37 %) and chlorophylls were a minor component (9–15 %). At the two shallowest sites, 45 and 60 m, chlorophylls were of greater importance, making up 54 % and 37 % of the surface sediment pigments respectively. At the transitional site, 75 m, xanthophylls dominated the surface sediments, accounting for 42 % of recovered pigments. At the anoxic sites, the most abundant pigment was pheophorbide-a, followed by zeaxanthin and beta-carotene. Under oxygenated bottom waters, pheophorbide-a also demoniated the pigmentsuite, followed by chlorophyll-a (Figure 26). At all sites, alloxanthin and chlorophyllide-a were minor components of the pigment suites (<5 %). Despite comprising 7.6 ± 1.4 % of total pigments at 45 m water depth, chlorophyll-c_2 was minor at all other sites (<4 %). Principal component analyses of pigments suites were conducted twice:

- With all 6 sites at down-core intervals using only site conditions (Figure 34-Figure 36).
- With 5 sites (data not available for 60 m depth) at down-core intervals using both site conditions, sediment geochemistry (Figure 37-Figure 39).

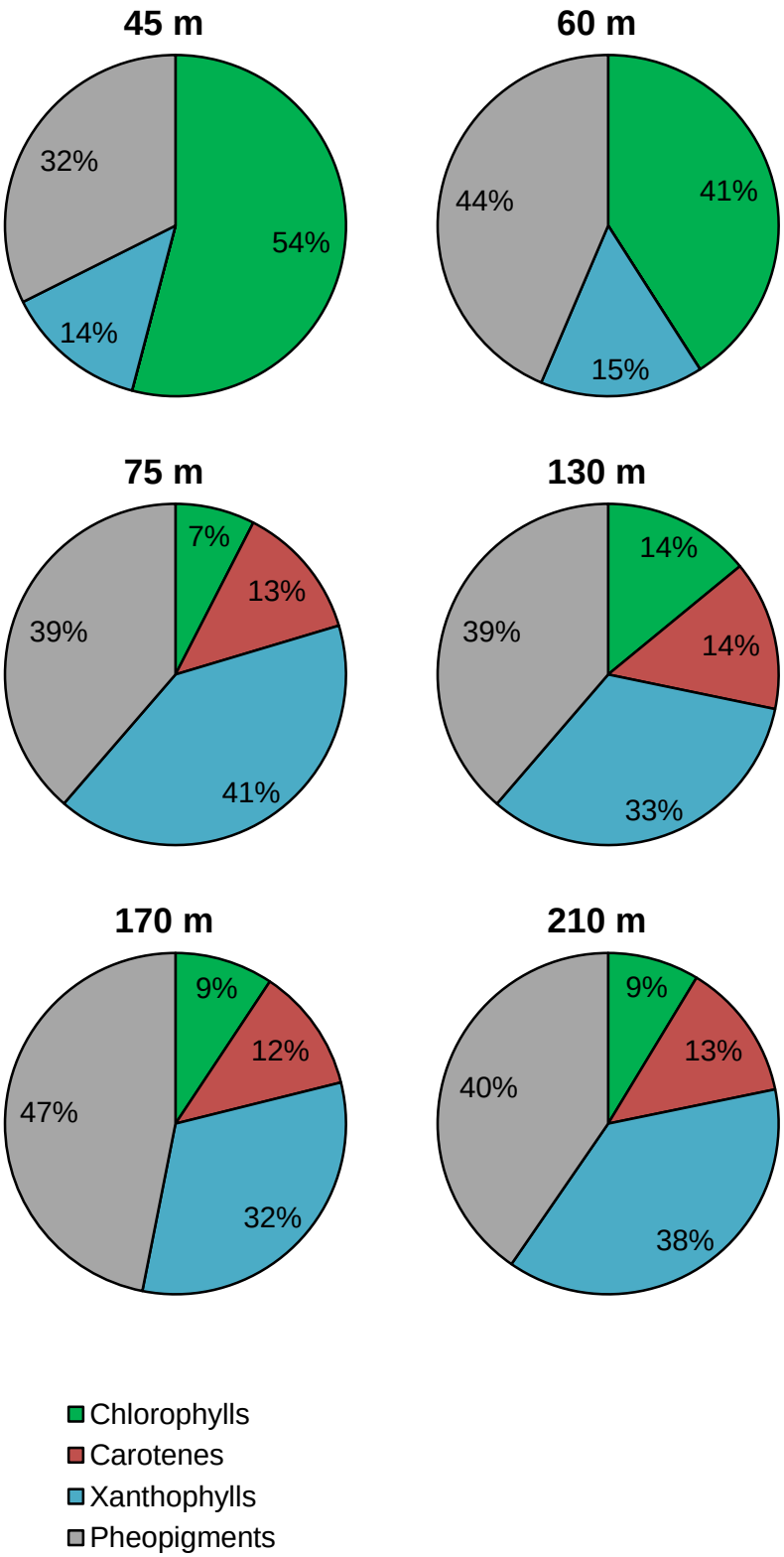


Figure 33. Pigment suites at all sites across the Baltic Sea Gotland Basin, separated by the broad pigment groups plus the pheopigments.

4.3.3.1. PCA Approach 1: All Sites, Site Conditions Only

The principal component analysis of all 6 sites revealed scores that separated sites along the PC1 axis, which accounted for 34.2 % of the variance (Figure 34). The 45 m and 60 m sites had the most negative PC1 scores, and displayed larger ranges in PC1 which increased (positively) downcore. The remaining sites all had higher scores along this axis, but displayed smaller ranges in PC1 scores. Negative PC1 scores were a function of increasing oxygen concentrations so it was revealing that the "transitional" site at 75 m is distinct from the oxygenated sites and sits amongst the anoxic sites (Figure 35). Negative PC1 scores were also aligned with total concentrations of chlorophyll-a, chlorophyll-b, chlorophyll-c_2, and fucoxanthin. Temperature, depth and salinity all exerted influence over positive PC1 scores, which was consistent with the inverse trend between water depth and oxygen concentrations at these sites. Sites were not fully separated over the PC2 axis, which accounted for 19.3 % of the variance, and displayed similar ranges to each other. The range of PC2 scores was a function to the length of sediment core retrieved as indicated by the influence of within-sediment interval depth ("mid-point") on the PC2 axis (Figure 35). Although the most abundant pigment, pheophorbide-a did not have much influence over the PC1 scores, it appeared to have a large influence over PC2 scores (Figure 35, Figure 36). Negative PC2 scores were a function of beta-carotene, alloxanthin and chlorophyllide-a. The absence of these three pigments in sediments at the two shallow oxygenated sites (45 and 60 m) explains the limited separation of downcore intervals of the sites over the PC2 axis. In summary, PC1 scores increased systematically downcore at the anoxic sites, and PC2 scores decreased systematically at the anoxic sites.

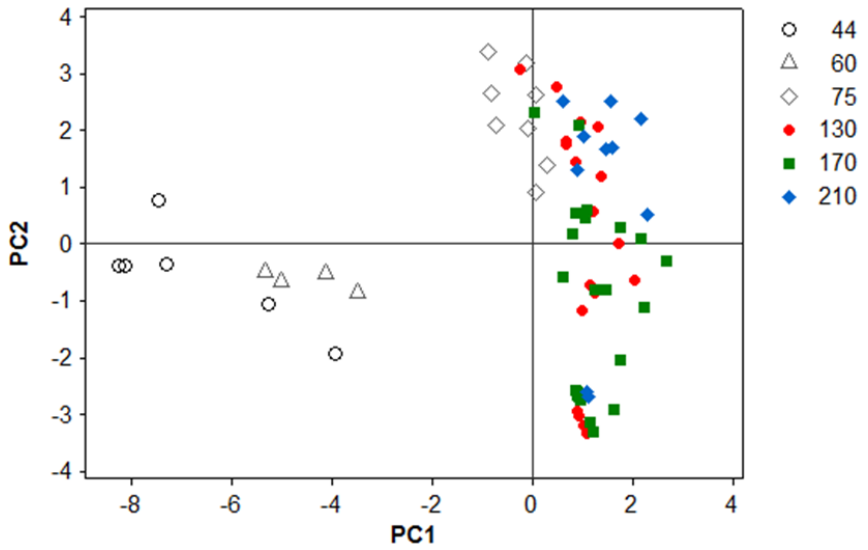


Figure 34. Results of the PCA approach 1: sample PC1 and PC2 scores.

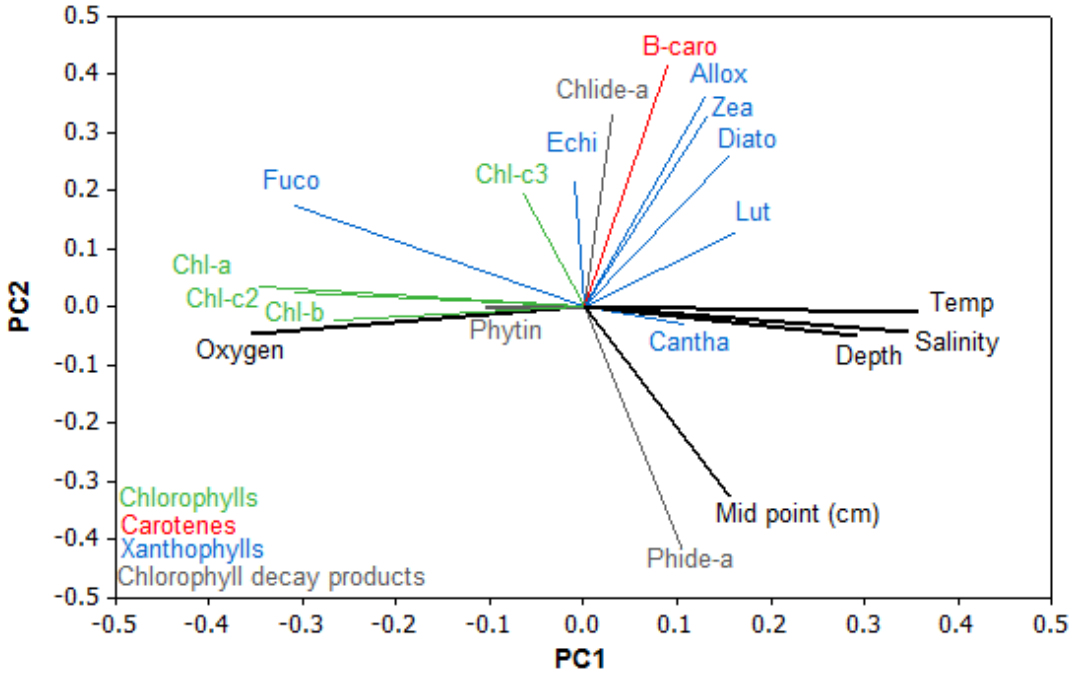


Figure 35. PCA approach 1: Loading plot showing the PC1 and PC2 factor coefficients of individual pigments (variables: site conditions only). For comparison of absolute values, see Figure 36.

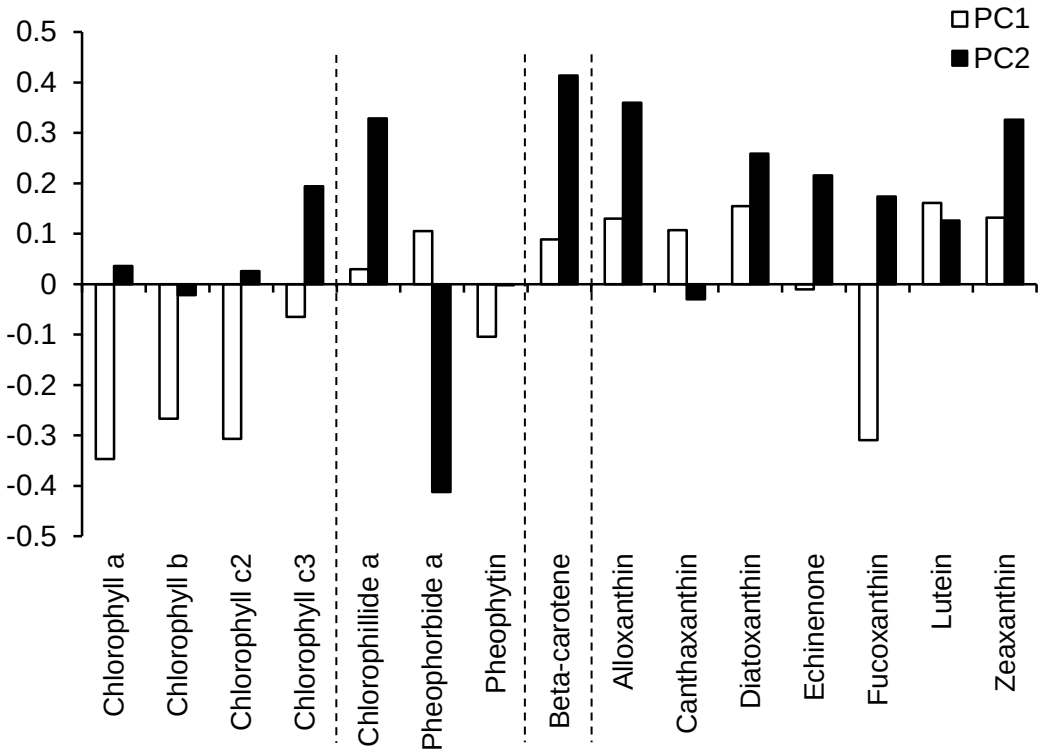


Figure 36. PCA approach 1: PC1 and PC2 factor coefficients all pigments in order of chlorophylls, their degradation products, carotenes, and xanthophylls (variables: site conditions only).

4.3.3.2. PCA Approach 2: 5 Sites, Sediment Geochemistry And Texture

A second PCA was needed to be able to assess the influence of sediment geochemistry and textural conditions on pigment suites, for which data was not available for the site at 60 m. This principal component analysis of five sites revealed scores that separated sites along the PC1 axis, which accounted for 33.3 % of the variance (Figure 37).

Again, the 45 m site had the most negative PC1 scores, and displayed larger ranges in PC1 which increased (positively) downcore. The remaining sites had higher scores along this axis and displayed similar ranges in PC1 scores. Like with PCA1, negative PC1 scores were a function of increasing oxygen concentrations and the "transitional" site at 75 m is sat amongst the anoxic sites (Figure 37). Again, negative PC1 scores were also aligned with total concentrations of chlorophyll-a, chlorophyll-b, chlorophyll-c_2, and fucoxanthin. Similarly, sites were not fully separated over the PC2 axis, which accounted for 18.6 % of the variance, and displayed similar ranges to each other. However, the anoxic 210 m site was mostly separated from the other transitional and anoxic sites, due to sediment textural properties (Figure 35). Negative PC2 scores were a function of % clay and % silt, whereas positive PC2 scores were a function of % sand.

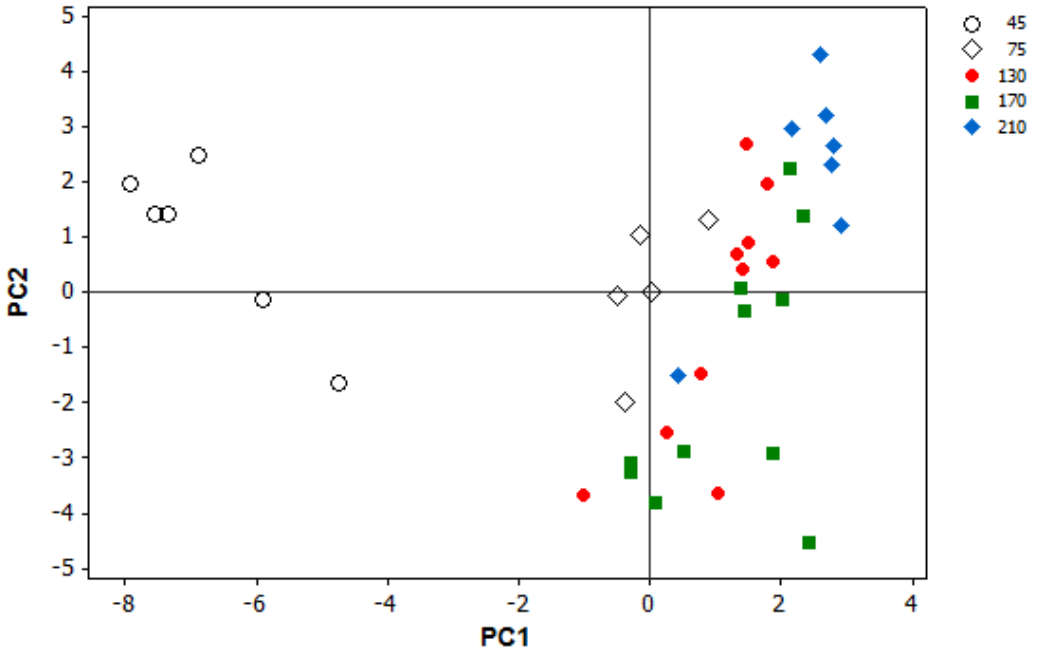


Figure 37. Results of the PCA approach 2: sample PC1 and PC2 scores.

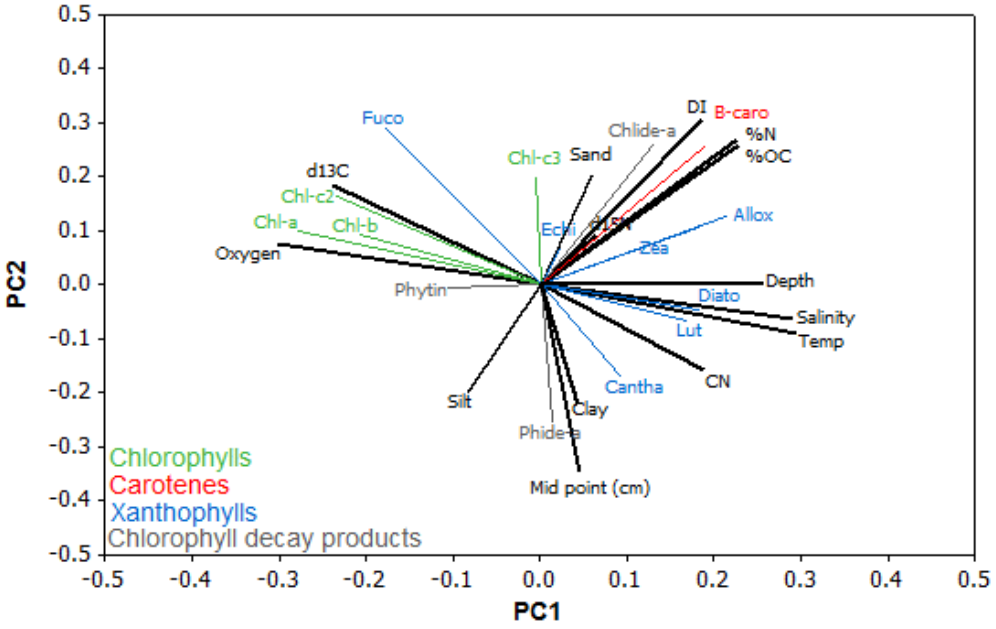


Figure 38. PCA approach 2: Loading plot showing the PC1 and PC2 factor coefficients of individual pigments (variables: site conditions, sediment geochemistry and textural properties). For comparison of absolute values, see Figure 39.

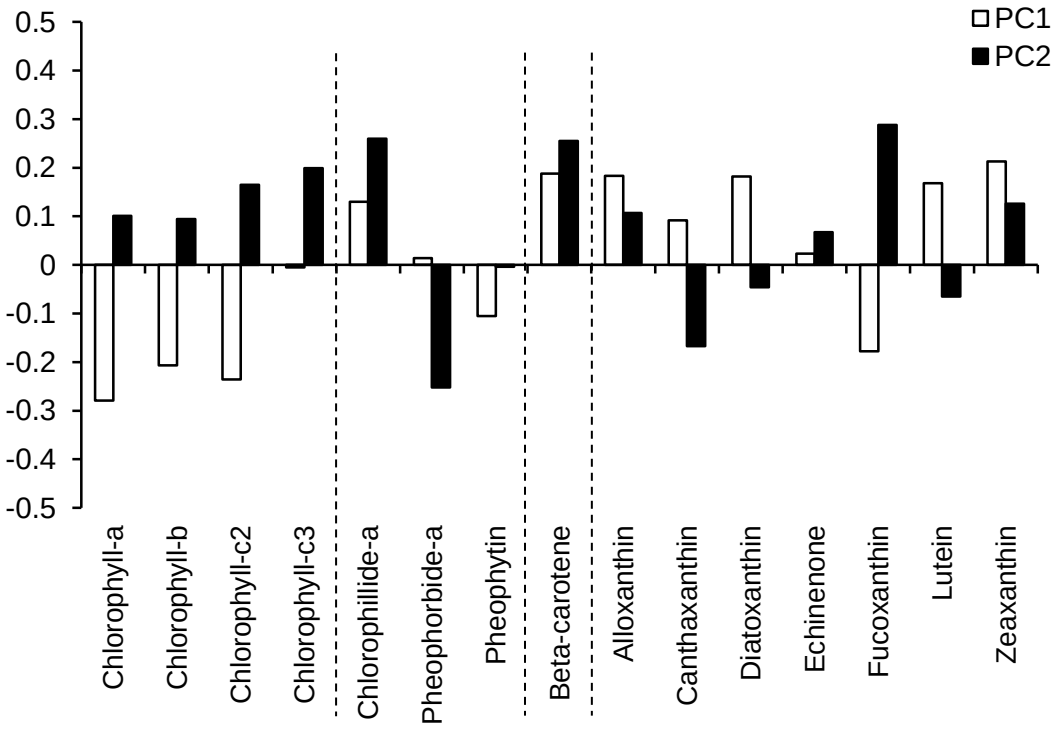


Figure 39. PCA approach 2: PC1 and PC2 factor coefficients all pigments in order of chlorophylls, their degradation products, carotenes, and xanthophylls (variables: site conditions, sediment geochemistry and textural properties).

4.3.4. Pigment Correlations

Two correlation analyses were conducted, with downcore pigment data ($P \leq 0.01$) and also with surficial ($P \leq 0.05$) pigment and environmental concentrations. Different significance levels were used due to the averaging effect of surface sediments to assess cross-margin trends.

4.3.4.1. Inter-Pigment Correlations

Surface total pigment concentrations correlated positively to a few key pigments (Table 11): pheophorbide-a ($\rho = 0.99$), beta-carotene ($\rho = 0.98$), diatoxanthin ($\rho = 0.96$), lutein ($\rho = 0.94$), fucoxanthin ($\rho = 0.93$), and zeaxanthin ($\rho = 0.90$) (all at $P \leq 0.05$). Similarly, some of the xanthophylls were significantly positively correlated to each other with strong relationships: e.g. between lutein and zeaxanthin ($\rho = 1.00$), alloxanthin and zeaxanthin ($\rho = 0.97$), lutein and diatoxanthin ($\rho = 0.97$) (all at $P \leq 0.05$). Chlorophyll-a and chlorophyll–b were strongly correlated to each other ($\rho = 098$, $P \leq 0.05$). Significant strong negative correlations were found between echinenone and canthaxanthin, diatoxanthin, fucoxanthin and pheophorbide-a, which may be an artefact of very low echinenone concentrations across the region.

Downcore correlations were similar to surface correlations. Downcore, total pigment concentrations correlated positively with the majority of pigments, but more strongly with carotenoids and pheopigments (Table 12): e.g. beta-carotene ($\rho = 0.96$), pheophorbide-a ($\rho = 0.95$), zeaxanthin ($\rho = 0.93$), lutein ($\rho = 0.87$), diatoxanthin ($\rho = 0.86$), alloxanthin ($\rho = 0.78$) and fucoxanthin ($\rho = 0.78$), and (all at $P \leq 0.01$). Both beta-carotene and pheophorbide-a concentrations were significantly positively correlated with all xanthophylls except echinenone, which was either absent or found in minor concentrations across the region.

Similarly, many xanthophylls were positively correlated to each other, with strong relationships between alloxanthin, diatoxanthin, lutein and zeaxanthin ($\rho = 0.73–0.94$). While chlorophyll-a and chlorophyll–b were strongly correlated to each other in the surface sediments ($\rho = 0.98$, $P \leq 0.05$), this correlation weakened downcore ($\rho = 0.67$, $P \leq 0.01$), Additionally, while chlorophyll-c3 and canthaxanthin were significantly positively correlated to each other at the surface ($\rho = 1.00$, $P \leq 0.05$), this relationship was not as strong downcore ($\rho = 0.56$, $P \leq 0.01$.)

Table 11. Surface sediment pigment correlation coefficient matrix using Pearson's product-moment correlation. Coefficients in bold and blue shading are significant at the 0.05 level (2-tailed).

	Chl-a	Chl-b	Chl-c_2	Chl-c_3	B-caro	Allox	Cantha	Diato	Echi	Fuco	Lut	Zeax	Chlide	Phide	Phytin
Chl-b	**0.98**														
Chl-c_2	0.09	0.11													
Chl-c_3	0.75	-	0.55												
B-caro	0.46	-	0.99	-0.24											
Allox	-0.52	-0.87	0.54	-0.96	0.72										
Cantha	0.67	-	-0.42	**1.00**	0.83	0.38									
Diato	-0.64	-0.62	0.76	-0.01	0.86	0.78	0.52								
Echi	-0.62	-	-	-	-0.96	-0.49	**-1.00**	**-1.00**							
Fuco	0.39	0.26	0.74	**0.97**	0.95	0.49	0.93	0.74	**-1.00**						
Lut	-0.62	-0.61	0.82	-0.05	0.81	0.75	0.43	**1.00**	-1.00	0.72					
Zeax	-0.58	-0.73	0.56	-0.75	0.94	**0.97**	0.67	**0.89**	-0.81	0.66	0.86				
Chlide	0.83	-	0.14	-0.97	0.62	0.91	0.49	0.24	-0.45	0.43	0.21	0.80			
Phide	0.05	-0.06	0.84	0.86	0.92	0.63	0.72	**0.94**	**-1.00**	**0.92**	**0.94**	0.79	0.26		
Phytin	0.57	-	-0.80	-0.08	-	-	-	-	-	-0.25	-	-	-	-0.55	
Total	0.05	-0.10	0.82	0.89	**0.98**	0.77	0.78	**0.96**	-0.99	**0.93**	**0.94**	**0.90**	0.44	**0.99**	-0.41

Table 12. Downcore pigment correlation coefficient matrix using Pearson's product-moment correlation. Coefficients in bold and grey shading are significant at the 0.01 level (2-tailed).

	Chl-a	Chl-b	Chl-c_2	Chl-c_3	B-caro	Allox	Cantha	Diato	Echi	Fuco	Lut	Zeax	Chlide	Phide	Phytin
Chl-b	**0.67**														
Chl-c_2	0.30	0.12													
Chl-c_3	0.49	0.74	0.38												
B-caro	**0.69**	0.88	**0.69**	**0.79**											
Allox	0.29	-0.57	0.42	-0.04	**0.68**										
Cantha	**0.78**	0.86	0.47	0.56	**0.69**	**0.47**									
Diato	0.17	-0.33	0.39	0.53	**0.82**	**0.75**	**0.41**								
Echi	0.10	-0.30	0.00	-	-0.02	0.21	-0.04	0.01							
Fuco	**0.49**	0.39	**0.54**	**0.89**	**0.82**	0.28	**0.71**	**0.44**	0.04						
Lut	0.13	-0.27	**0.55**	0.43	**0.81**	**0.73**	**0.44**	**0.94**	-0.18	**0.47**					
Zeax	0.30	-0.34	0.49	**0.62**	**0.93**	**0.86**	**0.67**	**0.86**	-0.05	**0.60**	**0.85**				
Chlide	**0.58**	0.90	0.53	**0.88**	**0.71**	0.23	**0.60**	0.23	0.01	**0.84**	0.31	**0.63**			
Phide	**0.42**	0.08	**0.68**	0.34	**0.81**	**0.75**	**0.59**	**0.79**	-0.08	**0.59**	**0.85**	**0.82**	0.38		
Phytin	0.37	-0.42	-0.23	0.12	0.08	0.17	0.13	0.05	0.00	0.21	-0.02	0.04	0.26	-0.07	
Total	**0.48**	0.13	**0.66**	**0.66**	**0.96**	**0.78**	**0.70**	**0.86**	-0.06	**0.78**	**0.87**	**0.93**	**0.70**	**0.95**	0.05

4.3.4.2. Pigment-Environment Correlations

Surface total pigment concentrations correlated positively to depth (ρ = 0.95), salinity (ρ = 0.94), temperature (ρ = 0.87), %N (ρ = 0.94), and degradation index (DI) (ρ = 0.89) (P ≤ 0.05) (Table 13). Fucoxanthin was the only pigment that showed the a significant positive correlation with the same environmental conditions. While oxygen concentration did not have a significant correlation with total pigment concentrations, it did have significant negative correlations with chlorophyllide-c_3 (ρ =-0.97), canthaxanthin (ρ =-0.97) and fucoxanthin (ρ =-0.83) (P ≤ 0.05). The same pigments, and pheophorbide-a, showed negative relationships with surface sediment $\delta^{13}C$. Alloxanthin showed a correlation with sediment texture: negative with % silt (ρ =-0.95), and positive with % sand (ρ = 0.95) (P ≤ 0.05). There were no significant correlations between pigments and surface %OC, % clay or C:N ratios. Fucoxanthin and total pigment concentrations displayed significantly strong positive relationships with the degradation index of organic carbon (DI): ρ = 0.93, and 0.89 respectively.

Correlations between sediment geochemical parameters were also calculated, to check for inter-correlation between multiple variables across the margin (Table 14). Notable correlations include a significant negative relationship between oxygen concentrations and degradation state (ρ =-0.94), and a positive correlation between surface nitrogen contents and degradation state (ρ = 0.98, P ≤ 0.05).

Downcore correlations were similar to cross margin correlations, but more significant (Table 15). At the 1 % significance level, total pigment concentrations were strongly positively correlated with %OC (ρ = 0.90), %N (ρ = 0.89) and DI (ρ = 0.83) and weakly negatively with downcore depth (mid-point, ρ =-0.52). All individual pigments displayed negative correlations with increasing sediment depth, but only beta-carotene showed a strong correlation (ρ =-0.73). Significant correlations were observed between individual pigments and %OC, %N and DI. The strongest correlations with %OC were beta-carotene, alloxanthin, zeaxanthin, and pheophorbide-a (ρ = 0.77–0.95), despite a lack of significant surface sediment relationships with %OC. The same pigments showed the strongest relationships with %N downcore (ρ = 0.76–95). With the addition of diatoxanthin, the same pigments presented significantly strong positive relationships with downcore degradation indices (ρ = 0.71–90). There were no significant correlations between any pigments and downcore $\delta^{15}N$ or C:N ratios.

Correlations between sediment geochemical parameters were also calculated, to check for inter-correlation between multiple variables downcore (Table 16). %OC and %N contents tracked each other down core ($\rho = 1.00$) ($P \leq 0.01$). the degradation state of organic matter (DI) was also significantly correlated to both %OC and %N ($\rho = 0.88$) ($P \leq 0.01$).

Table 13. Surface sediment pigments environmental variable correlation coefficient matrix using Pearson's product-moment correlation. Coefficients in bold and blue shading are significant at the 0.05 level (2-tailed).

	Depth	O_2	Salinity	Temp	%Clay	%Silt	%Sand	$\delta^{13}C$	$\delta^{15}N$	%OC	%N	C:N	DI
Chl-a	-0.00	-0.20	0.02	0.09	-0.03	-0.33	0.27	-0.74	-0.54	0.38	0.82	0.24	0.83
Chl-b	-0.20	0.06	-0.25	-0.20	-0.17	-0.36	0.26	-0.12	**1.00**	0.36	0.33	0.15	0.14
Chl-c_2	0.81	-0.64	0.63	0.54	-0.35	-0.65	0.61	-0.62	0.16	0.10	0.77	0.64	0.68
Chl-c_3	0.78	**-0.97**	**0.95**	**0.98**	0.47	0.02	-0.10	**-0.99**	-0.20	0.81	0.89	0.90	0.92
B-caro	**0.96**	-0.89	0.94	0.70	-0.53	-0.54	0.54	-0.80	0.54	-0.00	0.93	0.11	0.88
Allox	**0.92**	-0.81	**0.88**	0.79	-0.95	**-0.95**	**0.95**	-0.28	-0.08	-0.66	0.88	-0.52	0.85
Cantha	0.69	**-0.97**	0.93	**0.96**	-0.08	-0.09	0.09	**-0.99**	0.41	0.44	0.77	0.12	0.79
Diato	**0.88**	-0.74	0.83	0.71	-0.46	-0.47	0.47	-0.52	0.81	-0.04	0.68	0.46	0.53
Echi	-0.85	0.96	-0.94	-1.00	0.26	0.27	-0.27	0.99	-0.77	-0.34	-0.82	-0.34	-0.79
Fuco	**0.82**	**-0.83**	**0.87**	**0.86**	0.13	-0.25	0.18	**-0.93**	0.00	0.65	**0.94**	0.77	**0.93**
Lut	0.87	-0.68	0.77	0.64	-0.48	-0.49	0.49	-0.44	0.80	-0.10	0.63	0.46	0.47
Zeax	**0.96**	-0.86	**0.96**	0.87	-0.78	-0.79	0.78	-0.60	0.29	-0.33	**0.98**	-0.17	0.92
Chlide	0.76	-0.70	0.74	0.57	-0.79	-0.79	0.79	-0.31	-0.32	-0.51	0.85	-0.72	0.91
Phide	**0.90**	-0.74	**0.88**	0.80	0.02	-0.32	0.26	**-0.82**	0.25	0.55	0.87	0.78	0.82
Phytin	-0.31	0.00	-0.04	0.07	0.06	0.36	-0.21	0.03	-0.97	-0.13	-0.05	-0.50	-0.05
Total	**0.95**	-0.8	**0.94**	**0.87**	-0.019	-0.382	0.318	-0.88	0.09	0.53	**0.94**	0.74	**0.89**

Table 14. Cross margin surface sediment geochemistry correlation coefficient matrix using Pearson's product-moment correlation. Coefficients in bold and blue shading are significant at the 0.05 level (2-tailed).

	Depth	O_2	Salinity	Temp	%Clay	%Silt	%Sand	$\delta^{13}C$	$\delta^{15}N$	%OC	%N	C:N
O_2	**-0.70**											
Salinity	**0.93**	**-0.85**										
Temp	0.81	**-0.95**	**0.96**									
%Clay	-0.32	-0.29	0.05	0.28								
%Silt	-0.64	0.15	-0.34	-0.15	**0.90**							
%Sand	0.59	-0.07	0.27	0.07	**-0.93**	**-1.00**						
$\delta^{13}C$	-0.77	**0.98**	**-0.95**	**-0.99**	-0.30	0.13	-0.05					
$\delta 1^{5}N$	-0.03	0.40	-0.20	-0.34	0.00	0.18	-0.14	0.28				
%OC	0.26	-0.63	0.57	0.69	0.82	0.57	-0.63	-0.71	0.08			
%N	**0.95**	-0.87	**0.99**	**0.93**	-0.09	-0.48	0.41	**-0.92**	-0.25	0.44		
C:N	0.50	-0.81	0.67	0.75	0.54	0.19	-0.26	-0.82	0.14	0.80	0.62	
DI	0.87	**-0.94**	**0.98**	**0.97**	0.06	-0.36	0.29	**-0.97**	-0.36	0.52	**0.98**	0.68

Table 15. Downcore pigment and sediment geochemistry correlation coefficient matrix using Pearson's product-moment correlation. Coefficients in bold and grey shading are significant at the 0.01 level (2-tailed).

	Mid-point	$\delta^{13}C$	$\delta^{15}N$	%OC	%N	C:N	DI
Chl-a	**-0.47**	0.11	0.17	**0.65**	**0.65**	0.05	**0.61**
Chl-b	-0.35	-0.23	-0.10	0.18	0.23	0.01	0.20
Chl-c_2	**-0.58**	-0.20	0.46	**0.59**	**0.58**	0.41	0.47
Chl-c_3	-0.46	-0.53	-0.14	0.53	0.55	0.13	0.54
B-caro	**-0.73**	-0.01	0.05	**0.89**	**0.88**	0.09	**0.81**
Allox	**-0.48**	**0.53**	0.36	**0.77**	**0.76**	-0.12	**0.72**
Cantha	-0.26	0.17	-0.01	**0.69**	**0.69**	0.01	**0.66**
Diato	**-0.48**	0.20	0.32	**0.74**	**0.72**	0.05	**0.72**
Echi	-0.32	0.24	-0.14	-0.28	-0.27	0.00	0.02
Fuco	**-0.61**	-0.38	0.01	**0.68**	**0.69**	0.21	**0.62**
Lut	**-0.41**	0.27	0.31	**0.73**	**0.71**	0.01	**0.66**
Zeax	**-0.54**	0.34	0.16	**0.95**	**0.95**	-0.18	**0.90**
Chlide	**-0.61**	-0.19	-0.49	**0.57**	**0.61**	-0.39	**0.65**
Phide	**-0.47**	-0.05	0.34	**0.80**	**0.77**	0.27	**0.71**
Phytin	-0.11	0.09	-0.09	0.07	0.08	-0.05	-0.09
Total	**-0.52**	-0.09	0.26	**0.90**	**0.89**	0.21	**0.83**

Table 16. Downcore sediment geochemistry correlation coefficient matrix using Pearson's product-moment correlation. Coefficients in bold and grey shading are significant at the 0.01 level (2-tailed).

	$\delta^{13}C$	$\delta^{15}N$	%OC	%N	C:N
$\delta^{15}N$	0.09				
%OC	-0.25	0.29			
%N	-0.24	0.26	**1.00**		
C:N	**-0.54**	0.26	0.27	0.22	
DI	-0.16	0.21	**0.88**	**0.88**	0.14

4.3.5. Extraction Solvent Comparison

While ethanol was the only extraction solvent available at sea, a comparative extraction was performed on freeze-dried sediments (from 45 m water depth) using acetone. Overall, concentrations of both total and individual pigments in the surface sediment were comparable (Figure 40). However, where ethanol was used as a solvent, no pigments were extracted below the 4 cm sediment depth, whereas acetone extracted pigments to the base of the core (Figure 41A). Ethanol-extracted sediments yielded seven different pigments (chlorophyll-a, chlorophyll-c_2, chlorophyll-c_3, fucoxanthin, pheophorbide-a, pheophytin), none of which were found below 4 cm sediment depth. Acetone extraction measured concentrations of 14 individual pigments (only chlorophyllide-a was not found), many to the full core depth.

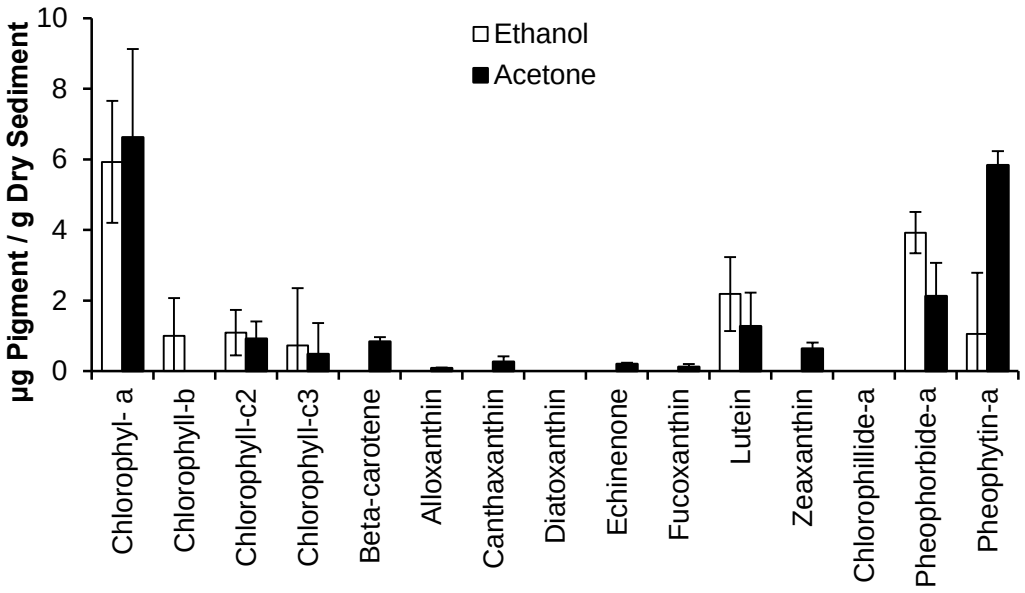


Figure 40. Comparison of average pigment concentrations in the surface sediments (0–3 cm) at the Balti Sea 45 m site using different extraction solvents; ethanol vs. acetone (error bars represent range, n=2)

Chlorophyll-a concentrations displayed similar surface sediment trends irrespective of solvent choice but became undetectable below 4 cm in ethanol (Figure 41B). While the other chlorophylls (b, c_2 and c_3) also showed similar profiles for ethanol and acetone, low concentrations were measured and are therefore not shown here.

Two derivatives of chlorophyll-a were found at the 45 m site, under both extraction methods: pheophytin-a and pheophorbide-a. Greater concentrations of pheophytin

were measured when acetone was used as the extraction solvent, both in the surface sediments and downcore (Figure 41C). Pheophytin was found in increasing concentrations down-core when extracted with acetone but only found in top 1 cm when extracted with ethanol. Greater concentrations of pheophorbide-a were measured in surface sediments extracted with ethanol than with acetone, but only acetone extracted pheophorbide-a at intervals greater than 4 cm sediment depth. (Figure 41D). Chlorophyllide-a was not extracted from sediments with either ethanol or acetone, and thus is presumed to not be present.

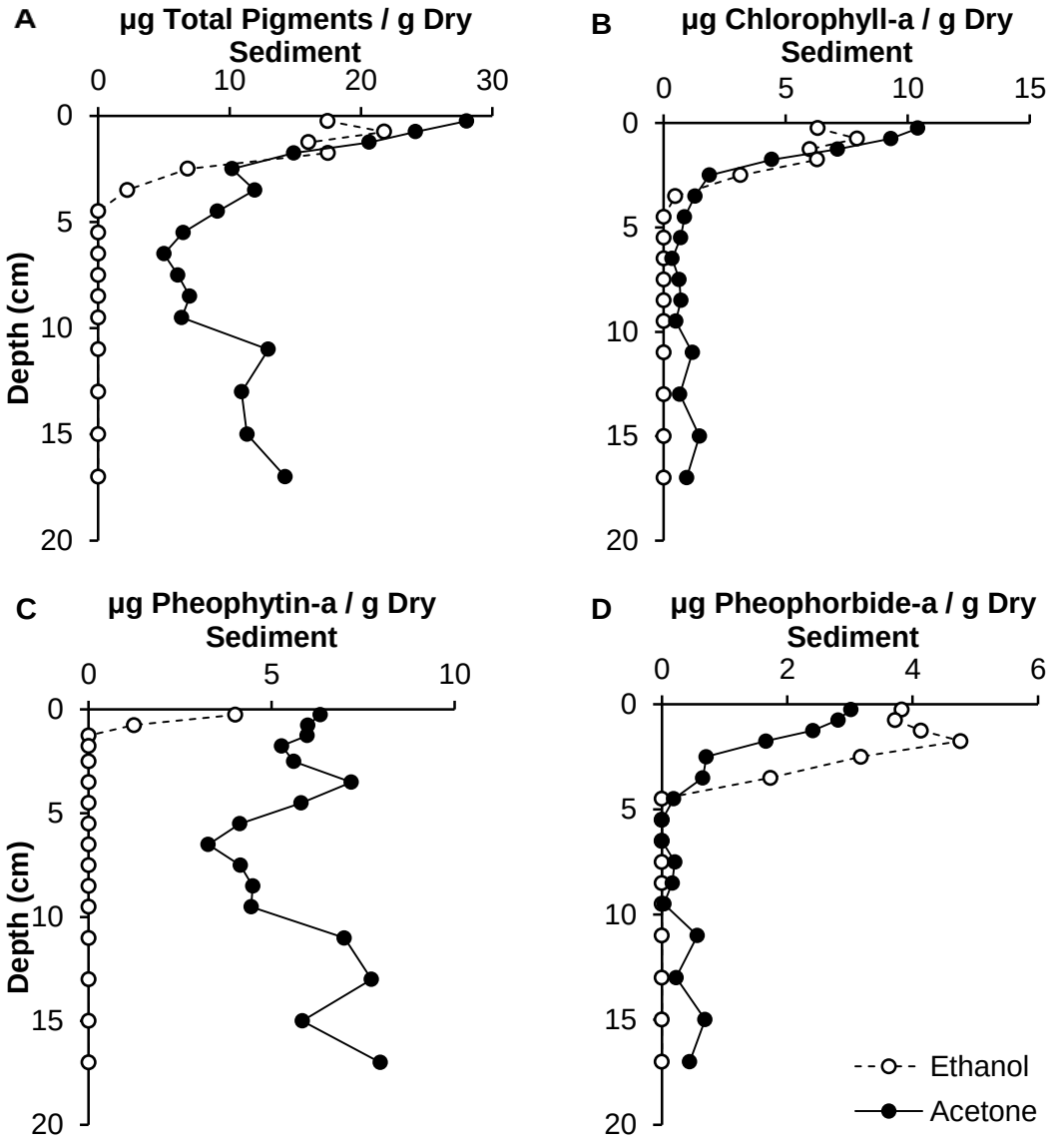


Figure 41. Down-core pigment concentrations at the Baltic Sea 45 m site using different extraction solvents: A: total pigments, B: chlorophyll-a, C: pheophytin-a, D: pheophorbide-a.

4.3.6. Pheopigment:Chlorophyll-A Ratios

The pheopigment:chlorophyll-a ratios compare the abundance of chlorophyll-a with its observed decay product, pheophorbide, allowing an assessment of degradation state of the sediments. Simply put, lower values can indicate fresh sedimentary pigment material, while higher values can indicate more degraded material. However, higher ratios may also be the result of pheophorbide accumulation and preservation in the sediment, following the degradation of available chlorophyll-a. It is also important to note that pheophorbide may also be degraded further to pheophytin, and then to colourless compounds, neither of which were resolved in this study.

Across the Gotland Basin, pheophorbide-a:chlorophyll-a ratios ranged from 1 to 27 and zero values were reported where either or both pigments were not detected (*Figure 42* and Figure 43). Highest ratios were found in sediments at the anoxic sites at 210 m and 170 m water depth. Averaged pheophorbide-a:chlorophyll-a ratios (over the surficial 3 cm of sediment) were ranged from 0.7 at the shallow oxygenated 45 m site to 13–15 at the 170 m and 210 m sites (*Figure 42*). At 45 m, 60 m, 75 m, and 130 m, pheophorbide-a:chlorophyll-a ratios increased downcore, indicating greater degradation at depth (Figure 43). Conversely, ratios appeared to decreased downcore at 170 m, and there was large downcore variability, but no trend, at 210 m water depth. These trends are not as expected, as fresh organic matter is thought to accumulate in anoxic sediments and degrade more slowly than in the presence of oxygen. However, pheophytin was not resolved in ethanol in this study (see 4.3.5), meaning that a major pheopigments may be missing from the analysis. It is thought that the inability to resolve both pheopigments in the same extraction process has resulted in unusual ratios. However, as a solvent comparison was only performed on one core, it is not possible to conclude either way if the ratios are an artefact of solvent issues or of degradation processes.

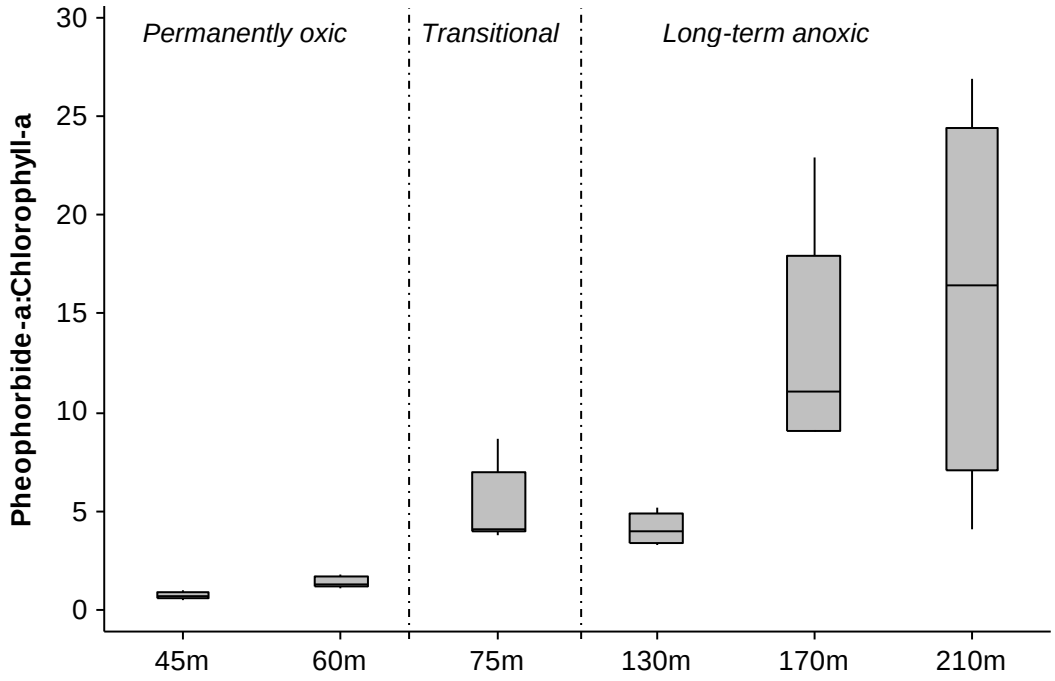


Figure 42. Box plot of surface sediment pheophorbide-a:chlorophyll-a ratios across the Gotland Basin of the Baltic Sea.

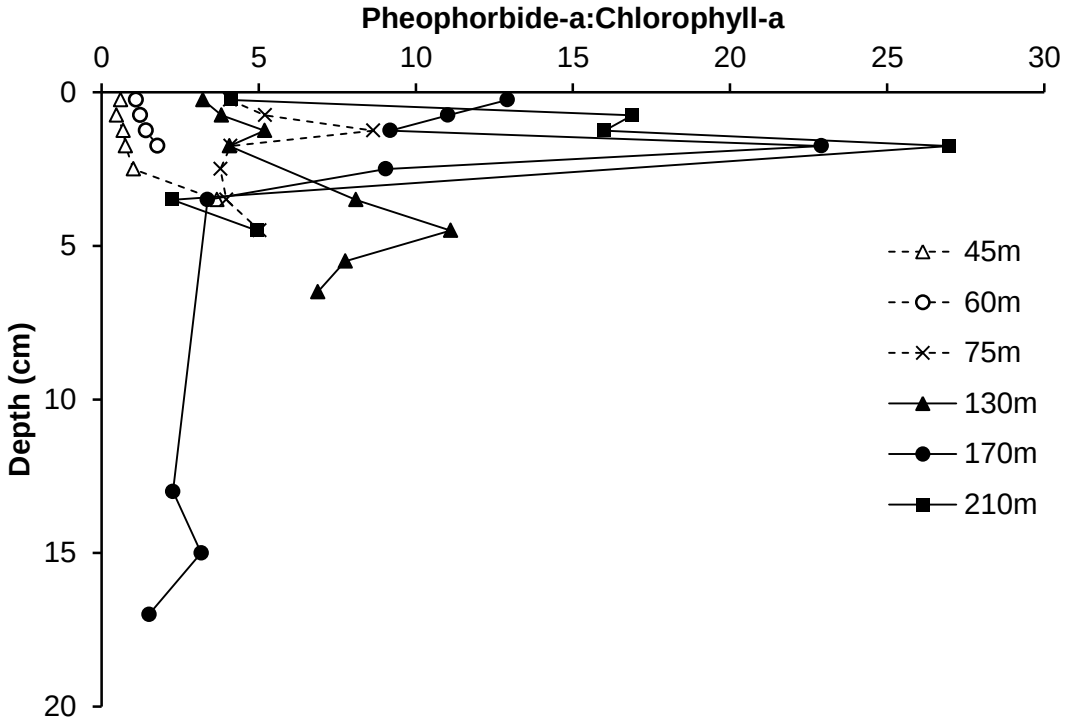


Figure 43. Downcore pheophorbide-a:chlorophyll-a ratios across the Gotland Basin of the Baltic Sea.

4.3.7. Decay Experiments

Decay experiments were conducted to assess the current degradation state of and potential for further decay of pigments in sediments from three sites in the Gotland basin (60, 130 and 210 m). Sediments were sub-sampled over 8-10 days, to measure any changes in pigment suite across the experiment. The full methodology is detailed in Chapter 3: Materials and Methods.

Surface samples, including the fluff layer, yielded greatest concentrations of total pigments at all three sites (Figure 44). At the 60-m site, total pigment concentrations in the 0–1 cm interval were more than double those in the 1–2 cm interval throughout the duration of the experiment (Figure 44a). Similarly at the 130-m site, total pigment concentrations in the fluff layer were significantly higher than those in samples from down-core intervals (Figure 44b). No temporal trend was observed at any depth interval. At the deepest site, at 210 m, total pigment concentrations generally decreased down-core at all time-points (Figure 44c). The lack of temporal trends in any experiment, except 210 m, indicates that the organic matter at these sites is already heavily degraded.

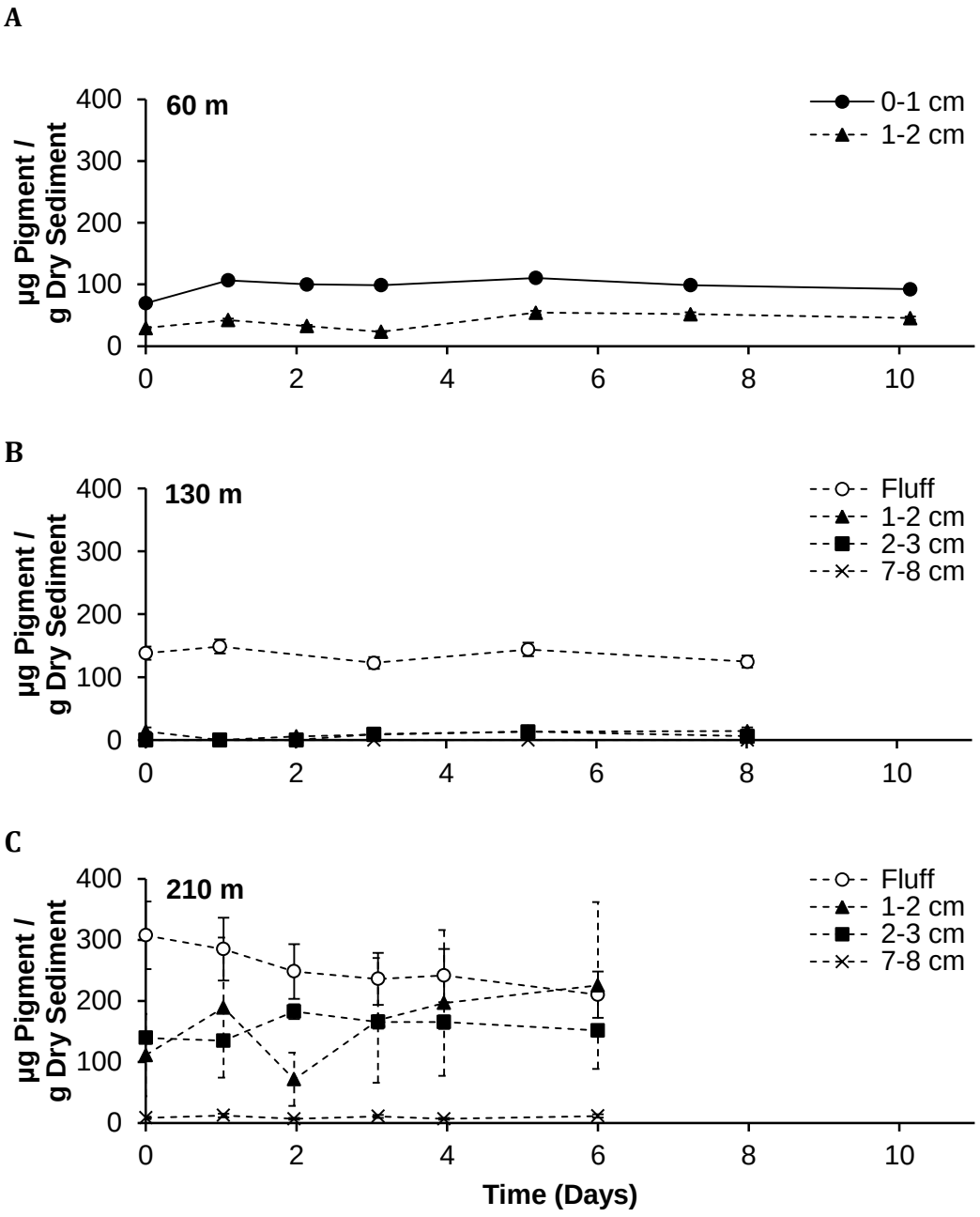


Figure 44. Temporal trends in total pigment concentrations at the 60 m (A), 130 m (B) and 210 m (C) sites. Of the Gotland Basin, Baltic Sea. Error bars represent the range, n= 2.

4.4. Discussion

4.4.1. Limitations

Aside from the limitations that arose from the availability of an extraction solvent at sea (ethanol), several other limitations should be acknowledged. It has been observed that freeze-drying of sediments before extraction (as was done here with acetone extractions), can reduce the pigment concentrations in sediments by an average of 60 % (Riaux-Gobin et al., 1987). Pigments are typically found in low concentrations, and in many isomeric forms which make them difficult to analyse. Furthermore, co-elution of compounds during chromatography means misidentification or incorrect quantification is possible. Given this risk, only standard-checked pigments were reported in this study to avoid misidentification of compounds. As discussed previously, pigments are sensitive to light, heat and oxygen, which makes handling during extraction and quantification difficult.

4.4.2. Summary Of Results

Pigment concentrations displayed high variability within the surface sediments (0–3 cm). Average total pigments varied across the Gotland basin from 15 ± 5.5 to 265 ± 107 μg /g dry sediment. Maximal values were observed at sites with long-term anoxic bottom-waters and the highest organic carbon contents. Lowest concentrations were found at shallow sites with the high bottom-water oxygen concentrations and low organic carbon contents. Individual pigments largely showed the same cross-margin pattern.

The chlorophyll-a concentrations observed here are an order of magnitude higher than those observed by Bianchi et al. (2002) in Baltic Seston sediments. Chlorophylls contributed 37–54 % of the total surface pigments in the oxic shallow sites. This is in line with previous findings that chlorophyll-a can represent 20–70 % of sedimentary pigments in relatively shallow environments (Sun et al., 1994). The surficial carotenoid concentrations found at the anoxic sites are similar to those observed by Łotocka et al. (2004) at 90 m water depth in the Gotland Basin. The concentrations here are much higher than those found in eastern Mediterranean sediments (Bianchi et al., 1996), and an order of magnitude lower than pigment concentrations reported on the Peru continental shelf (Repeta and Gagosian, 1987).

All pigments were found to decrease with increasing sediment depth, irrespective of pigment stability. These findings are in line with rapid downcore pigment loss in previous studies (Abele-Oeschger, 1991; Łotocka et al., 2004; Woulds and Cowie, 2009). Notable sub-surface peaks were observed at the 170 m site.

At the anoxic sites, pheopigments dominated the surface sediment pigment suites (32–37 %). At the oxygenated sites, 45 and 60 m, chlorophylls dominated the surface sediments (37–54 %). At the transitional site, 75 m, xanthophylls were the most abundant pigment group (42 %). The dominance of pheopigments at the deepest sites is in line with previous findings of in the Gotland Deep and the Gdansk deep (Kowalewska et al., 1999). Similarly while intact pigments were missing, large abundances of pheopigmens were observed on the Oman margin of the Arabian Sea (Shankle et al., 2002).

Significant positive relationships were seen between several carotenoids, both in the surface sediments and downcore. Total surface pigment correlations were positively correlated to depth, temperature, salinity, %N and DI. Only alloxanthin displayed any correlation with sediment texture. Downcore concentrations of individual pigments were generally correlated positively with %OC, %N and DI.

The only temporal trend observed during the decay experiments was a decrease in total pigments in the fluff layer from 210 m.

Acetone extraction yielded a greater number, and concentration, of individual pigments than ethanol-extraction. While surface sediment concentrations of pigments were comparable in the two different extraction solvents, ethanol and acetone, down-core trends were markedly different. Pheophytin was not resolved in ethanol but large concentrations were extracted using acetone. This clearly limits the extent to which the pigment data can be interpreted confidently.

Pheophorbide-a:chlorophyll-a ratios were highest at the deep anoxic sites. At the shallow oxygenated sites and at 130 m depth, ratios increased downcore, indicating greater degradation at depth downcore. Conversely, ratios appeared to decrease with sediment depth at the 170 m site. Given the issues raised by the comparison of solvent extraction methods, these ratios should be interpreted with care.

4.5. Pigments Suites And Sources

The suite of sedimentary pigments can be used to indicate the source and diagenesis history of organic matter in marine sediments. The presence of chlorophylls, especially chlorophyll-a, is proxy for algal productivity in the water column. In combination with their known degradation products, pheopigments, chlorophylls may also indicate freshness and/or degradation state of sedimentary organic matter. Accessory pigments, such as the carotenoids, often display taxonomic specificity and can be used as biomarkers for specific algal groups, and thus, sedimentary organic matter source. However, caution is required when interpreting pigment suites. The organic matter than arrives at the sediment may have been degraded in the water column (e.g. zooplankton grazing), or undergone decay upon burial in the sediments. Thus, the pigment suites observed in marine sediments are not always an equivalent representation of the pigments initially produced, or those that arrived at the sediment-water interface.

Across the Gotland Basin, pheophorbide–a dominated the pigment suites at all sites except at 45 m. In general, minor contributions were also made by chlorophyll-a and several carotenoids, including beta-carotene, diatoxanthin, fucoxanthin, lutein and zeaxanthin. The importance of these carotenoids is similar to those observed by Łotocka et al. (2004) at 90 m in the Gotland Basin: fucoxanthin and zeaxanthin. At 45 and 60 m, chlorophyll-a represented 35.8 ± 4.7 % of the total pigments. This in agreement with previous findings that chlorophyll-a is a major component of pigment suites in shallow settings, representing 20–70 % of pigments (Sun et al., 1994). However, the low chlorophyll-a concentrations compared to pheopigments implies that there has been advanced decay of the sedimentary organic matter. Pheophorbide and pheophytin can indicate grazing by phytoplankton and/or zooplankton in water column before sedimentary deposition (Shuman and Lorenzen, 1975; Bianchi et al., 2000), and the pheopigments that is ultimately produced has been shown to be species-specific (Louda et al., 1998). Aside from the limitation here that pheophytin was not resolved in ethanol, and thus at all sites, the use of pheopigments as grazing indicators has been questioned (Villanueva and Hastings, 2000; Louda et al., 2002). Chlorophyll decay to pheopigments has been observed in the absence of zooplankton or phytoplankton grazing, and is thought to also be produced as a result of microbial decay and cell lysis (Villanueva and Hastings, 2000; Louda et al., 2002). The significant

contribution of pheophorbide to the pigment suites, especially at the anoxic sites, strongly suggests that there has been water column herbivory before deposition.

Due to the taxonomic specificity of many carotenoids, they can be used to indicate organic matter source (Bianchi et al., 1996). In this study, the dominant carotenoids were beta-carotene, diatoxanthin, fucoxanthin, lutein and zeaxanthin. Beta-carotene and diatoxanthin are both present in trace amounts in many algal classes, and thus not hugely useful biomarkers on their own (Jeffrey and Vesk, 1997).

The presence of fucoxanthin is thought to indicate diatom biomass, and lutein is a common marker for green algae (Wright and Jeffrey, 1987). Fucoxanthin, and to a smaller extent zeaxanthin, is also characteristic of crysophytes (golden algae) (Jeffrey and Vesk, 1997). Four families of crysophytes are known to inhabit the central basin of the Baltic Sea: *Dinobryon*, *Ollicola*, *Uroglena* and *Spumela* spp. (Hällfors, 2004). Fucoxanthin has a lower stability than many other carotenoids and has been shown to be rapidly degraded in the presence of grazing zooplankton, so its contribution to the pigment suite should be treated with caution (Repeta and Gagosian, 1982; Abele-Oeschger, 1991; Leavitt and Hodgson, 2001).

Zeaxanthin is indicative of red algae, picoplankton and cyanobacteria (Jeffrey and Vesk, 1997). While cyanobacterial blooms in the region are widespread, zeaxanthin is known to be present in *Aphanizomenon* sp. but not in *Nodularia* sp. (Bianchi et al., 2000a; Poutanen and Nikkila, 2001). While echinenone is almost unique to cyanobacteria, it can be less stable than zeaxanthin and so high zeaxanthin concentrations have been used to indicate cyanobacterial biomass in the Baltic Sea (Bianchi et al., 2000b; Bianchi et al., 2002; Łotocka et al., 2004). This is the case here, given that echinenone was either absent or found in small concentrations in the Gotland Basin sediments.

In summary, the pigment suites of the Gotland Basin sediments suggest relatively degraded organic matter. The high concentrations of pheophorbide-a alludes to substantial water column herbivory or sedimentary microbial decay. The dominance of fucoxanthin and zeaxanthin within the carotenoids indicates that cyanobacteria and diatoms are important organic matter sources to the region, with additional contributions from golden, green and red algae.

4.6. Controls On Pigment Distribution

Total pigments in the surface sediments were positively correlated with water depth ($\rho = 0.95$), salinity ($\rho = 0.94$), temperature ($\rho = 0.87$), total nitrogen ($\rho = 0.94$) and degradation index ($\rho = 0.89$) ($P \leq 0.05$) (Table 13). While not significant at the 5 % level, total pigments were strongly correlated with oxygen concentrations ($\rho = -0.80$). However, oxygen concentrations did significantly and negatively correlate with depth ($\rho = -0.70$), salinity ($\rho = -0.85$), temperature ($\rho = -0.95$) and DI ($\rho = -0.94$) ($P \leq 0.05$) (Table 14) – implying that the effect of redox conditions may be masked by other factors. Similar but stronger correlations were seen at depth within sediment cores. Downcore concentrations of total pigments correlated with %OC ($\rho = 0.90$), %N ($\rho = 0.89$), and DI ($\rho = 0.83$) ($P \leq 0.01$). The same significant correlations were observed for downcore concentrations of chlorophyll-a, chlorophyll-c_2, all carotenoids (except echinenone), chlorophyllide-a and pheophorbide-a. Echinenone was either absent from sediments, or not extracted in large enough quantities for analysis.

This opens the question of whether oxygen concentrations are the main driver for pigment distributions, as it is for total organic matter degradation state (DI), or one of the other environmental variables is primarily responsible.

4.6.1. Oxygen

Despite the historical debate surrounding effect of oxygen on organic matter preservation, it is generally accepted that the absence**,** or low concentration, of oxygen in bottom-waters promotes preferential organic matter accumulation and preservation in marine sediments (Canfield, 1989, 1994; Demaison and Moore, 1980; Paropkari et al., 1992; Thiede and Vanandel, 1977). It has been further clarified that "oxygen exposure time" is especially important and there are systematic relationships between organic matter concentrations, composition, degradation state and burial efficiency with increasing oxygen exposure time (e.g. Hartnett et al., 1998; Hedges et al., 1999; Keil and Cowie, 1999).

Total sedimentary pigments in this study showed negative relationships with bottom-water oxygen concentrations ($\rho = -0.80$). Total pigment concentrations were greatest at the anoxic and hypoxic sites, suggesting that the absence of oxygen is retarding pigment decomposition and/or enhancing total sedimentary pigment accumulation.

The lowest pigment concentrations occurred in sediments at the oxic sites where oxygen is likely to have increased the degradation of labile pigments arriving at the seafloor. All carotenoids, except echinenone, displayed strong negative correlations between surface pigment abundance and bottom water dissolved oxygen concentrations, ranging from ρ =-0.68 (lutein) to ρ =-0.97 (canthaxanthin, $P \leq 0.05$). Furthermore, the PCA of pigment suites revealed that the PC1 axis, which was indicative of oxygen concentrations, accounted for 33.3 % of the variance between sites. Lower (and negative) PC1 scores were associated with oxic sites, and thus the greater availability of oxygen.

However, chlorophyll-a concentrations did not show a strong negative relationship with oxygen across the area, as there was no systematic change in surficial chlorophyll-a abundances across the region.

Oxygen concentrations held significant negative correlations with sedimentary organic matter degradation state (ρ =-0.94, $P \leq 0.05$) implying that oxygen availability may play a key role in determining not just total pigment concentrations, but also the freshness of organic matter in the surface sediments. In laboratory incubations of both surface and buried sediments, Hulthe et al. (1998) assessed the degradation of both labile and refractory organic matter with and without oxygen. The study showed that the presence of oxygen significantly increased the degradation of refractory organic matter while labile organic matter degraded regardless of oxygen availability. Further laboratory incubations of anoxic muddy sediments in in the Baltic Sea (Kiel Bight, Germany) showed that sedimentary pigment decay rates were strongly influenced by oxygen concentrations, with faster decay occurring in oxygenated compared to anoxic sediments (Abele-Oeschger, 1991). The authors measured chlorophyll and carotenoid concentrations over several weeks and found that lutein exhibited greater stability against chemical and microbial breakdown than chlorophyll-a under oxic conditions. The trends observed here in the Gotland Basin support the observations made by Hulthe et al. (1998) and Abele-Oeschger (1991).

The relationships between oxygen concentration and pigment abundance were not as strong or as significant as expected. However, low oxygen availability, i.e. at the deep anoxic and hypoxic sites, appears to influence pigment distributions by increasing the accumulation of pigments in the sediments rather than by preventing the degradation

of more labile pigments (e.g. chlorophyll-a) at the sediment-water interface. The preferential preservation of pigments over total organic carbon in the absence of oxygen has previously been observed (King, 1994) and this explains the trends observed across the Gotland Basin. Furthermore, the effect of oxygen as control on organic matter distribution may be masked by other factors, which may also be interlinked, such as water depth, faunal re-working, organic matter source and sediment texture.

4.6.2. Organic Matter Content

Surface pigment concentrations did not systematically correlate with surficial sediment organic carbon contents. However, total pigment concentrations downcore did correlate with organic carbon contents ($\rho = 0.9$, $P \leq 0.01$), (Figure 45). This positive correlation was observed at all sites except at 45 m, where oxygen concentrations were highest. Downcore concentrations of organic carbon were significantly and positively correlated with all pigments except chlorophyll-b, chlorophyll-c_3, echinenone and pheophytin (the latter two being all but absent from most samples). Thus the distribution of pigments in the deeper sediment is likely to be controlled by the same factors that control sedimentary organic matter contents : i.e. oxygen exposure times and organic carbon source. While OETs are not known in this study, they are a function of sedimentation rate and oxygen concentrations. The high accumulation of pigments at the anoxic sites may be due to a combination of decreased oxygen and rapid sedimentation of organic matter, but this cannot be confirmed.

The ratio of organic carbon to total pigments differs down-core and between sites across the margin (Figure 46). Anoxic sites show much higher values (0.2–3.6) than oxygenated sites (<0.2). While the distribution of pigments does not appear to track bulk organic carbon content down-core at the anoxic sites, it does at the oxygenated sites. This suggests there is preferential loss of pigments and thus of labile organic matter where oxygen is not present.

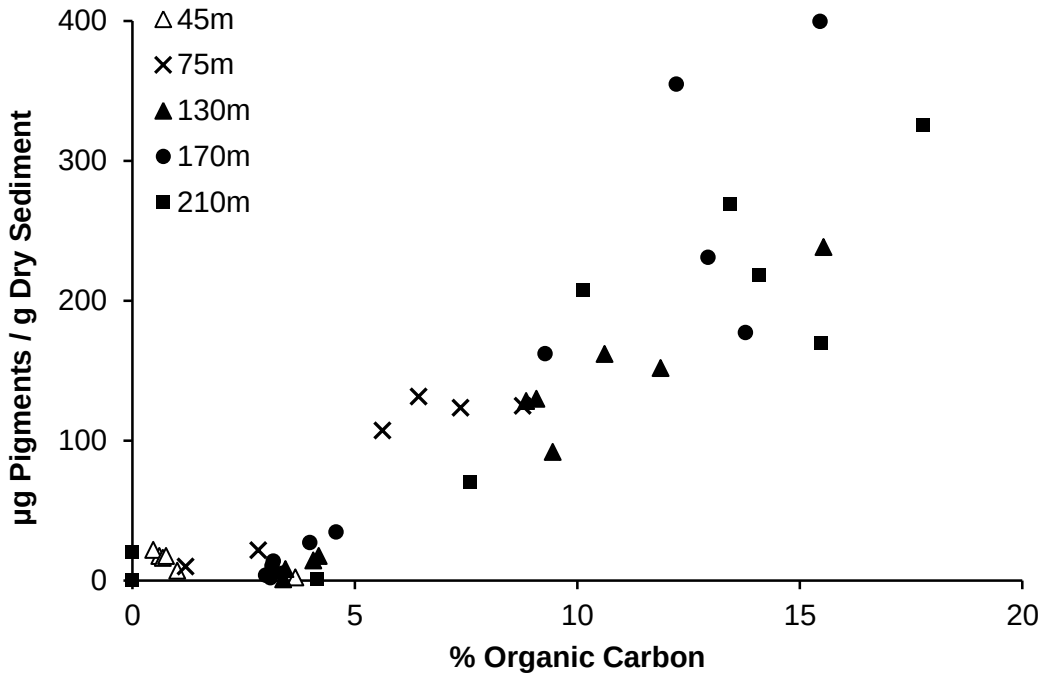


Figure 45. Sedimentary organic carbon content vs. total pigment concentrations downcore at sites across the Gotland Basin, Baltic Sea.

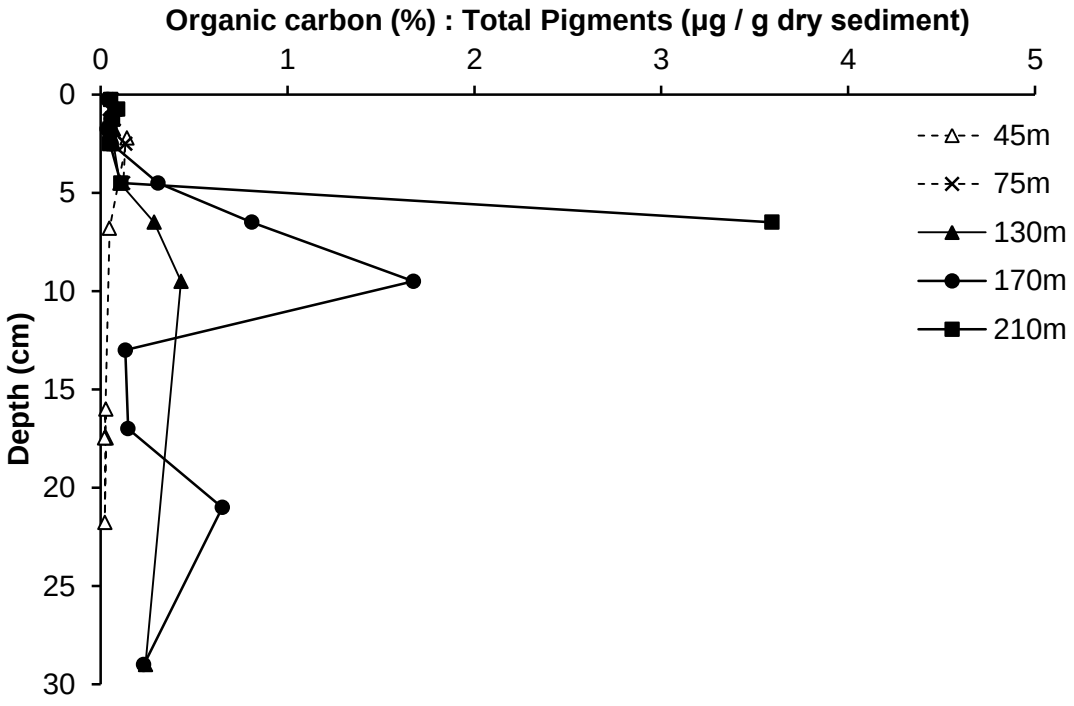


Figure 46. Organic carbon:total pigment ratios down-core at sites across the Gotland Basin, Baltic Sea.

4.6.3. Sediment Texture

Only alloxanthin showed a significant correlation with sediment texture: negative with %silt (ρ =-0.95), and positive with %sand (ρ = 0.95) ($P \leq 0.05$). This was surprising as previous work has shown that sediment textural features such as grain size and surface area play key roles in determining marine sedimentary organic matter contents and preservation (e.g. Orr et al., 1958; Calvert et al., 1995; Pedersen et al., 1992; Bergamaschi et al., 1997; Hedges and Keil, 1995; Mayer, 1994; Keil et al., 1994). Fine-grained sediments have been found to have higher concentrations of organic carbon due to the similar hydrodynamic transport properties of both organic and fine particles, and sorption of organic matter onto mineral surfaces (Hedges and Keil, 1995; Mayer, 1994). However, the opposite trend was observed here for alloxanthin concentrations which positively correlated with sand contents, i.e. a larger grain size. While factors including sediment texture, hydrodynamic sorting and reworking play key roles, their importance appears to increase where oxygen exposure is short, as indicated by enhanced organic matter preservation (e.g. Keil and Cowie, 1999). While it is a surprise that pigment concentrations showed no clear trends with sediment textural properties, it may be that the effect is overprinted by other factors. Furthermore, downcore changes in grainsize were not available which may have yielded more information.

4.6.4. Faunal Activities

Studies have shown that significant amounts of pheophorbide-a can be produced from chlorophyll-a in the water column by metazoan grazing (Shuman and Lorenzen, 1975; Welschmeyer and Lorenzen, 1985; Bianchi et al., 1988, 1991; Louda et al., 2002; Villanueva and Hastings, 2000). Controlled feeding experiments reveal that elevated concentrations of pheophorbides often reflect high levels metazoan grazing activity (Millie et al., 1993). However, these pheopigments may also be formed during decomposition of chlorophylls by abiotic factors, including oxygen, light, and temperature (Louda et al., 1998). The link between abiotic and biotic factors is complicated by the knowledge that while anoxia retards pigment degradation it also limits benthic macrofaunal communities which are known to stimulate sedimentary pigment decay (Bianchi et al., 2002). Nonetheless, chlorophyll-a degradation products are often used to infer biogeochemical processes such as heterotrophic activity,

chemical transformation and megafaunal breakdown of chlorophylls in the sediment or the water column (e.g. Mackas and Bohrer, 1976; Welschmeyer and Lorenzen, 1985; Bianchi et al., 1988,2002).

Knowing that grazing by macro- and meso- zooplankton can produce pheophorbide-a during chlorophyll-a degradation, sedimentary pheophorbide-a concentrations can be used to estimate abundance of zooplankton-degraded organic matter. However the pheophorbide-chlorophyll-a ratios calculated in this study should be treated with caution due to the ambiguity created by the choice of extraction solvent. If no artefacts have been created by solvent choice, the high rations found in the anoxic sediments suggest that faunal-grazed organic matter is most abundant in the deep of the Gotland Basin. Accordingly, low pheopigment-chlorophyll ratios imply that water column faunal grazing is minimal above the shallow oxic sites.

Benthic faunal communities were only studied at two sites (60 and 210 m, see Chapter 5). The shallow oxic 60 m site was dominated by metazoan macrofauna, whereas sedimentary at 210 m water depth were almost devoid of fauna, bar a limited foraminifera community. Given the dependence of metazoan macrofauna on oxygen concentrations, it is assumed that only the oxic sites could support a benthic community capable of bioturbation. The smallest surficial pigment concentrations were found at these oxic sites and downcore concentrations were consistently smaller than at the anoxic and hypoxic sites. This increased decay of sedimentary pigment may be due to bioturbation by active benthic fauna, which can increase the oxygen penetration depth into the sediment by burrowing, and stimulate microbial activity to enhance further pigment degradation (Sun and Dai, 2005). The low pheopigment-chlorophyll ratios at the oxic site with a large macrofauna community dispute the enhanced degradation of pigments by fauna. However, the absence of burrowing fauna and low oxygen availabilities at the deep anoxic sites could be responsible for the high total pigments concentrations observed there. Although zooplankton-degraded organic matter can be estimated by pheophorbide-a concentrations, the role of microbial degradation is much harder to estimate. A large bacterial community exists at 210 m (see Chapter 6), but no specific biomarkers for microbial pigment degradation were identified in this study.

In summary, there is limited evidence for faunal-mediated degradation, but this is interlinked with the role of oxygen.

4.6.5. Water Depth

In this study, total pigment concentration was significantly positively correlated with water depth ($\rho = 0.95$, $P \leq 0.05$) across the Gotland Basin. This positive correlation between total pigment correlation and water depth can be explained by dominant pigments (i.e. beta-carotene, fucoxanthin, lutein, pheophorbide-a, zeaxanthin) which displayed significant positive correlations with water depth ($\rho = 0.82–0.96$, $P \leq 0.05$). The flux of organic matter that reaches the seafloor is known to decrease as a function of the log of water depth (Suess, 1980; Lee et al., 1998). Thus it is not surprising that some previous studies have observed a negative correlation between sedimentary pigment concentrations and water depth, as a longer sinking time often equates to greater decay (e.g. chlorophyll-a, Grahl et al., 1995).

While it appears that pigment concentrations and distributions are correlated to water depth in the Baltic Sea, this relationship is the opposite of the expected trend. It is thought that increased water depth, leads to longer exposure to oxygen during sinking and thus may be partially responsible for the pigment concentrations that reach the seafloor (e.g. Lee et al., 2000; Pfannkuche et al., 2000; Shankle et al., 2002). The lack of significant negative correlations between water depth and any individual pigment, indicates that its influence has been masked by other effects. Therefore, factors, such as oxygen concentrations, organic matter source, or sediment textural properties may be more influential on pigment distribution in the region (e.g. Morata and Renaud, 2008). The depths in this study are within a small range, and the variation in sediment concentrations is much greater. It is also worth noting that water depth and oxygen concentrations are intrinsically linked ($\rho = -0.70$, $P \leq 0.05$) and thus oxygen may be masking the expected effect of water depth.

4.7. Sub Surface Peaks In Concentration

Of the six cores analysed, one (170 m water depth) showed distinct sub surface peaks between 10 and 20 cm sediment depth. Peaks were observed in down-core concentrations of alloxanthin, canthaxanthin, chlorophyll-a, diatoxanthin, lutein, pheophorbide-a and zeaxanthin. There are several potential causes: episodes of lateral

transport of sediment; vertical transport of organic matter down-core, or increased preservation at discrete times in the past.

Lateral transport of pigments across the Gotland basin may have occurred due cross-margin currents depositing fresh or suspended material to the site. Resuspension is common physical transport process and its effect on marine sedimentary organic material cycling has been documented both along coastal margins and in the deep sea (e.g. Gross et al., 1988; Thomsen et al., 1994; Almroth-Rosell et al., 2012). It may occur due to tides, wind waves, sea level differences, density gradients, faunal activity, or human disturbance of the sea floor such as dredging and trawling activities (Almroth-Rosell et al., 2011; Graf and Rosenberg, 1997; Jonsson et al., 2005). While the tidal effect in the Baltic Sea is negligible, it is thought that sediments up to 80 m water depth may be resuspended annually due to the influence of waves (Jonsson et al., 2005), and movement of resuspended sediment from shallower to deeper areas have been found to be significant in both field and modelling studies of the Baltic Sea (e.g. Christiansen et al., 2002; Almroth-Rosell et al., 2011). In this case, it is plausible that lateral transport could have led to enhanced pigment preservation at the 170-m site but the lack of sub-surface peaks at either of the other two deeper sites (130 m and 210 m) raises questions.

Vertical transport within sediments by benthic organisms (e.g. polychaetes) is known to transport labile organic material from surface sediments to depths of up to 15 cm (Levin et al., 1997; Graf, 1989). However, this mechanism seems unlikely as no macrofauna able to induce vertical mixing have been documented at anoxic sites in the Baltic Sea thus far. Greater supply of pigment material, or at least larger quantities reaching the sediment could lead to enhanced pigment contents – but distinguishing between the two was not possible here without sediment traps. Increased organic matter preservation in sediments has been found to be influenced by increased sedimentation rates which lead to rapid burial of organic material (Henrichs and Reeburgh, 1987). A historical period of increased primary production in the surface waters would result in higher sedimentation rates and lead to larger quantities of organic material being deposited at the sea floor (Slater and Kroopnik, 1984). Increased preservation or decreased degradation at a previous time of deposition could account for greater pigment preservation at depth. In addition, changes in the

grain size of sediment delivered to the site could have resulted in enhanced pigment preservation.

In this study, oxygen availability has been observed correlated negatively with pigment abundance in the Gotland Basin. Therefore, historical decreases in bottom-water oxygen concentrations could have affected the concentration observed in deeper sediments. However, the 170 m site is already anoxic so an oxygen control seems unlikely.

4.8. Pigments As Indicators Of Organic Matter Degradation State

The preservation state of organic matter in the Gotland Basin sediments has been independently assessed using amino-acid suites to produce the degradation index (DI), where high DI values indicate fresh, or less degraded organic matter (Dawe and Middelburg, 1998; Cowie et al., unpubl.). The "freshest" organic matter was observed at the anoxic 210 m site (0.94 ± 0.03) which coincided with the peak in organic carbon content (15.2 ± 1.9 %). DI values displayed a strong significant positive correlation with total surface pigment ($\rho = 0.89$, $P \leq 0.05$) and fucoxanthin concentrations ($\rho = 0.93$, $P \leq 0.05$), and strong positive correlations with many individual pigments: e.g. zeaxanthin ($\rho = 0.92$), chlorphyll-c_3 ($\rho = 0.92$), pheophorbide-a ($\rho = 0.82$), chlorophyllide-a ($\rho = 0.91$), beta-carotene ($\rho = 0.88$), alloxanthin ($\rho = 0.85$) (not significant at the 5 % level). Downcore correlations between individual pigments were also strongly positive, and significant ($P \leq 0.01$) for all pigments except chlorophyll-b, chlrorophyll-c_2, chlorophyll-c_3, echinenone and pheophytin-a. The strongest correlations downcore were seen between DI and zeaxanthin ($\rho = 0.90$, $P \leq 0.01$) and beta-carotene ($\rho = 0.81$, $P \leq 0.01$), and thus inventories of these pigments may be indicative of sedimentary organic matter degradation state.

Sedimentary pigments are often found to be a highly reactive component of marine organic matter, and the observations here in the Gotland basin suggest that pigments are associated with, and may be used to predict, high quality organic matter (e.g. Lee et al., 2001).

4.8.1. Pheopigments

The oxic sites contained the smallest concentrations of pheopigments, which is either due to a smaller source (e.g. zooplankton-grazed material) or further degradation to the colourless compounds that could not be resolved in this study. The absolute pheopigment concentrations decreased downcore at all sites, and returned to background levels most rapidly at the oxic 45 m site. These downcore and cross margin trends suggest that pheophorbide-a decay is sensitive to oxygen, both cross margin and downcore. The weight % contribution of pheophorbide-a to total pigments increased downcore, especially at the anoxic sites (Figure 47). This increased dominance of pheophorbide with sediment depth suggests that preferential pheophorbide-a preservation has occurred in the absence of oxygen.

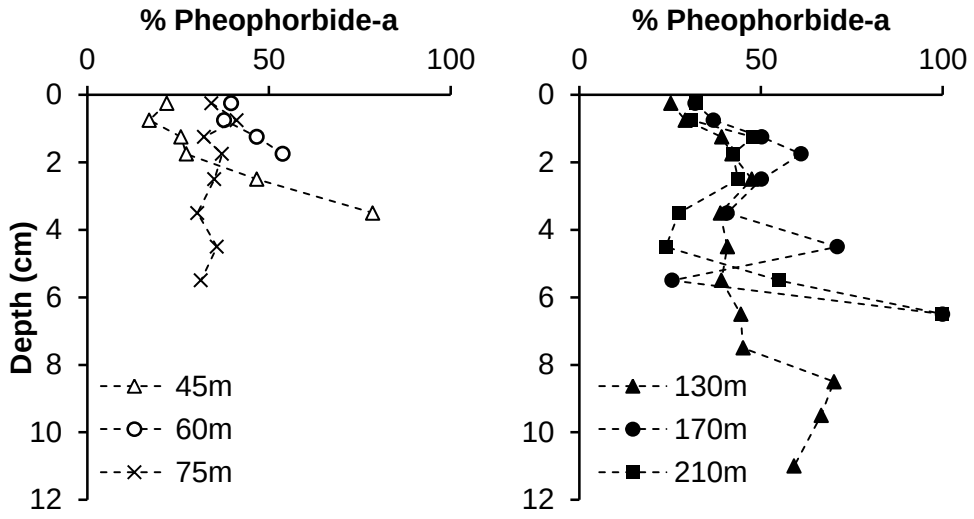


Figure 47. Downcore contribution of pheophorbide-a to total pigment suites at all sites across the Baltic Sea Gotland Basin.

4.8.2. Carotenoids

Surface concentrations of carotenoids were generally greatest at the anoxic sites, implying that this pigment group is primarily influenced by oxygen availability. Analysis of the weight percentages of individual pigments downcore, yielded information about the relative relativities of the carotenoids. Downcore profiles of weight percentages showed that beta-carotene, alloxanthin, and zeaxanthin (not shown) contributed approximately the same proportion of the total pigments at all sites and did not change downcore. This is in contrast to the observation of Repeta (1989) Reperta (1989) that carotenes are less readily decayed than other accessory

pigments. Downcore profiles of diatoxanthin (Figure 48), fucoxanthin (Figure 49), and lutein (Figure 50) revealed contrasting relative relativities. Both diatoxanthin and fucoxanthin showed increasing weight percentage downcore, suggesting they were selectively preserved compared to other pigments. Furthermore, the surface and downcore concentrations of fucoxanthin were much lower in the oxic and hypoxic sediments than at the anoxic sites, which indicates that enhanced oxygen availability reduces this selective preservation. Weight percentages of lutein generally decreased downcore, indicating that lutein is more readily degraded than other pigments. A wide range of carotenoid decay products have been identified (e.g. Repeta and Gagosian, 1984; Hopmans et al., 2005) but it was not possible to detect them in this study. In summary, downcore profiles showed diatoxanthin and fucoxanthin to be the most selectively preserved carotenes, lutein to be the most readily degraded. Cross-region trends found a general accumulation of carotenes in the surface sediments at anoxic sites.

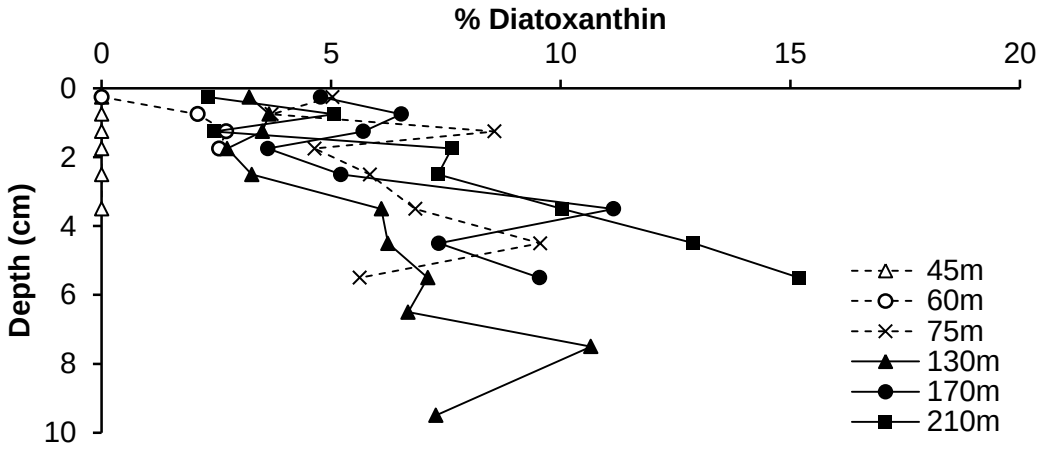


Figure 48. Downcore contribution of diatoxanthin to total pigment suites across the Gotland Basin.

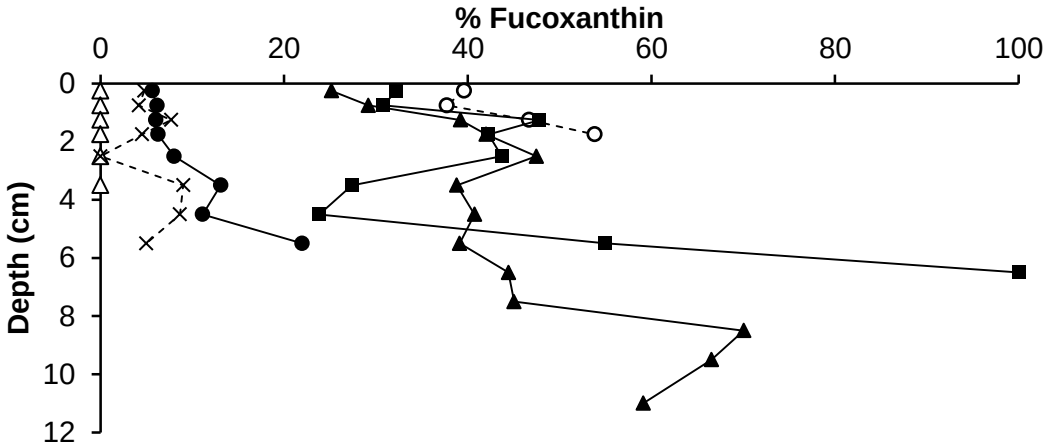


Figure 49. Downcore contribution of fucoxanthin to total pigment suites across the Gotland Basin.

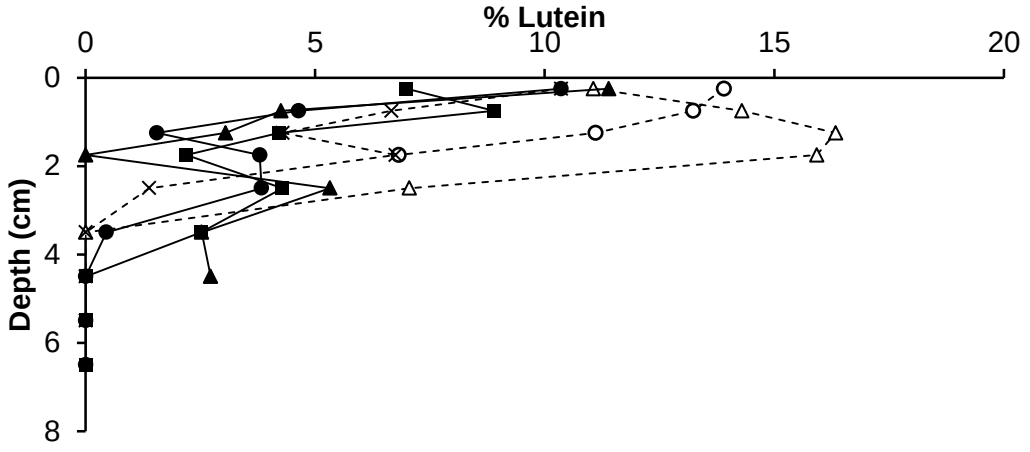


Figure 50. Downcore contribution of lutein to total pigment suites across the Gotland Basin.

4.9. Conclusions

- Systematic differences were observed in pigment suite and degradation state between sites.
- Systematic differences were observed in pigment suite and degradation state downcore.
- Total pigment concentrations declined downcore at all sites.
- Pheophorbide-a dominated the surface sediment pigment suite at all sites, suggesting that pigment-containing organic matter is degraded.
- Maximal pigment concentrations were found at the deepest sites of the Gotland Basin, where oxygen was absent, faunal communities were small, organic carbon was greatest, grain size was largest and organic matter was freshest.
- Greatest total pigment concentrations were found at sites with large carotenoid concentrations and relatively fresh organic matter (as shown by the DI values).
- Oxygen availability appears to be the controlling factor, given its role in the wider degradation of OM and control on faunal communities.
- Many pigments correlated with DI, suggesting they themselves are good indicators of sedimentary organic matter degradation state.
- Despite extensive grazing in the water column, a large proportion of the phytoplankton bloom reaches the sediment, as indicated by the preservation of intact carotenoids.
- Algal-class specific biomarkers were identified and were found to accumulate in the sediments.
- The only systematic decay trend during the 10-day incubation experiments, occurred at the anoxic 210 m site, where both the organic matter and pigment suites were freshest.
- The solvent extraction comparison showed that solvent choice can yield contrasting pigment extraction – most notably for pheophytin-a.

5. SHORT-TERM PROCESSING OF ORGANIC MATTER BY BENTHIC FAUNA

5.1. Introduction

Continental margins receive significant amounts of OM from terrestrial and marine sources, and it is estimated that over 80 % of all OC preservation takes place in these areas (Berner, 1982). The cycling and burial of OM in these regions is therefore significant in the global cycles of C and N, and other major biogenic elements, and in ocean productivity and climate (Berner, 1982, 1989; Berner et al., 2007; Berner and Kothavala, 2001; Walsh, 1991). For example, long-term carbon burial largely controls the atmospheric accumulation of O_2, on geological timescales (Berner, 1982). Furthermore, buried OM is the main potential source of fossil fuels and can also be used to reconstruct records of palaeo-environments (Cowie et al., 1999). Therefore, it is crucial to identify and understand the factors which control the sources, distribution, and preservation of OM along continental margins.

Much research has been conducted to determine the controls on OM distribution and preservation, and has identified several factors including O_2 availability and/or exposure time, differential OC sources, OM reactivity, sorptive preservation and organic-mineral interactions, water depth, sediment accumulation rates, winnowing and re-deposition, primary productivity, and biological processing (Calvert et al., 1995; Cowie et al., 1999; Hedges and Keil, 1995; Mayer, 1994; Schulte et al., 1999; van der Weijden et al., 1999). While there have been numerous reviews of the relationships between sedimentary OM burial efficiency and local oceanographic conditions, the relative importance of these factors remains unresolved. Many of the factors are interrelated, making them difficult to deconvolve, and their relative influences are likely to vary between environments (e.g. coastal margins vs. the open ocean). Consequently, it is often an interplay of factors that generates observed cross-margin OM trends.

The least well understood aspect of OM cycling and burial in marine sediments is the role of benthic fauna living on and in the sediments. Continental margins are food-limited environments where seasonal pulses of phytodetritus from the surface ocean

form an important supply to benthic communities (Billett et al., 1983). Both OM quality and availability and oxygen concentrations are known to heavily influence the presence, size, composition, and response of benthic faunal communities to added organic matter (e.g. Levin, 2003; Levin et al., 2000; Woulds et al., 2009). In turn, benthic organisms are known to affect the amount of sedimentary OM, its distribution, preservation and chemical composition (e.g. Aller, 1982; Bianchi et al., 1988; Sun, 2000; Sun et al., 1993). Seafloor communities influence marine sedimentary OM cycling and burial via a number of activities including digestion (Lauerman et al., 1997), bioturbation or burrowing (Levin et al., 1997; Sun et al., 1999; Thomas and Blair, 2002), respiration (Aberle and Witte, 2003; Witte et al., 2003b), irrigation and ventilation (Aller and Aller, 1998; Sun et al., 1999; Sun et al., 2002), and through microbial stimulation (Aller, 1982; Levin et al., 1997; Sun et al., 1999). Thus, dynamic relationships exist between benthic faunal communities, sediment geochemistry, and oxygen availability.

Early studies concerning the role of benthic fauna in marine sedimentary OM cycling revealed that a benthic response to OM addition is not always apparent (e.g. Sayles et al. 1994; Pfannkuche et al. 1999; Smith and Kaufmann 1999) and that faunal biomass is not a sufficient proxy for biological OM processing (Pfannkuche et al. 1999). As a consequence, ^{13}C and ^{15}N stable isotopes have widely been used to investigate the feeding habits of benthic communities and have been shown to be excellent source indicators that can be used to reconstruct food webs (e.g. Fry and Sherr 1984; Minigawa and Wada 1984; Peterson and Fry 1987). In order to trace a multitude of benthic processes and biogeochemical cycles, artificial enrichments of these isotopes are used to allow direct tracking of benthic systems as they are incorporated into naturally occurring compounds or substrates (e.g. bicarbonate, glucose, algal detritus and ammonium) (Cowie and Woulds, 2011).

The majority of previous isotope tracing studies have been restricted to single processes or species, using artificial microcosms with only a fraction of the natural benthic community (e.g. Armentero et al. 2010;Forster et al. 1995; Sun et al. 1999, 2002; Thomas and Blair 2002;Van de Bund et al. 2001). While microcosm experiments allow the control of the factors such as oxygen concentrations, temperature and light, and are therefore replicable, the differences between the artificial system and the natural ecosystem may mean ecological realism is limited. In order to truly study the

effects of fauna on sedimentary OM cycling, experiments are needed that consider the effects of the whole benthic community response to environmental factors. The development of such whole-community experiments is vital in addressing the role of benthic fauna in OM cycling and burial, in order to develop comprehensive models of seafloor OM cycling, by measuring organic matter pathways in benthic environments across both continental margin and deep sea sediments (e.g. Middelburg et al. 2000; Moodley et al. 2005; Woulds et al. 2007). Currently, most stable isotope tracing experiments involve the deliberate addition of isotopically labelled material to incubated samples, which is then traced into various C and N pools (e.g. sediments, different faunal groups, bacteria, and both the organic and inorganic dissolved forms). This allows the quantification of a variety of benthic processes, including respiration, assimilation by different taxa, and feeding guilds. Only then is it possible to characterise C and N cycling on short term timescales and thus investigate the relationships between benthic faunal activities and OM cycling.

Previous experimental work has indicated that benthic communities rapidly intercept and ingest most of the OM flux delivered to the seafloor (Blair et al. 1996, 2001; Cahet and Sibuet 1986; Cahet et al. 1990; Levin et al. 1997; Lauerman et al. 1997; Miller et al. 2000) but that the response varies between faunal groups such as bacteria, foraminifera and megafauna (e.g. Armentero et al. 2010; Boetius and Lochte 1996; Lochte and Turley 1988; Gooday et al. 1993; Tyler et al. 1990; Witte 1996; Woulds et al. 2007 and references therein).

Some previous whole-community experiments suggest that foraminifera and bacteria dominate the uptake of added isotopic label, and thus OM remineralisation, in marine sediments (e.g. Moodley et al. 2000, 2002; Witte et al. 2003 b). Conversely, other studies found that the macrofauna are key players in faunal OM processing in terms of OM transport, burial, uptake, and respiration (e.g. Heip et al. 2001; Levin et al. 1997; Witte et al. 2003a, b; Woulds et al.2007). In addition, several factors are known to influence benthic biological processing of OM: oxygen, OM quality and quantity (Bühring et al. 2006; Sayles et al. 1994; Soetaert et al. 1996;Woulds et al. 2007), temperature (Moodley et al. 2005; Woulds et al. 2007), and faunal size and abundance (Middelburg et al. 2000; Woulds et al. 2007). Thus, further work is required to determine how the key variables such as O_2 concentrations, OM quality, and

community structure combine to affect biological processing of OM in marine sediments.

Oxygen minimum zones (OMZs) are areas of low-oxygen that typically occur at intermediate depths of between 200 m and 1000 m and persist for at least decades (Rabalais et al., 2010). The presence of an OMZ, and its upper- and lower-boundaries, are influenced by natural processes and cycles such as monsoons (Helly and Levin, 2004; Wyrtki, 1966) and high surface water productivity, long residence times, and restricted water circulation are largely responsible for their formation. Furthermore, some regions experience upwelling which causes increased productivity rates which lead to increases in oxygen demand and thus contribute to hypoxia (Helly and Levin, 2004). The combination of high organic matter supply, high surface water productivity, and low oxygen concentrations makes these areas major sites of carbon burial. Thus the presence of an OMZ is thought to enhance OM delivery to, and burial in, the deep sea (Devol and Hartnett 2001). OMZs are typically characterised by specialized low biodiversity benthic communities that have lower oxygen tolerance thresholds (Levin et al., 2000) achieved by physiological and morphological adaptations and the ability to utilize chemosynthesis-based nutritional pathways (Levin, 2003). Continental margins underlying OMZs are therefore excellent natural laboratories for biogeochemical studies as they display large ranges in productivity, OM fluxes, depositional redox conditions and benthic communities (Levin, 2003). While recent modelling studies suggest that OMZs will expand as a result of global warming (Doney, 2010; Stramma et al., 2008) very little is known about how decreasing oxygen concentrations will impact benthic biogeochemical and ecological processes.

5.2. Aims And Hypotheses

This study examines the short-term processing of OM by benthic faunal communities in response to changing oxygen concentrations. Study sites span the Indian Margin OMZ of the Arabian Sea and the coastal to deep water range of the Baltic Sea. Both study areas provide a natural range of bottom-water oxygen concentrations, OM availability, and benthic faunal communities. ^{13}C and ^{15}N enriched OM was used as a tracer of labile OM to mimic seasonal pulses of OM to the seafloor. Shipboard incubation experiments were conducted under both ambient and manipulated oxygen

concentrations s in order to identify the key factors controlling biological processing of OM at the seafloor: the role of community structure, and the impact of oxygen concentrations.

Thus, the following hypotheses were addressed:

- Benthic faunal communities play a significant role in determining the short-term fate of organic matter in Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin) sediments.
- The role of benthic fauna in short-term organic matter cycling is strongly influenced by local oxygen conditions and organic matter quality in both the Baltic Sea (Gotland Basin) and Arabian Sea (Indian Margin).
- Benthic faunal sedimentary OM processing is:
    - dominated by foraminifera where oxygen is depleted and organic matter quality is low (e.g. in the OMZ core of the Arabian Sea, and at the deep anoxic sites of the Baltic Sea).
    - evenly shared between macrofauna, and foraminifera where oxygen is not limited and organic matter quality is high (e.g. outside of the OMZ in the Arabian Sea, and at oxygenated sites in the Baltic Sea).

5.3. Methodology

5.3.1. Incubation Experiments

Shipboard experiments were performed on whole sediment cores retrieved by either a submersible (Arabian Sea) or a megacorer (Baltic Sea). Ex-situ experiments afforded the ability to manipulate both the oxygen conditions and the substrate type added to incubated sediments. Experiments were initiated by the addition of ^{13}C and ^{15}N enriched substrate (650 mg C m^{-2} labelled algae) slurries to cores, which was then allowed to settle. Cores were incubated at ambient seafloor temperatures in the dark, submerged in tanks of filtered seawater. Overlying waters in the cores were ambient bottom waters collected by the submersible, while the tanks were filled with filtered surface waters as there was no mechanism for collecting large volumes of bottom water. The dissolved O_2 concentrations in the water tanks were set at either “normal” (ambient), “low” or “high” i.e. artificially raised or lowered by 5 % dissolved oxygen saturation. These small changes from the ambient O_2 conditions were chosen in order

to test the hypothesis that oxygen exerts a threshold type effect on benthic faunal processing of OM, and that small changes in O_2 may have large impacts on these OM processing patterns. Following incubation termination after five days, cores were sliced and sampled for pore waters by centrifugation at intervals of 0–1, 1–2, 2–3, 3–5, 5–7 and 7–10 cm. Sediments samples were halved and either freeze-dried for further geochemical studies or preserved in diluted formalin for later faunal extraction. Formalin was used to preserve the sedimentary fauna until laboratory analysis, which occurred up to 6 years later in the case of Arabian Sea samples.

Shipboard sample collection and experimental work was conducted by Clare Woulds in the Arabian Sea (2008), and by the author (Carol White) in the Baltic Sea (2010). All laboratory work was run by the author, except where analyses were run externally (e.g. isotopic analysis at LSMSF Lancaster).

5.3.2. Laboratory Analyses

Sediments from the tracer incubation experiments were washed and sieved at 300 μm before microscopic inspection. Fauna were picked and photographed before being acidified with HCl and analysed for their ^{13}C and ^{15}N content by mass spectrometry. Full details are given in Chapter 3: Materials and Methods.

5.4. Results

5.4.1. Site Conditions

A summary of site conditions is shown in Table 2, full site details can be found in Chapter 3 (Materials and Methods).

On the Indian margin of the Arabian Sea, minimal dissolved oxygen concentrations were observed at the shallowest site (500 m; 0.5 μm). The intermediate site situated at the OMZ boundary was hypoxic (814 m; 1.8 μm). The deepest study site was outside of the OMZ and considerably more oxygenated, but also remained hypoxic (1156 m; 22.4 μm). Bottom-water temperature decreased offshore (12.3 °C to 7.3 °C) while salinity remained consistent (~35 PSU). Organic carbon content was greatest within the OMZ (500 m; 7 %), where dissolved oxygen concentrations were lowest, and decreased offshore.

The two sites in the Baltic Sea displayed contrasting dissolved oxygen conditions, from 0 μm (sulphidic) in the deepest part of the basin (210 m) to 100 μm near shore (60 m). Temperatures were lower than those observed at the Arabian Sea sites (4.2–6.4 °C). Baltic Sea waters were brackish rather than saline, as reflected by the observed lower salinities (8.7 – 12.5 PSU).

Foraminifera were present at all sites in both study areas, although only one individual was seen at 60 m in the Baltic Sea. Metazoan macrofauna were present at all Arabian Sea sites, but only at the shallow Baltic Sea site (60 m). Foraminifera showed the greatest domination of the benthic community under the lowest oxygen conditions, at the 500 m and 210 m sites. In the Arabian Sea, metazoan macrofauna, predominantly polychaete species, displayed the greatest abundance at the OMZ boundary (814 m) where both the organic matter (4.7 % OC) and dissolved oxygen concentrations (1.8 μm O_2) were adequate.

5.4.2. Faunal Distribution, Abundance And Biomass

An overview of faunal communities, averaged across all experimental core, at each of the sites in the two study areas can be found in Table 17 and Figure 52. Differences between treatments will be addressed in later sections, some of which may be due to of seafloor heterogeneity.

Total biomass is made up of both living tissue and dead structures constructed by the organism, such as shells and tests. Biomass can be described as the total mass of an individual (i.e. wet or dry) or in terms of a chemical component (e.g. carbon, specific lipids) but there is no standardised definition or procedure for measuring biomass. Following recommendations by Brey et al. (1998) and similar benthic isotope-labelling studies, biomass is expressed here in terms of total organic carbon or nitrogen, where appropriate.

Cross-margin trends in faunal abundance and biomass in both regions are shown in Figure 51 and Figure 52. Foraminifera abundance and biomass was greater in the Arabian Sea than in the Baltic Sea. In contrast, metazoan macrofauna abundance and biomass at the Baltic Sea 60 m site was greater than at all Arabian Sea sites.

In the Arabian Sea, foraminifera abundance and biomass decreased with increasing water depth. However, metazoan macrofauna abundance and biomass peaked at the

OMZ edge site 814 m. In the Baltic Sea, only the 60 m site had a large faunal community, dominated by metazoan macrofauna.

5.4.2.1. Arabian Sea

500 m

Mean foraminifera density at the 500 m Indian Margin site was 241431 ± 44587 (1 SD) ind.m^{-2} (Table 17, Figure 53). Mean metazoan macrofauna abundance was lower, at 757 ± 1071 (1 SD) ind.m^{-2}. The dominant faunal groups were *Globorotalia menardii* (19.2 %), *Orbulina* spp. (18.2 %), and *Pullenia* spp. (16.0 %) and comprised 90 % of all fauna at the site. All metazoan macrofauna were *polychaetes*, and made up 3.2 % of present counted individuals.

Mean foraminifera biomass was 518 ± 171 (1 SD) mg C m^{-2} and 182 ± 25 (1 SD) mg N m^{-2}. Polychaete biomass was 7.0 ± 4.0 (1 SD) mg C m^{-2} and 5.8 ± 1.9 (1 SD) mg N m^{-2}. 68 % of the total carbon biomass was made up of *Orbulina* spp. (23.0 %), *Globorotalia menardii* (17.7 %), *Haplophragmoides* spp. (14.2 %). and *Pullenia* spp. (13.3 %). While only representing 3.2 % of all faunal individuals, polychaetescontributed to 9.9 % of the carbon biomass. Nitrogen biomass was dominated by *Orbulina* spp. (21.0 %), followed by polychaete spp. (17.5 %) and *Haplophragmoides* spp. (15.5 %). Polychaetes disproportionately made up a large portion of the nitrogen biomass (17.5 %) compared to their low abundance (3.2 %)

Foraminifera abundance and biomass did not display any down-core trends (Figure 58). In contrast, metazoan abundance and biomass was concentrated in the surface sediments (0–2 cm) and were zero in the 2–3 cm interval.

814 m

Mean foraminifera density at the 814 m Indian Margin site was 134444 ± 41471 (1 S.D.) ind.m^{-2} (Table 17, Figure 54). Mean polychaete abundance was lower, at 3030 ± 1365 (1 S.D.) ind.m^{-2}. The dominant faunal group was *Globorotalia menardii* (44 %), and together with *Pullenia* spp. (25 %) and *Orbulina* spp. (21 %) comprised 90 % of all fauna at the site. Polychaetes made up 2.2 % of present fauna, and were the only metazoan macrofauna found.

Mean foraminifera biomass was 260 ± 66 (1 S.D.) mg C m^{-2} and 44 ± 10 (1 S.D.) mg N m^{-2}. Polychaete biomass was 35 ± 27 (1 S.D.) mg C m^{-2} and 12 ± 8 (1 S.D.) mg N m^{-2}. Total carbon biomass was largely in the form of *Globorotalia menardii* (35.2 %), followed by *Orbulina* spp. (26.5 %) and *Pullenia* spp. (18 %). While only representing 2.2 % of the total number of individuals, polychaetes contributed to 11.9 % of the carbon biomass. Nitrogen biomass was dominated by *Orbulina* spp. (29 %), followed by polychaetes (20.9 %) and *Pullenia* spp. (17.2 %). Again, polychaetes disproportionately made up a large portion of the nitrogen biomass compared to their low abundance.

Foraminifera abundance and biomass generally increased down-core from 0–3 cm sediment depth (Figure 59). In contrast, polychaete abundance and biomass was concentrated in the surface sediment (0–1 cm).

1156 m

Mean foraminifera density at the 1156 m Indian Margin site was 129962 ± 19115 (1 S.D.) ind.m^{-2} (Table 17, Figure 55). Mean polychaete abundance was lower, at 1073 ± 609 (1 S.D.) ind.m^{-2}. The dominant faunal group was *Orbulina* spp. (28.7 %), followed by *Globorotalia menardii* (24.8 %) and *Chilostomella* spp. (11.2 %). Metazoan macrofauna consisted entirely of polychaete individuals and made up 0.8 % of living fauna.

Mean foraminifera biomass was 194 ± 87 (1 S.D.) mg C m^{-2} and 72.4 ± 27.6 (1 S.D.) mg N m^{-2}. Metazoan macrofauna biomass was 10.2 ± 5.5 (1 S.D.) mg C m^{-2} and 6.0 ± 4.8 (1 S.D.) mg N m^{-2}. Total carbon biomass was largely in the form of *Orbulina* spp. (28.7 %), *Globorotalia menardii* sp. (24.8 %) and Chilostomella spp. (11.2 %). While only representing 0.8 % of the total number of individuals, polychaete spp. contributed to 5.0 % of the carbon biomass. Nitrogen biomass was dominated by of *Orbulina* spp. (45.5 %) and *Haplophragmoides* spp. (13.9 %). Again, polychaetes disproportionately made up a large portion of the nitrogen biomass (7.6 %) compared to their low abundance.

Both foraminifera and metazoan abundance and biomass decreased down-core from 0 to 3 cm sediment depth (Figure 60). While foraminifera were observed at all sediment intervals, metazoans were not found in the 2–3 cm sediment depth interval.

5.4.2.2. Baltic Sea

60 m

Mean foraminifera density at the 60 m Baltic Sea site was 255 ind.m^{-2} (n = 1) (Table 17, Figure 56). Mean metazoan macrofauna abundance was higher at 3247 ± 810 (1 S.D.) ind.m^{-2}. The dominant faunal group was *Polychaete* spp. (70.3 %), and together with *Protobranchia* spp. (21.6 %) and *Hyperiidea* spp. (5.4 %), metazoans comprised 97.3 % of all fauna at the site.

Mean foraminifera biomass was 0.1 (n = 1) mg C m^{-2} and 0.1 (n = 1) mg N m^{-2}, unsurprising as only one individual was counted. Polychaete biomass was 46.6 ± 18.5 (1 S.D.) mg C m^{-2} and 19.4 ± 8.4 (1 S.D.) mg N m^{-2}. Total carbon biomass was dominated by the polychaetes (74.5 %). While only representing 5.4 % of the total number of individuals, *Hyperiidea* spp. contributed to 15.5 % of the carbon biomass. Nitrogen biomass was dominated by polychaete species (56.4 %), but again, *Hyperiidea* spp. disproportionately made up a large portion of the nitrogen biomass (27.2 %) compared to their low abundance.

Metazoan macrofauna abundance and biomass generally decreased down-core from 0–3 cm sediment depth (Figure 61).

210 m

Unlike at the shallow 60 m station, no Metazoan macrofauna were observed at 210 m (Table 17). The only faunal group identified was *Orbulina* spp. (100 %), with an abundance of 11014 ± 4952 (1 S.D.) ind.m^{-2} (Figure 57). Mean biomass was 14.4 ± 9.1 (1 S.D.) mg C m^{-2} and 6.4 ± 4.6 (1 S.D.) mg N m^{-2}. Foraminifera abundance and biomass were confined to the surface 0–2 cm sediment depth (Figure 62).

Table 17. Faunal abundance and biomass at all study sites (error bars represent ± 1 S.D. and n≥2 unless specified).

Site		Abundance		Biomass			
Study area	Depth	Metazoans	Foraminifera	Metazoans		Foraminifera	
	m	*ind.m^{-2}*	*ind.m^{-2}*	*mg C m^{-2}*	*mg N m^{-2}*	*mg C m^{-2}*	*mg N m^{-2}*
Arabian Sea	500	757 *(± 1071)*	241431 *(± 44587)*	0.3 *(± 0.4)*	0.5 *(± 0.6)*	518 *(± 171)*	182 *(± 25)*
	814	3030 *(± 1365)*	134444 *(± 41471)*	35.3 *(± 26.5)*	11.6 *(± 7.9)*	260 *(± 66)*	43.8 *(± 9.9)*
	1156	1073 *(± 609)*	129962 *(± 19115)*	10.2 *(± 5.5)*	6.0 *(± 4.8)*	194 *(± 87)*	72.4 *(± 27.6)*
Baltic Sea	60	3247 *(± 810)*	255 *(n = 1)*	46.6 *(± 18.5)*	19.4 *(± 8.4)*	0.1 *(n = 1)*	0.1 *(n = 1)*
	210	-	11014 *(± 4952)*	-	-	14.4 *(± 9.1)*	6.4 *(± 4.6)*

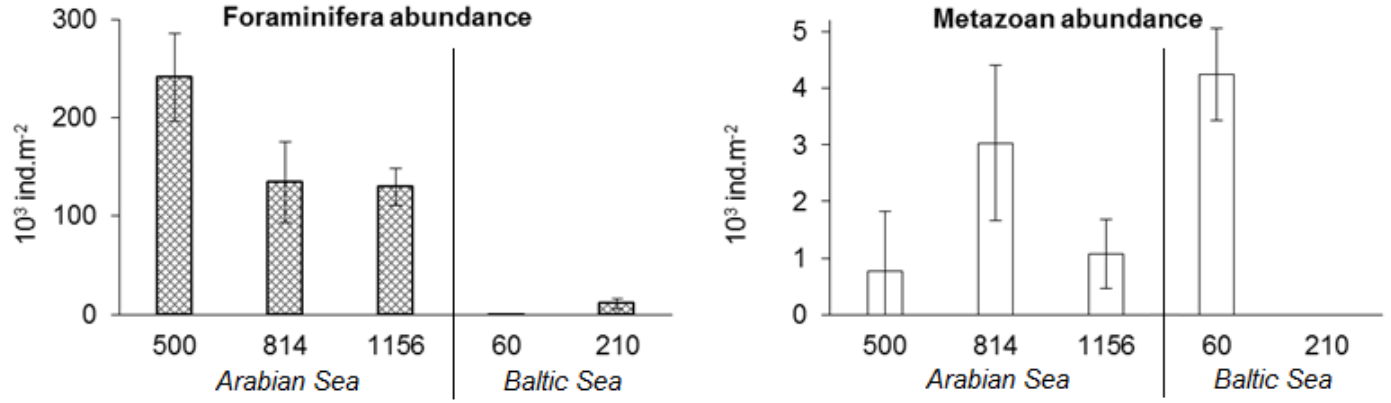


Figure 51. Faunal abundance at all sites in both study regions (0-3 cm sediment depth).

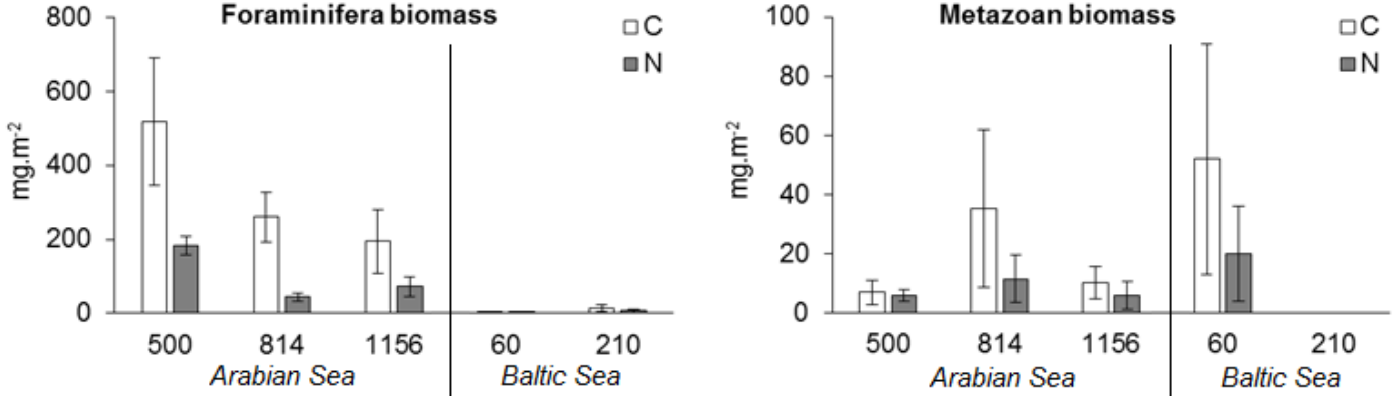


Figure 52. A comparison of faunal biomass at all sites in both study regions (0-3 cm sediment depth). Error bars represent ± 1 S.D. and n≥2.

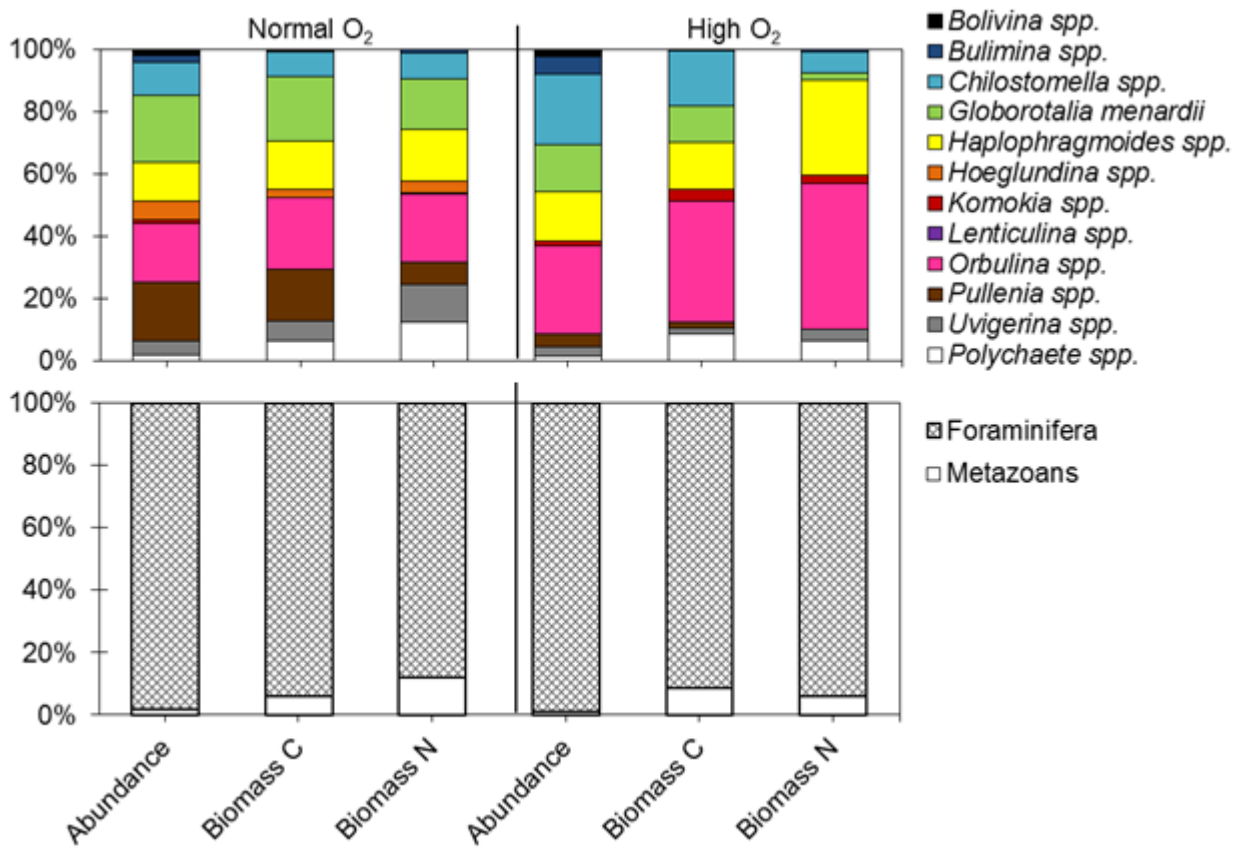


Figure 53. Faunal community composition across oxygen manipulation experiments at 500 m, Arabian Sea (0-3 cm sediment depth).

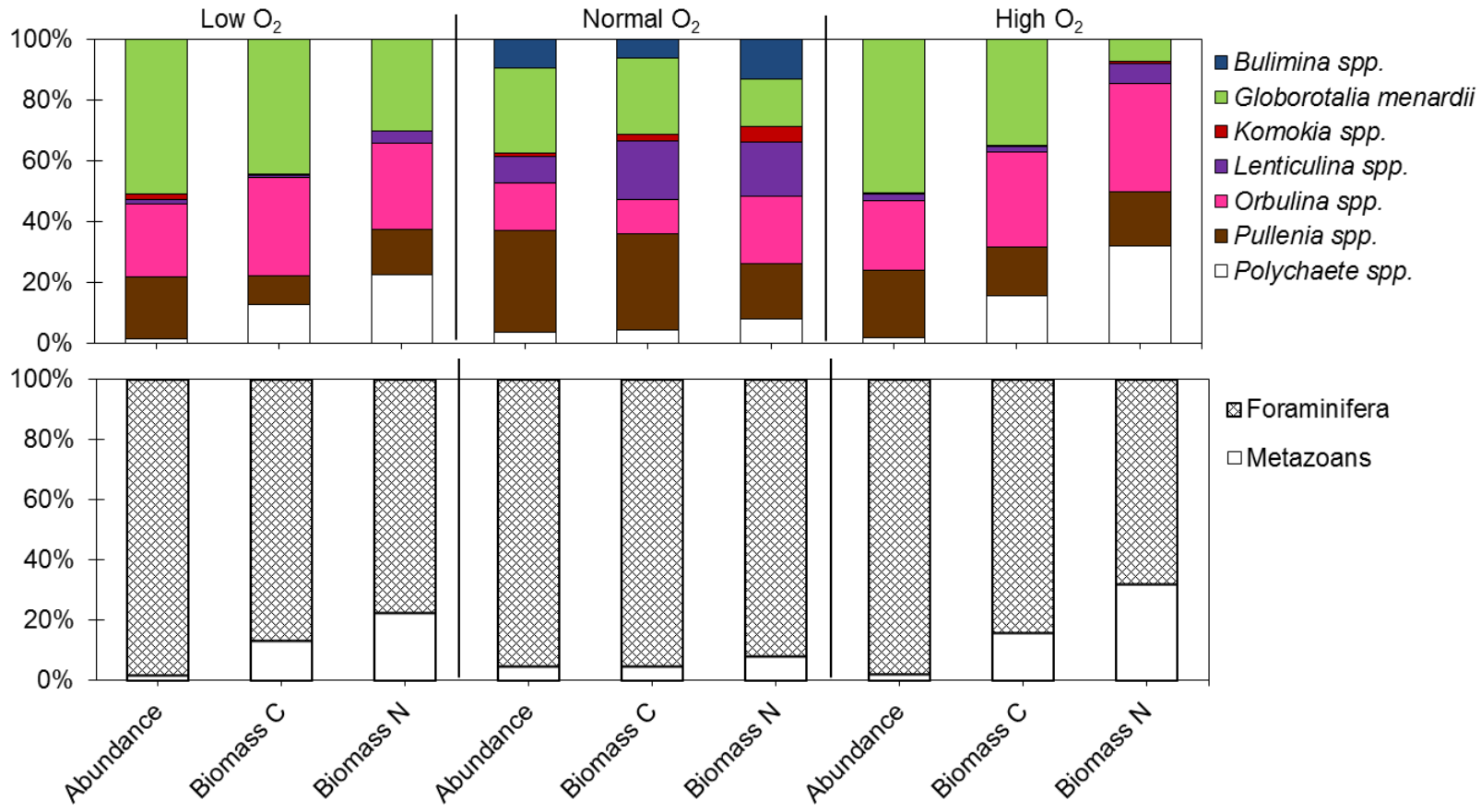


Figure 54. Faunal community composition across oxygen manipulation experiments at 814 m, Arabian Sea (0-3 cm sediment depth).

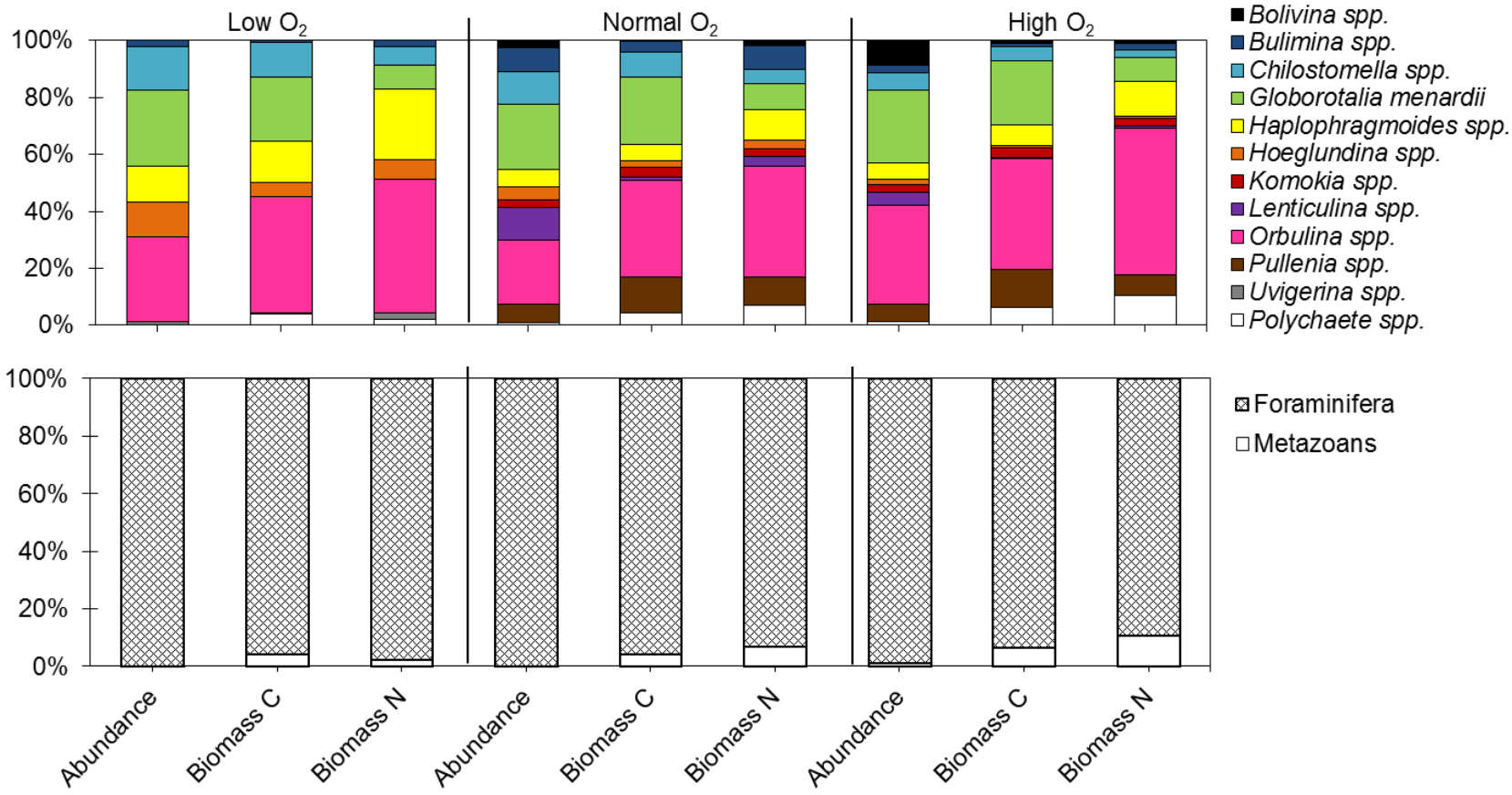


Figure 55. Faunal community composition across oxygen manipulation experiments at 1156 m, Arabian Sea (0-3 cm sediment depth).

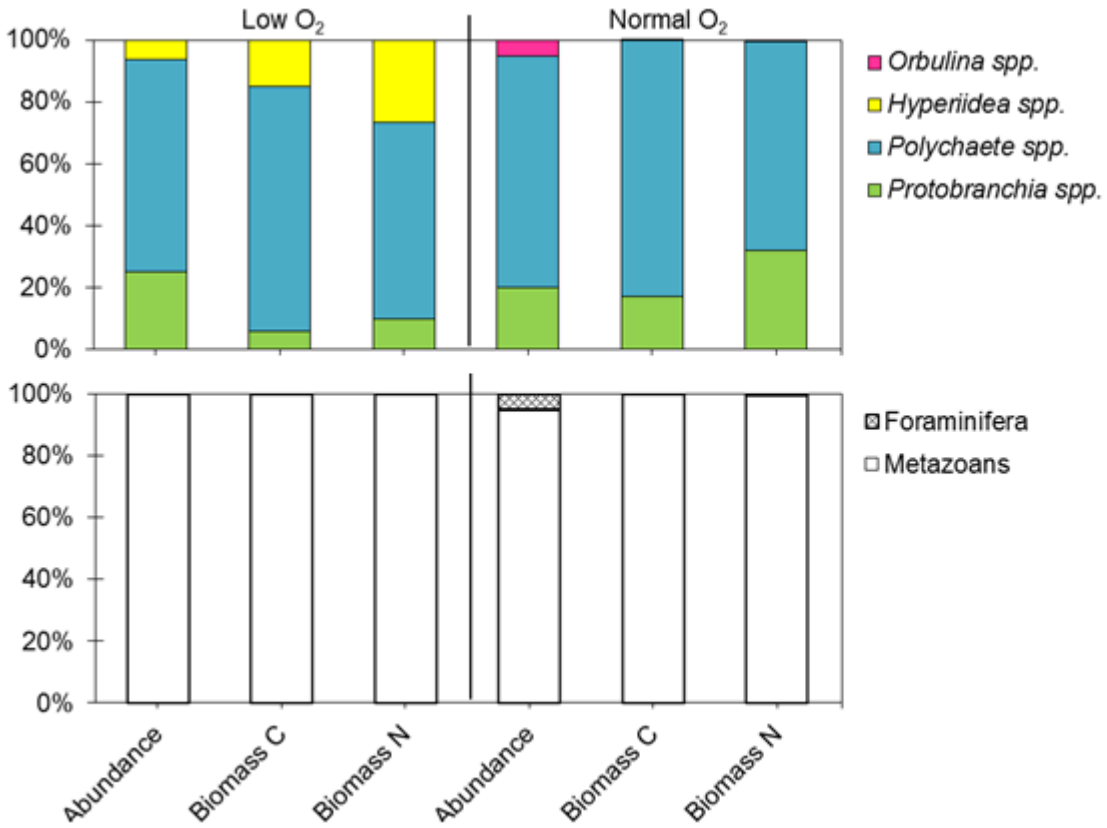


Figure 56. Faunal community composition across oxygen manipulation experiments at 60 m, Baltic Sea (0-3 cm sediment depth).

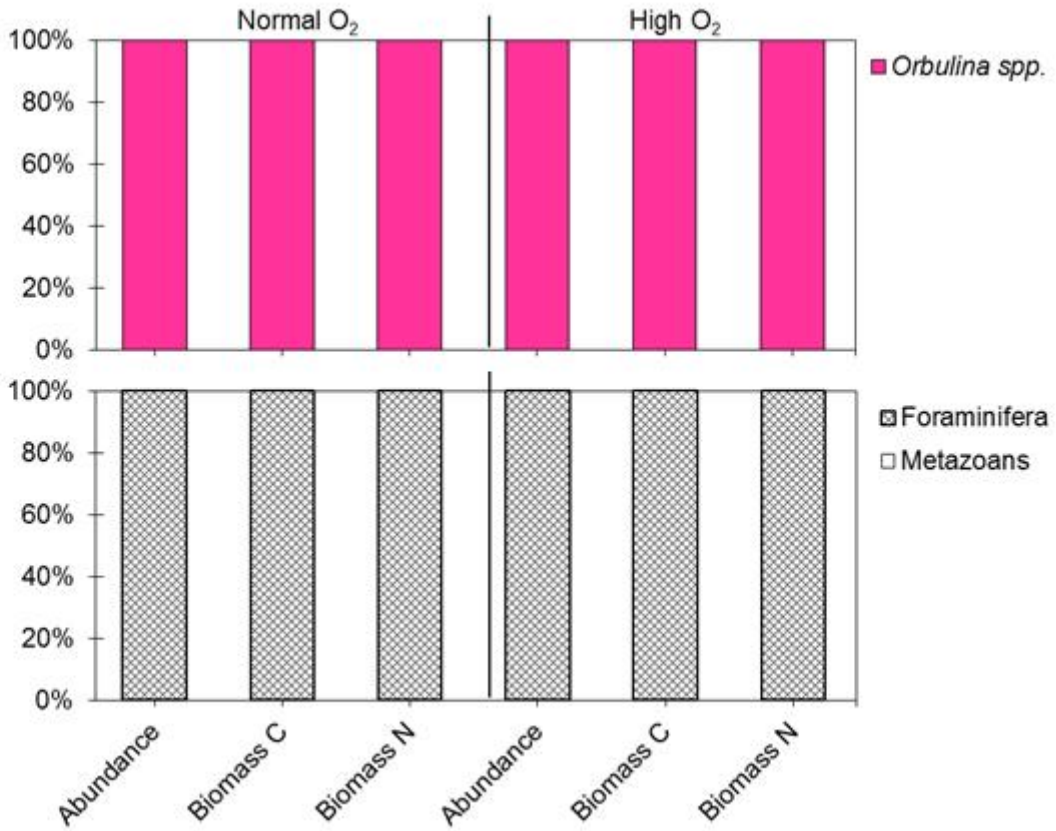


Figure 57. Faunal community composition across oxygen manipulation experiments at 210 m, Baltic Sea (0-3 cm sediment depth).

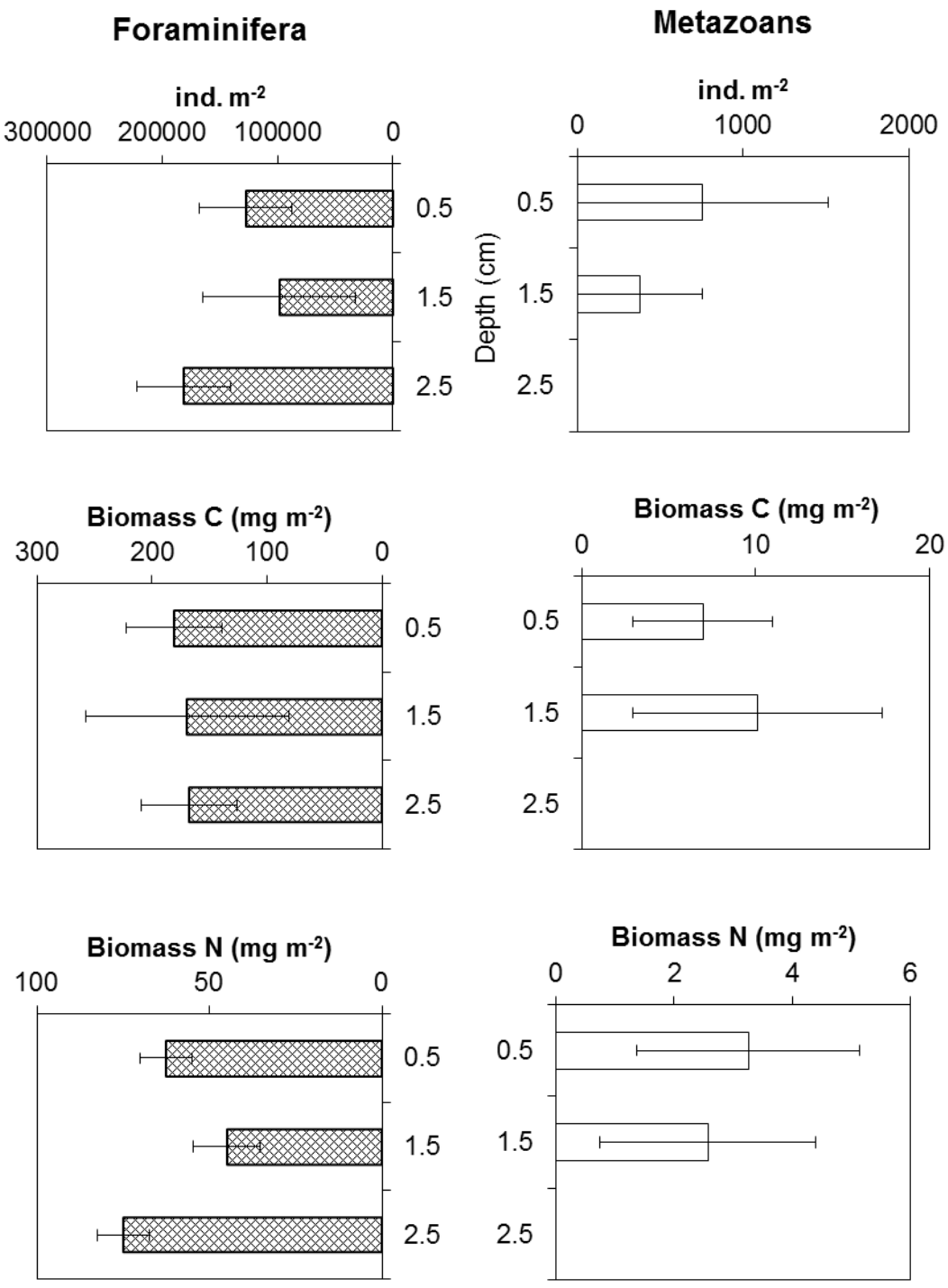


Figure 58. Vertical distribution of mean faunal abundance and biomass at 500 m, Arabian Sea (0-3 cm sediment depth, error bars represent ± 1 S.D. and n≥2).

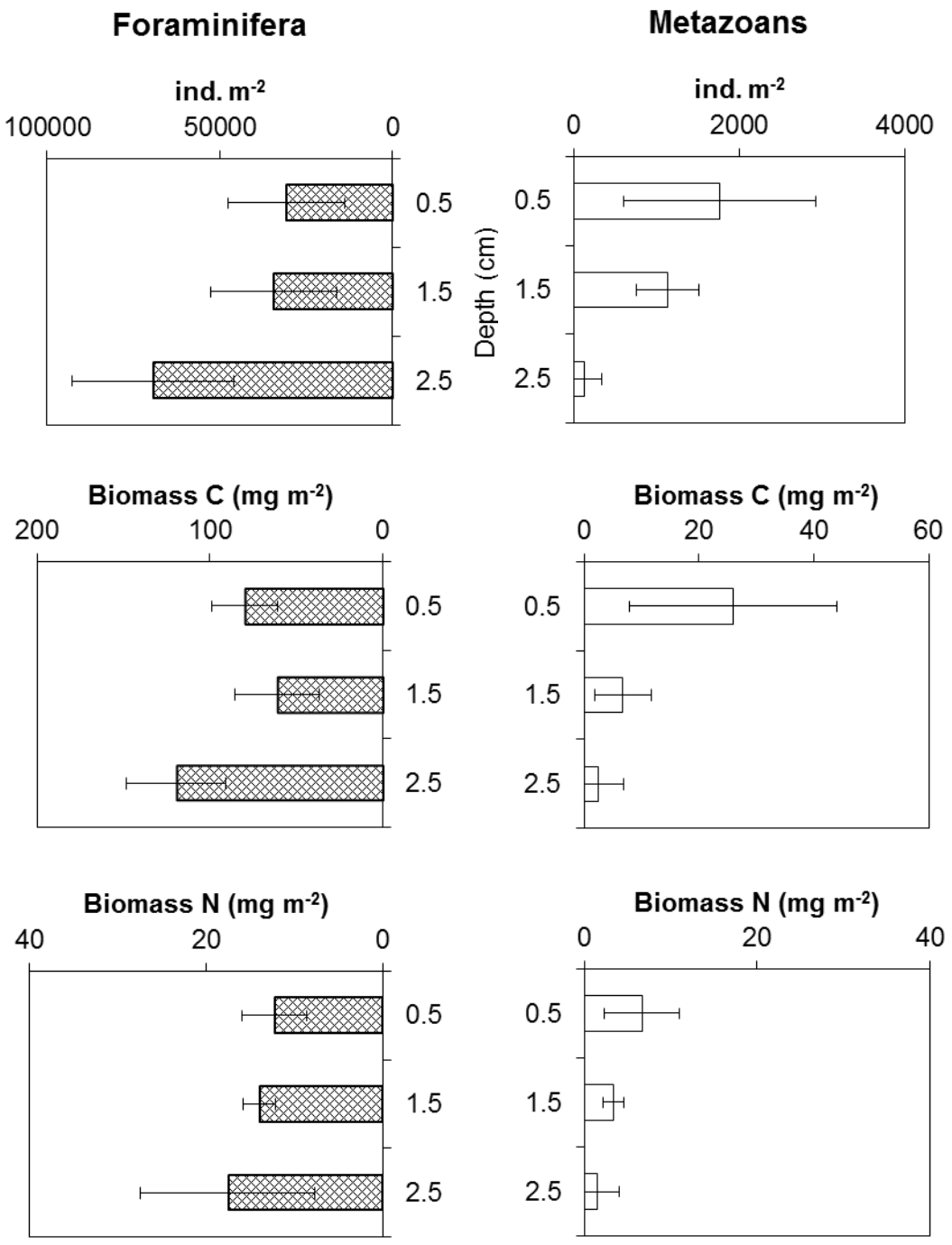


Figure 59. Vertical distribution of mean faunal abundance and biomass at 814 m, Arabian Sea (0-3 cm sediment depth, error bars represent ± 1 S.D. and n≥2).

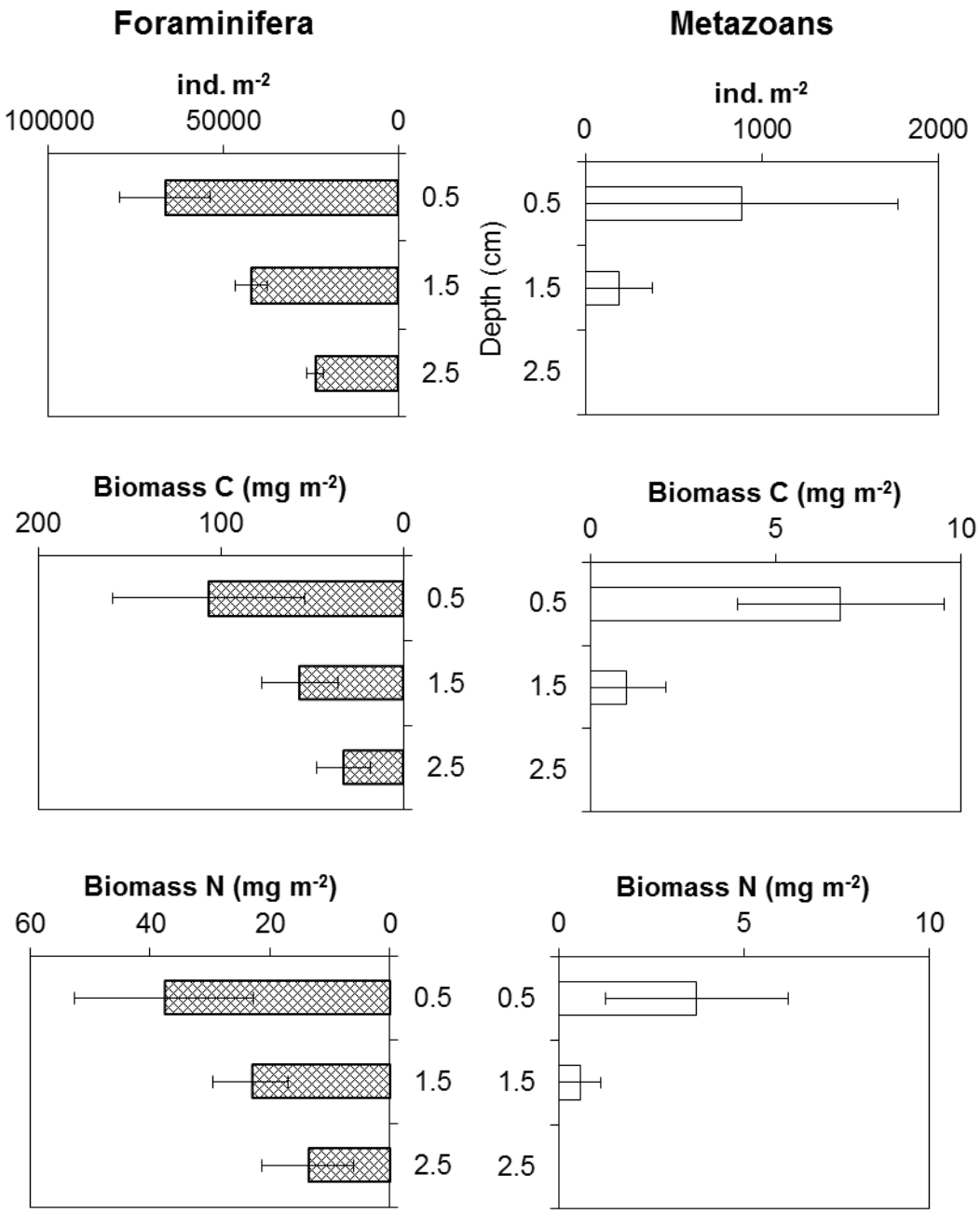


Figure 60. Vertical distribution of mean faunal abundance and biomass at 1156 m, Arabian Sea (0-3 cm sediment depth, error bars represent ± 1 S.D. and n≥2).

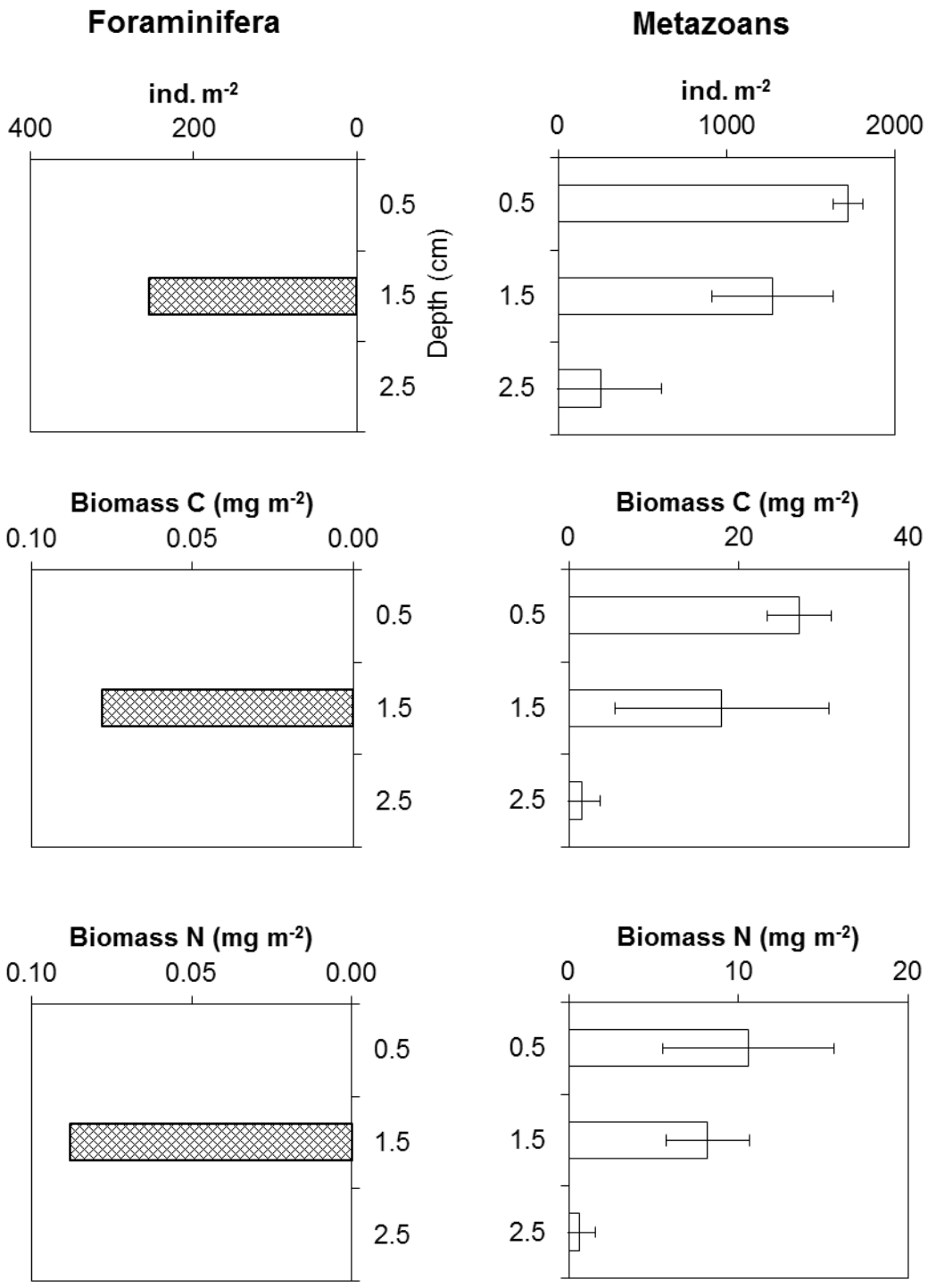


Figure 61. Vertical distribution of mean faunal abundance and biomass at 60 m, Baltic Sea (0-3 cm sediment depth, error bars represent ± 1 S.D. and n≥2).

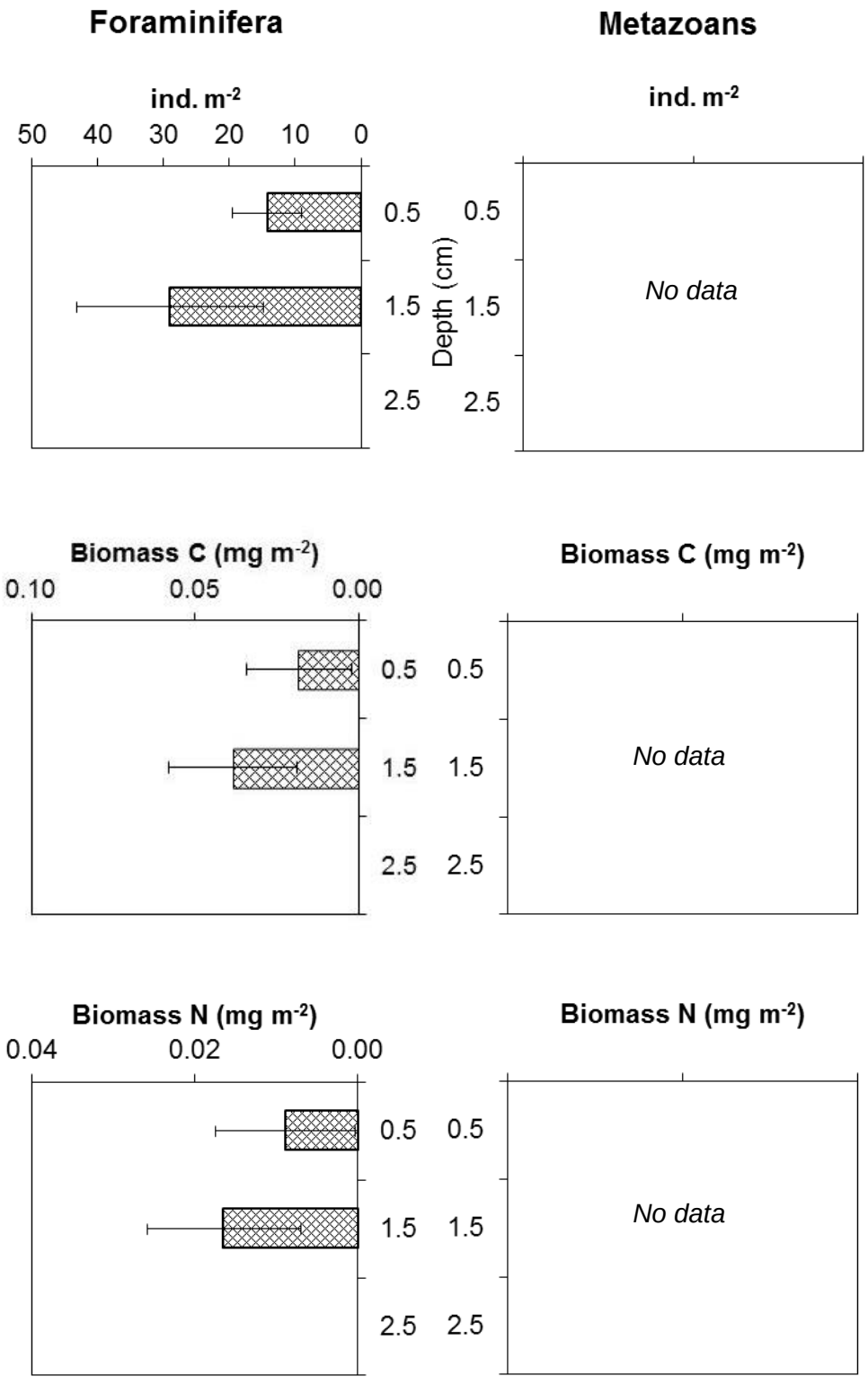


Figure 62. Vertical distribution of mean faunal abundance and biomass at 210 m, Baltic Sea (0-3 cm sediment depth, error bars represent ± 1 S.D. and n≥2).

5.4.3. Total Carbon Uptake

At all sites in both study areas, uptake of both added ^{13}C and ^{15}N occurred after five days of incubation in both experiments. Isotopic enrichment of fauna differed with both treatment (Figure 63) and faunal type (Figure 65, further described in section 5.4.4 below).

In the Arabian Sea experiments, 7.5 (± 3.5) % of added label was recovered in the faunal pools (Table 18). The highest recovery was at 814 m (14.1 %, high oxygen experiment) and the lowest values were observed at 1156 m, (1.6 %, low oxygen experiment). In the Baltic Sea experiments, only 0.9 (± 1.2) % of added label had been taken up by fauna (Table 18). Uptake of added label was 2–5 times higher in the Arabian Sea than the measureable uptake in the Baltic Sea. Carbon uptake at the shallow 60 m site (Figure 63) was 45 times higher than the negligible uptake levels at the deep 210 m site (Figure 63).

Decreased experimental oxygen concentrations had a measurable impact on faunal uptake at the most oxygenated sites, shown by reduced uptake levels at 1156 m and 60 m. Increased oxygen concentrations only had an effect at the OMZ edge site (814 m), where faunal uptake increased.

5.4.3.1. Arabian Sea

500 m

Under ambient O_2 concentrations uptake of label was 75.7 ± 7.7 mg C m^{-2} and 7.6 ± 2.0 mg N m^{-2}. When O_2 concentrations were increased, label uptake decreased to 61.9 ± 9.5 mg C m^{-2} and 4.9 ± 1.3 mg N m^{-2}. Of the ~650 mg C m^{-2} added to each incubation experiment, the recovery of added label in the faunal pool ranged from 9.5 % (high O_2) to 11.6 % (ambient O_2).

814 m

Under ambient O_2 concentrations uptake of label was 33.8 ± 19.3 mg C m^{-2} and 1.7 ± 1.2 mg N m^{-2}. Label uptake increased under manipulated O_2 concentrations, both when lowered and when elevated. When O_2 concentrations were lowered, C and N uptake increased to 50.1 ± 21.0 mg C m^{-2} and 2.0 ± 1.8 mg N m^{-2}. When O_2 concentrations were manipulated upwards, uptake increased further to 91.6 ± 25.7 mg C m^{-2} and 6.0 ± 3.5 mg N m^{-2}. While ~650 mg C m^{-2} was added to each

incubation experiment, the recovery of added label in the faunal pool ranged from 5.2 % (ambient O_2) to 14.1 % (high O_2).

1156 m

Under ambient oxygen concentrations uptake of label was 41.3 ± 1.9 mg C m^{-2} and 3.6 ± 1.6 mg N m^{-2}. Label uptake did not differ under elevated O_2 concentrations; 43.6 ± 5.7 mg C m^{-2} and 3.0 ± 10.7 mg N m^{-2}. When O_2 concentrations were artificially lowered, C and N uptake decreased to 10.5 ± 5.4 mg C m^{-2} and 0.5 ± 0.3 mg N m^{-2}. ~650 mg C m^{-2} was added to each incubation experiment, the recovery of added label in the faunal pool ranged from 1.6 % (low O_2) to 6.4 % (ambient O_2), to 6.7 % (high O_2).

5.4.3.2. Baltic Sea

60 m

Under ambient oxygen concentrations uptake of label was 16.1 ± 7.0 mg C m^{-2} and 0.5 ± 0.5 mg N m^{-2}. When oxygen concentrations were lowered, label uptake decreased to 6.7 ± 9.5 mg C m^{-2} and 0.3 ± 0.4 mg N m^{-2}. Although ~650 mg C m^{-2} was added to each incubation experiment, the recovery of added label in the faunal pool ranged from 1.0 % (low oxygen) to 2.5 % (ambient oxygen).

210 m

Under ambient oxygen concentrations uptake of label was 0.35 ± 0.06 mg C m^{-2} and 0.12 ± 0.12 mg N m^{-2}. When oxygen concentrations were increased, label uptake was negligible. Although ~650 mg C m^{-2} was added to each incubation experiment, the recovery of added label in the faunal pool was very low; from 0.01 % (high oxygen) to 0.05 % (ambient oxygen).

Table 18. Average percentage of total added label recovered in each of the faunal pools in both regions (n=2).

Site		O_2	% Label recovered		
Study area	**Depth** *m*		**Metazoans**	**Foraminifera**	**Total**
Arabian Sea	500	Ambient	0.4	11.2	11.6
		High	0.5	9.0	9.5
	814	Low	0.6	7.1	7.7
		Ambient	2.3	2.9	5.2
		High	3.4	10.7	14.1
	1156	Low	0.4	1.2	1.6
		Ambient	0.5	5.8	6.4
		High	1.5	5.2	6.7
Baltic Sea	60	Low	1.0	-	1.0
		Ambient	2.5	-	2.5
	210	Ambient	-	0.1	0.1
		High	-	0.0	0.0

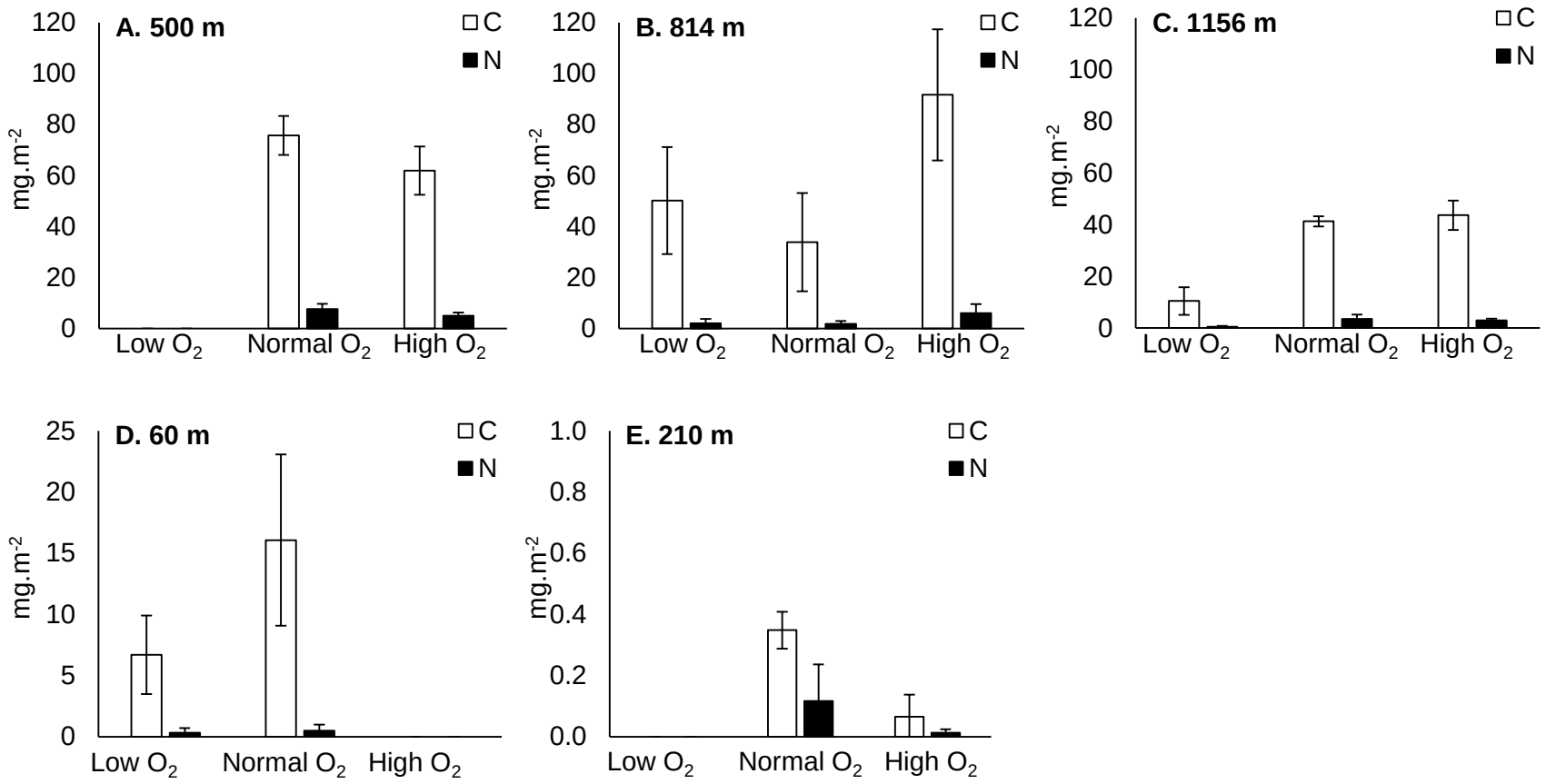


Figure 63. Faunal uptake of added label across the Baltic Sea, under differing experimental oxygen concentrations (error bars represent ± 1 S.D. and n≥2). Note the difference in x-axis scales.

5.4.4. Faunal Class Response

At all Arabian Sea sites and at 210 m in the Baltic Sea, faunal uptake of added label was dominated by foraminifera, matching the dominance of foraminifera abundance and biomass (Table 19). However, due to the near-absence of foraminifera at the oxygenated 60 m Baltic Sea site, carbon uptake was dominated by metazoan macrofauna.

Faunal class dominance of OM uptake changed with differences in both local and experiment oxygen concentrations (Figure 64). Generally, the contribution of each faunal group to total biomass matched the contribution to total OM uptake. However, a large shift in faunal class dominance of carbon uptake was seen at 814 m when oxygen concentrations were artificially reduced, corresponding with a decrease in the percentage of uptake accounted for by metazoan macrofauna. A similar trend was observed at the same site, which sits on the OMZ boundary, when oxygen concentrations were increased.

5.4.4.1. Arabian Sea

500 m

Carbon uptake was dominated by foraminifera under both ambient oxygen concentrations (96 %), and elevated oxygen conditions (94 %). An increase in relative uptake by metazoan macrofauna accompanied the increase in experimental oxygen concentration.

Absolute carbon uptake by all foraminifera decreased when oxygen concentrations were elevated, while metazoan uptake increased (Figure 65A). Other than relatively poor N uptake by *Globorotalia menardii*, there were no differences between carbon and nitrogen uptake. The most dramatic decreases in uptake were observed in the following taxa: *Bolivina* spp., *Hoeglundina* spp., *Pullenia* spp., and *Uvigerina* spp. (Figure 66).

814 m

Under ambient oxygen conditions, carbon uptake was nearly evenly split between foraminifera (55 %) and metazoan macrofauna (45 %). However, when oxygen

concentrations were altered, uptake became more dominated by foraminifera: 93 % under lowered oxygen concentrations, and 76 % under elevated oxygen conditions.

Metazoan macrofauna (polychaetes, e.g. *Spionidae*) responded to changes in dissolved oxygen concentrations; absolute label uptake increased under elevated oxygen conditions, and decreased when the oxygen concentration was lowered. Foraminifera responded in a similar fashion to macrofauna when oxygen levels were increased; uptake was 2–3 times higher. However, under decreased oxygen conditions, foraminifera responded differently: carbon uptake increased when oxygen concentrations were decreased, whereas nitrogen uptake did not change. Individual taxa had differing responses to changes in oxygen concentrations (Figure 67). Uptake by both *Lenticulina* spp. and polychaetes increased with elevated dissolved oxygen and decreased accordingly under lowered conditions. Both *Orbulina* spp. and *Globorotalia menardii*, two planktonic species observed to be actively up taking added label during the experiment, displayed enhanced uptake under both lowered and increased oxygen concentrations. *Pullenia* spp. showed an increase in uptake when dissolved oxygen was decreased. *Komokia* spp. showed a minor decrease in uptake in response to altered oxygen concentrations. *Bulimina* spp. was only present in one experiment and so cannot be examined for response to changes in conditions.

1156 m

Under ambient oxygen conditions, carbon uptake was dominated by foraminifera (92 %) with respect to metazoan macrofauna (8 %). When oxygen concentrations were increased, relative metazoan uptake increased to 23 %. Under lowered oxygen conditions, metazoan uptake also increased (24 %), due to the greater decrease in absolute uptake by foraminifera than by metazoan macrofauna.

Metazoan macrofauna (polychaetes spp.) responded to changes in dissolved oxygen concentrations; absolute carbon uptake increased under elevated oxygen conditions, and decreased when the oxygen concentration was lowered. However, foraminifera did not respond so strongly to increased O_2 concentrations, most taxa remained similarly labelled between experiments. However, under decreased oxygen conditions, foraminifera responded differently: absolute carbon uptake increased when oxygen concentrations were decreased, whereas nitrogen uptake did not change. Individual taxa had differing responses to changes in oxygen concentrations. Uptake by

Chilostomella spp., *Orbulina* spp., *Pullenia* spp. and metazoans increased with elevated dissolved oxygen and decreased accordingly under lowered conditions (Figure 68). In contrast *Bulimina* spp., showed decreased label uptake under both elevated and lowered oxygen conditions. Uptake by *Haplophragmoides* spp., did not change with increased oxygen concentrations, but did decrease when concentrations were/ lowered.

5.4.4.2. Baltic Sea

60 m

OM uptake at the 60 m Baltic Sea site was dominated by metazoans, both in terms of carbon and nitrogen, due to only a single foraminifera test being found. Metazoan carbon uptake decreased when oxygen concentrations were artificially lowered. No difference in nitrogen uptake was observed.

210 m

No metazoan macrofauna were observed at the 210 m Baltic Sea site, and thus OM uptake was dominated by foraminifera (*Orbulina* spp., 100 %). Uptake decreased when oxygen concentrations were elevated, both in terms of carbon and nitrogen.

Table 19. Carbon and nitrogen uptake at all study sites (error bars represent ± 1 S.D. and n≥2).

Site		O_2	Carbon uptake		Nitrogen uptake	
Study area	Depth		Metazoans	Foraminifera	Metazoans	Foraminifera
	m		*mg C m^{-2}*		*mg N m^{-2}*	
Arabian Sea	500	Ambient	2.82 (± 1.58)	72.88 (± 7.67)	0.24 (± 1.58)	7.32 (± 2.05)
		High	3.52 (n = 1)	58.40 (± 9.50)	0.26 (n = 1)	4.67 (± 1.30)
	814	Low	3.68 (± 2.07)	46.42 (± 20.18)	0.47 (± 0.32)	1.86 (± 0.92)
		Ambient	15.05 (± 8.15)	18.77 (± 5.68)	0.37 (± 0.37)	1.70 (± 0.70)
		High	21.85 (± 6.19)	69.80 (± 19.41)	1.90 (± 0.88)	4.02 (± 1.76)
	1156	Low	2.52 (± 3.56)	7.94 (± 5.36)	0.01 (± 0.01)	0.52 (± 0.26)
		Ambient	3.49 (± 3.84)	37.79 (± 1.94)	0.29 (± 0.13)	3.27 (± 1.62)
		High	9.90 (± 9.43)	33.74 (± 5.71)	0.26 (0.21)	2.73 (± 0.68)
Baltic Sea	60	Low	6.70 (± 3.20)	-	0.32 (± 0.39)	-
		Ambient	16.06 (± 7.00)	-	0.49 (± 0.49)	-
	210	Ambient	-	0.35 (± 0.06)	-	0.12 (± 0.12)
		High	-	0.07 (± 0.07)	-	0.01 (± 0.01)

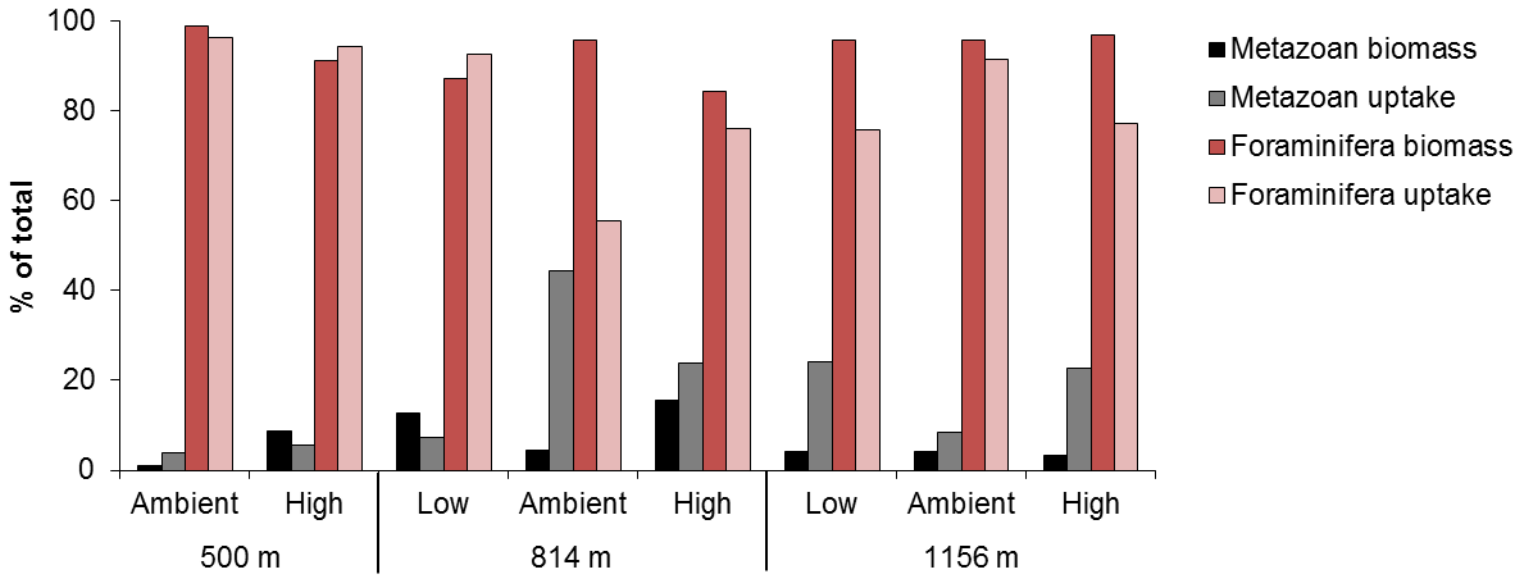
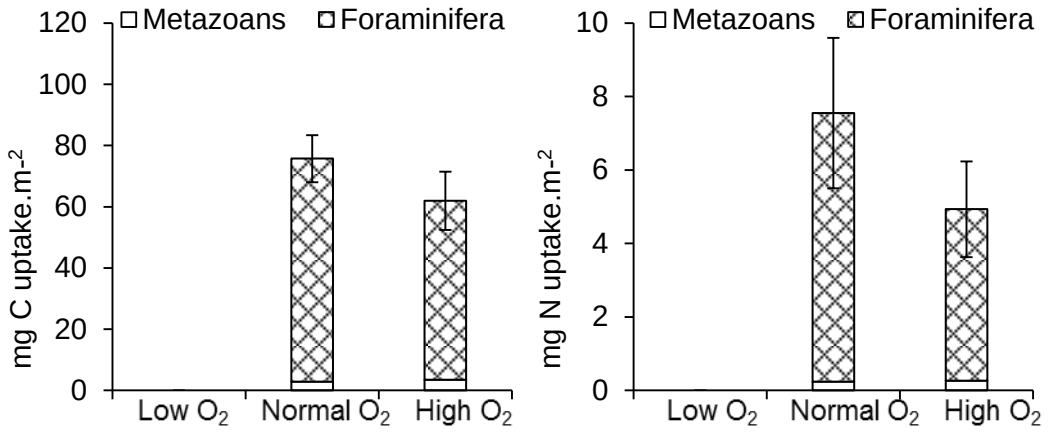
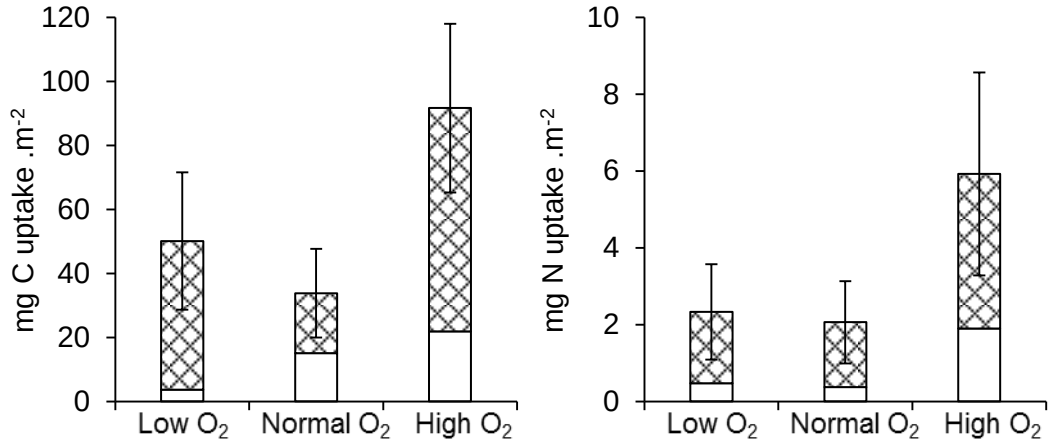


Figure 64. Percentage biomass of and uptake by metazoan macrofauna and foraminifera in each experiment in the Arabian Sea sediments.

A. 500 m



B. 814 m



C. 1156 m

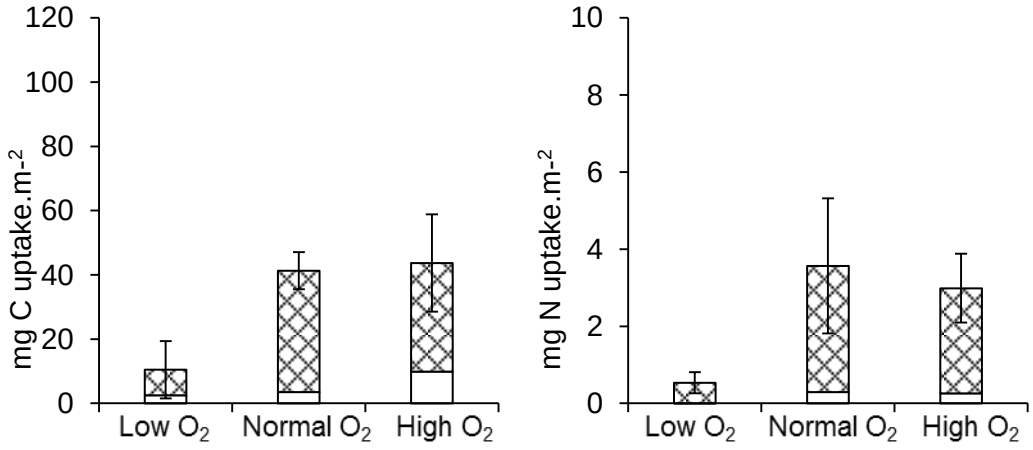


Figure 65. Incorporation of label by faunal groups under different experimental conditions (Arabian Sea). Error bars represent ± 1 S.D. and n≥2.

500 m

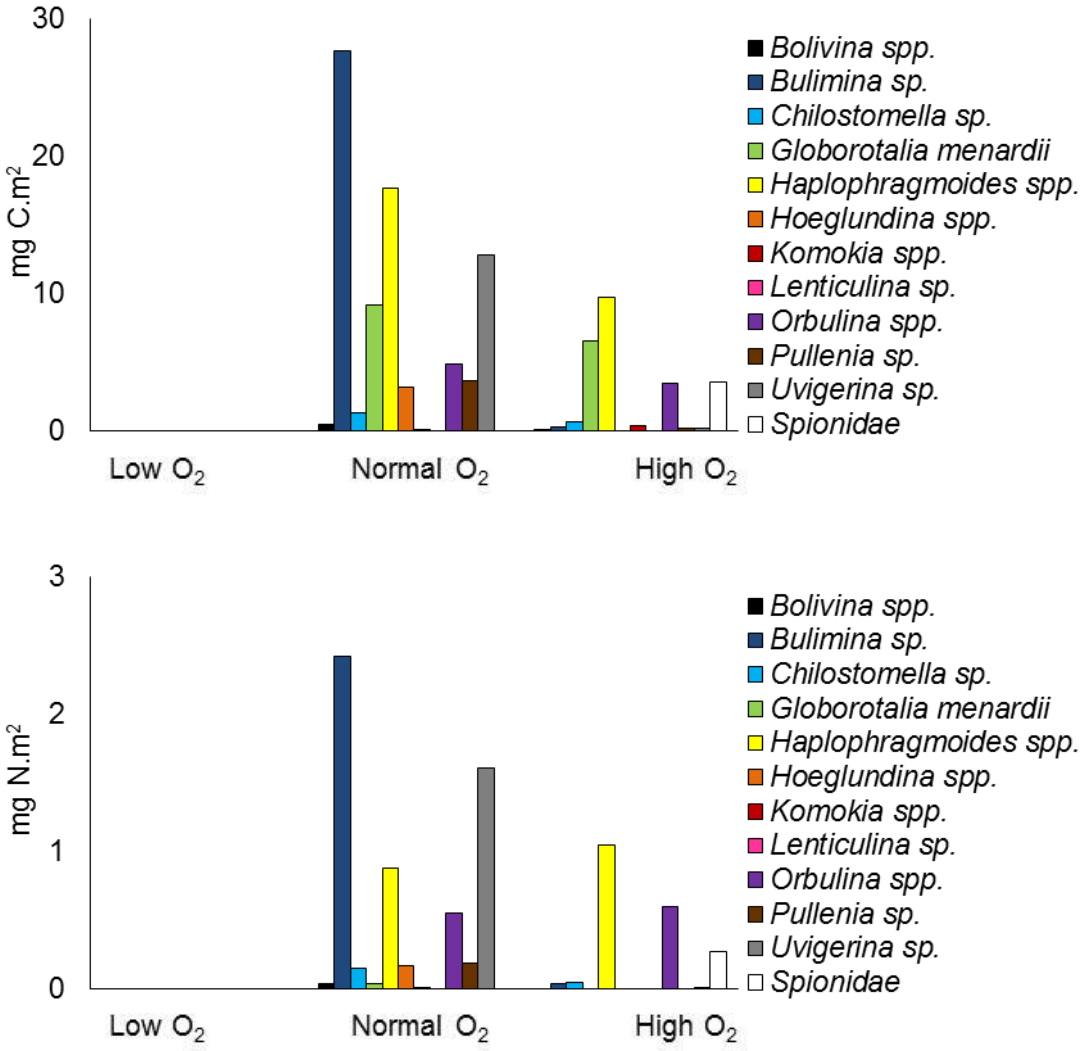


Figure 66. Uptake of added label by different faunal groups under differing experimental conditions: a) carbon, b) nitrogen at 500 m (Arabian Sea)

814 m

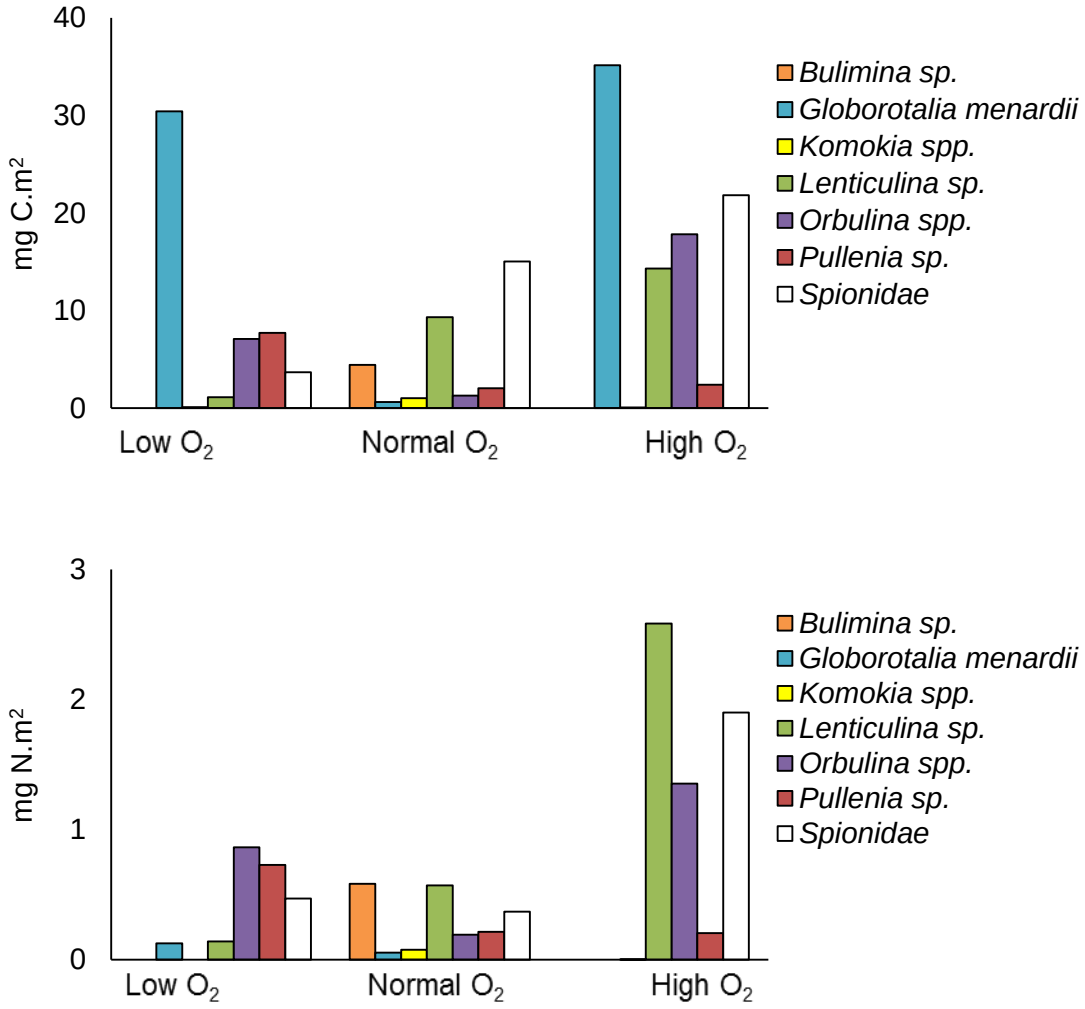


Figure 67. Uptake of added label by different faunal groups under differing experimental conditions: a) carbon, b) nitrogen at 814 m (Arabian Sea).

1156 m

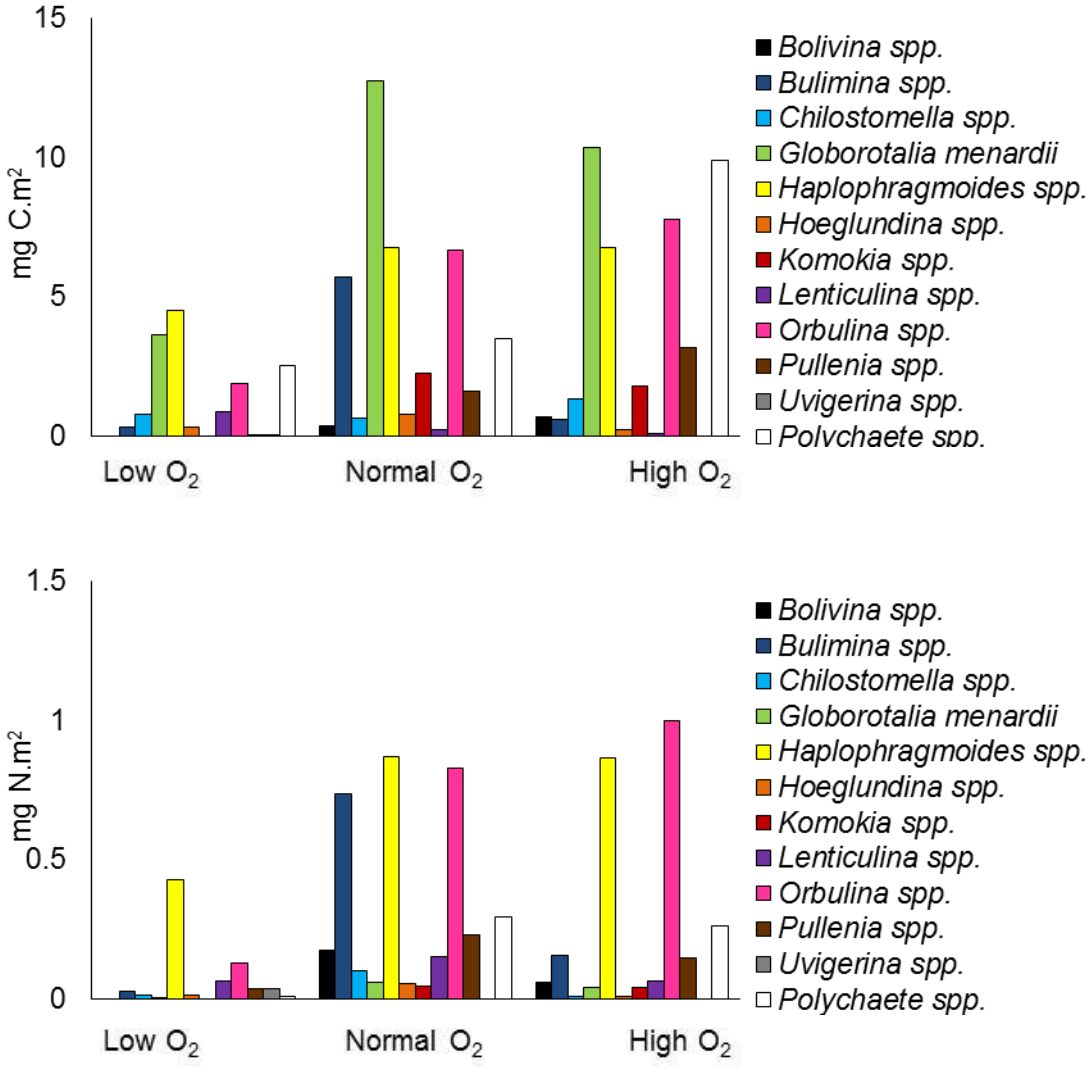


Figure 68. Uptake of added label by different faunal groups under differing experimental conditions: a) carbon, b) nitrogen at 1156 m (Arabian Sea)

5.4.5. Vertical Distribution Of Labelled Fauna

5.4.5.1. Arabian Sea

Labelled fauna were picked from all depths in each experiment, at all three sites (Figure 69). In general, more added label was recovered from fauna in the surface sediments than at depth (2–3 cm), with the exception of the artificially altered O_2 experiments at 814 m.

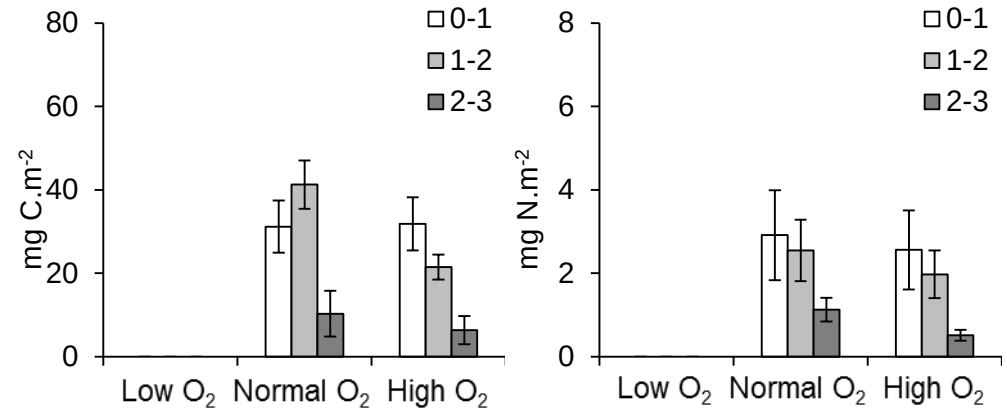
At 500 m and 814 m, a greater proportion of label was recovered from the surface sediment (0–1 cm interval) when O_2 concentrations were increased. At 814 m this was matched with a decrease the recovery of ^{13}C-labelled fauna when oxygen concentrations were artificially lowered. However, decreased oxygen conditions did not influence the vertical distribution of ^{15}N-labelled fauna at 814 m.

In contrast, at 1156 m, artificial manipulation of O_2 conditions did not lead to changes in the vertical distribution of labelled fauna.

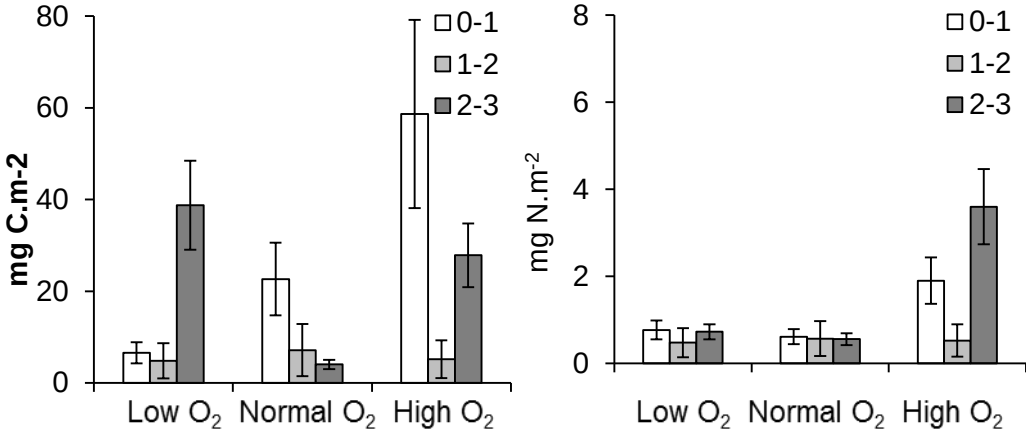
5.4.5.2. Baltic Sea

Labelled fauna were not present at all sediment depths in each experiment (Figure 70, Figure 69). Under ambient O_2 concentrations, more label was recovered from fauna in the surface 0–1 cm than at depth (1–3 cm), at both sites. However, under manipulated O_2 concentrations, this trend reversed.

A. 500 m



B. 814 m



C. 1156 m

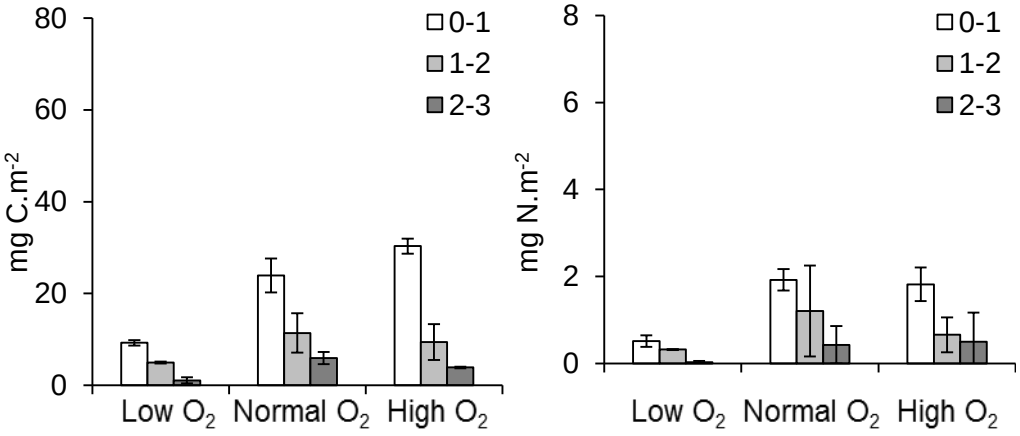
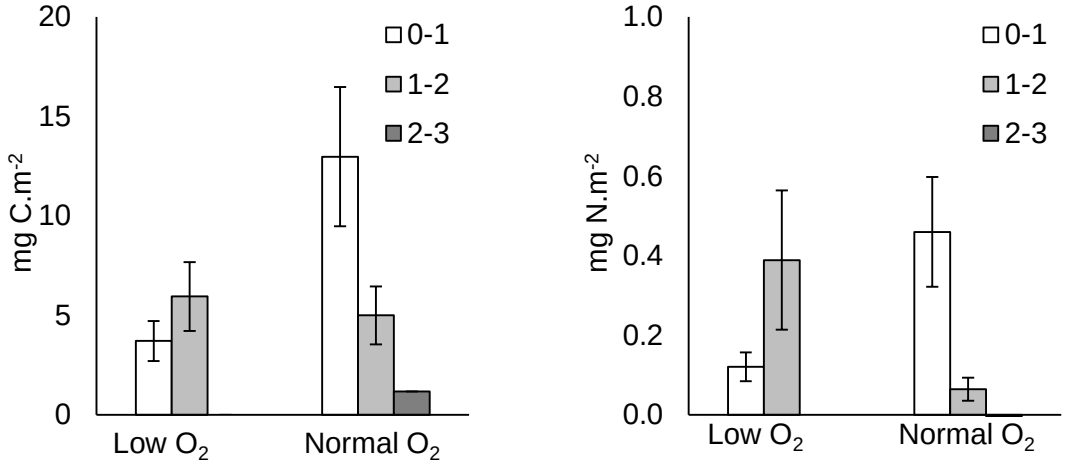


Figure 69. Vertical distribution of faunal C and N uptake under differing experimental conditions across the Arabian Sea. Error bars represent range, n=2.

A. 60 m



B. 210 m

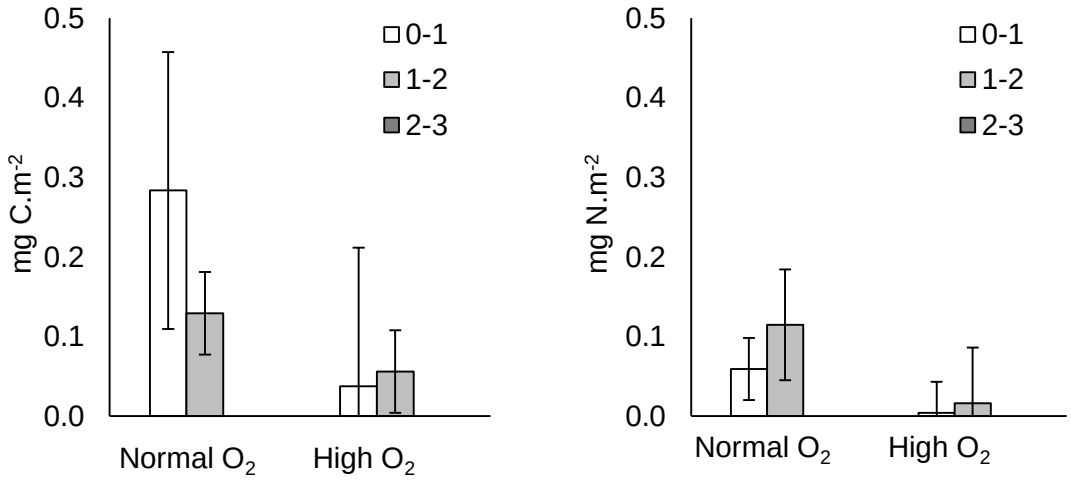


Figure 70. Vertical distribution of faunal C and N uptake under differing experimental conditions across the Baltic Sea. Error bars represent range, n=2. Note the difference in scale between the plots.

5.5. Discussion

5.5.1. Limitations And Data Quality

While isotope-labelling techniques afford the opportunity to study the role of benthic organisms in biogeochemical cycles, it is important to note that there are several limitations. Using stable isotopes to isotopically enrich substrates is often expensive and requires careful handling. Furthermore, problems may be encountered in producing isotopically labelled OM that mimics natural compounds, especially in deep-sea settings. For example, the fresh labelled-algal material used in this study is compositionally different to the degraded OM usually consumed by benthic fauna. However, the use of undegraded algal detritus in this study follows precedents set by previous seafloor labelling experiments, and therefore allows comparison with other studies and environments (e.g. Woulds et al., 2007; 2009; Moodley et al., 2002; Witte et al., 2003 a, b). It has been shown that faunal responses to OM addition in similar experiments may be influenced by both the absolute or relative amount of added carbon (Moodley et al., 2005). At all sites, a similar amount of algal carbon was added to experiments (650 mg C m^{-2}), irrespective of local sedimentary organic carbon concentrations. While this will have given different doses of "relative carbon" it also provides a degree of continuity by allowing the comparison of sites with different OM characteristics, faunal communities and oxygen availabilities, all known to influence benthic carbon processing. If faunal stimulation occurred due to greater relative carbon addition, it is expected to have occurred at the least OM-rich sites (1156 m and 814 m, Arabian Sea). However, the amount of carbon added was less than 1 % of sedimentary carbon at each site so this variation should not be important.

All experiments were conducting using a pair of sediment cores to provide replication. Both time and practical constraints at sea prevented further replication of experiments, and thus only A and B cores were available for analysis. Standard deviations were used to provide estimates of error margins, but may be heavily influenced by local heterogeneity in faunal communities.

When interpreting the results of isotope tracing experiments, it is crucial to assess (and subtract out) the baseline isotopic signatures. These have been shown to significantly vary within sampling areas and so an average must often be used (e.g. Vander Zanden and Rasmussen, 1999). In this study, we did not have access to

baseline isotopic signatures for each experiment and as a result, average signatures calculated from previous studies were used (Table 3). While this may be a source of error, the variation in background isotopic signatures is very small in comparison to those of highly labelled fauna. Therefore, the need to subtract baseline isotopic signatures is somewhat diminished, and the error introduced will not have been measurable.

The duration of incubation experiments must be considered, as there needs to be sufficient time for the tracer to be consumed, respired, and/or assimilated, sometimes more than once. Too short incubations may result in no label being transferred, and too long experiments may lead to dilution and recycling of added label (Evrard et al., 2010). Knowledge of the carbon and nitrogen cycling in the chosen environment may allow better estimates for determining the duration of tracing experiments. The resolution of time-series sampling should be high enough to allow sufficient tracking of the tracer through the system, as indicated by the results of Evrard (2007). All incubations in this study were approximately 5 days long, to maximise comparisons with previous experiments from similar environments, which thus also provided confidence that the experiment duration was appropriate (e.g. Woulds et al., 2007; 2009).

Furthermore, the quantity of tracer added has been shown to influence the benthic response (Buhring et al., 2006b). In benthic-lander experiments, Buhring et al. (2006b) found that a 10-fold increase in added tracer led to higher carbon turnover rates and bacterial assimilation. However, bacterial carbon processing contributed to a greater proportion of total carbon processing where tracer addition was lowest (Buhring et al., 2006b). This highlights the need for caution if comparing benthic OM processing patterns observed in studies using different quantities and qualities of OM tracers. A dose of 650 mg C m^{-2} was added to the incubations in this study in order to mimic the natural input of OM to the study sites (Cowie et al., 2014) and allow useful comparison to previous studies (Moodley et al., 2002; Woulds et al., 2009).

It has been argued that in-situ experiments afford more reliable results than those conducted ex-situ in the assessment of benthic biogeochemistry (e.g. Glud et al. 1994; Hall et al. 2007). While shipboard experiments provide greater access to, control of, and manipulation of experimental variables, studies have shown that some benthic

microorganisms are sensitive to changes in pressure induced by core sampling which may result in altered activity and ultimately death (e.g. Babu et al. 1990; Park and Clark 2002). Systematic differences have been reported between in-situ and ex-situ results in deep water environments but at depths less than 2000 m these potential artefacts in the data are not large enough to affect data interpretation, and can be compensated by greater replication of experiments (e.g. Aberle and Witte 2003; Anderson et al. 2008; Woulds et al. 2007). Specifically, Woulds et al. (2007) conducted both in-situ and ex-situ experiments in the Arabian Sea up to a depth of 1850 m and found no significant difference in experimental results. In this study the sites are considerably shallower than the suggested threshold of 2000 m and multiple cores were taken which may allow the assessment of local variability or patchiness in benthic processes and community levels as observed in many regions. Biomass differences observed between cores and treatments are thought be due to natural biological heterogeneity rather than as a result of experimental treatment.

5.5.2. Faunal Assemblages

Differences in faunal abundance and biomass were observed between sites, and within-site, between different experiments, in both the Arabian and Baltic Sea. While this is most likely due to heterogeneity of the seafloor, the influence of the experimental conditions cannot be ruled out. For example, missing taxa in the low-oxygen experiment at 814 m may be due to inhibited activity rather than seafloor patchiness. For ease of (limited) discussion of faunal assemblages, average biomass and compositions have been constructed for easier comparison (Figure 51, Figure 52, Figure 71, Figure 72). The faunal assemblages in the Arabian Sea were markedly different to those observed in the Baltic Sea, which is not surprising given the geographic difference in the regions and local conditions. However, the downcore trends were similar in both regions: see section 5.4.2.1.

In the Arabian Sea, foraminiferal abundance and biomass decreased with increasing water depth, which has previously been attributed to a corresponding decrease in food supply and bottom water temperatures (Levin et al., 2000; Rowe et al., 1982; Flach and Heip, 1996; Cosson et al., 1997; Thomsen et al., 1995). However, this trend is not present for metazoans, due to the presence of the OMZ and the emergence of the OMZ-boundary. Metazoan macrofaunal abundance and biomass peaked at the OMZ edge site 814 m, which has previously been observed on the Arabian Sea OMZ-boundary (Levin

et al., 2000; Woulds et al., 2007). This peak in metazoan macrofauna is attributed here to the combination of an increase in oxygen concentrations and abundant food availability, known as the "edge effect".

In the Baltic Sea, metazoans dominated (97.5 ± 3.5 %) the biomass at the oxygenated 60 m site, but disappeared completely at the anoxic 210 m site, most likely due to lack of oxygen. Foraminiferal abundance and biomass were considerably lower in the Baltic Sea than at the Arabian Sea sites, due to regional differences in biological communities. Metazoan macrofaunal abundance and biomass at 60 m was greater than at all Arabian Sea site, thought to be due to the site being fully oxygenated (100 μM)

The taxonomic composition of the foraminifera communities at our Arabian Sea sites are similar to that found by Gooday et al. (2009) on the nearby Pakistan margin of the Arabian Sea. However, in contrast the previously observed dominant foraminifera, *Uvigerina* sp. and Reophax sp. (Gooday et al. 2009; Woulds et al. 2007), were either minor or not present. In general, the polychaete abundance observed is much lower than previously observed on the Pakistan margin (Levin et al. 2009) which may be due to specialisation by fauna at the sites due to the fact that oxygen concentrations were lower than at an equivalent depth on the Pakistan margin. At 814 m, metazoan macrofauna (polychaete dominated) abundance was comparable to that found by Hunter et al. (2012) at a similar depth in the same region (this study 3030 ind. m^{-2}, Hunter et al. (2012) ~5000 ind. m^{-2}). Given the slightly lower abundance in this study, it is no surprise that the carbon and nitrogen biomass of polychaetes was also smaller than that observed by Hunter et al. (2012) (35.3 vs. ~80 mg C m^{-2}, and 11.6 vs.~10–15 mg N m^{-2}). It was not possible to identify individual polychaete species in this study. However, the carbon biomass values are comparable those observed by (Pozzato et al., 2013) at a very similar site (885 m, 2 μM) on the same Indian Margin OMZ; 2528 mg C m^{-2} of macrofauna (note their macrofauna included some foraminifera, but fewer than 100 individuals across all experiments).

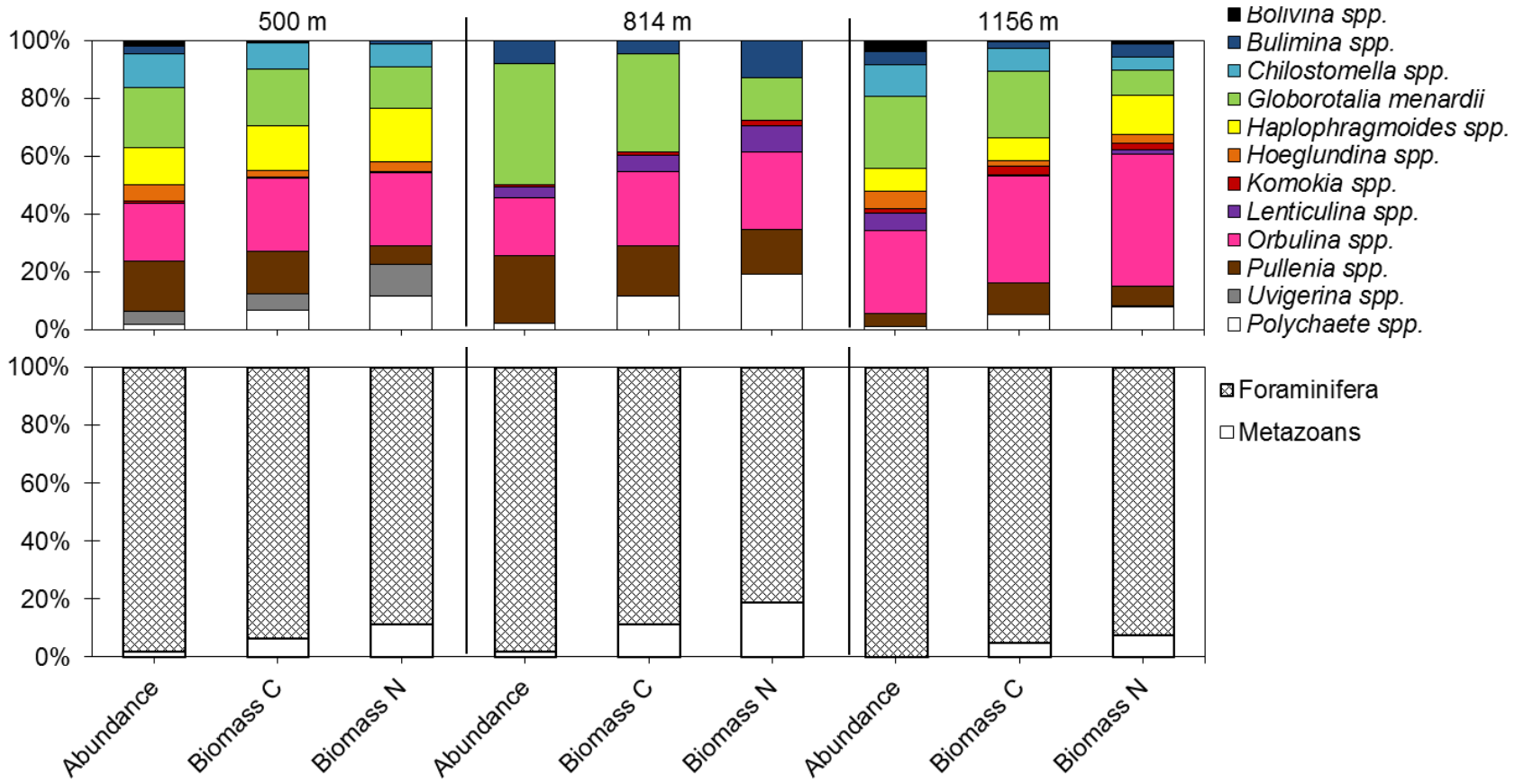


Figure 71. Average faunal community composition for each Arabian Sea site (averaged across experimental conditions, n≥4).

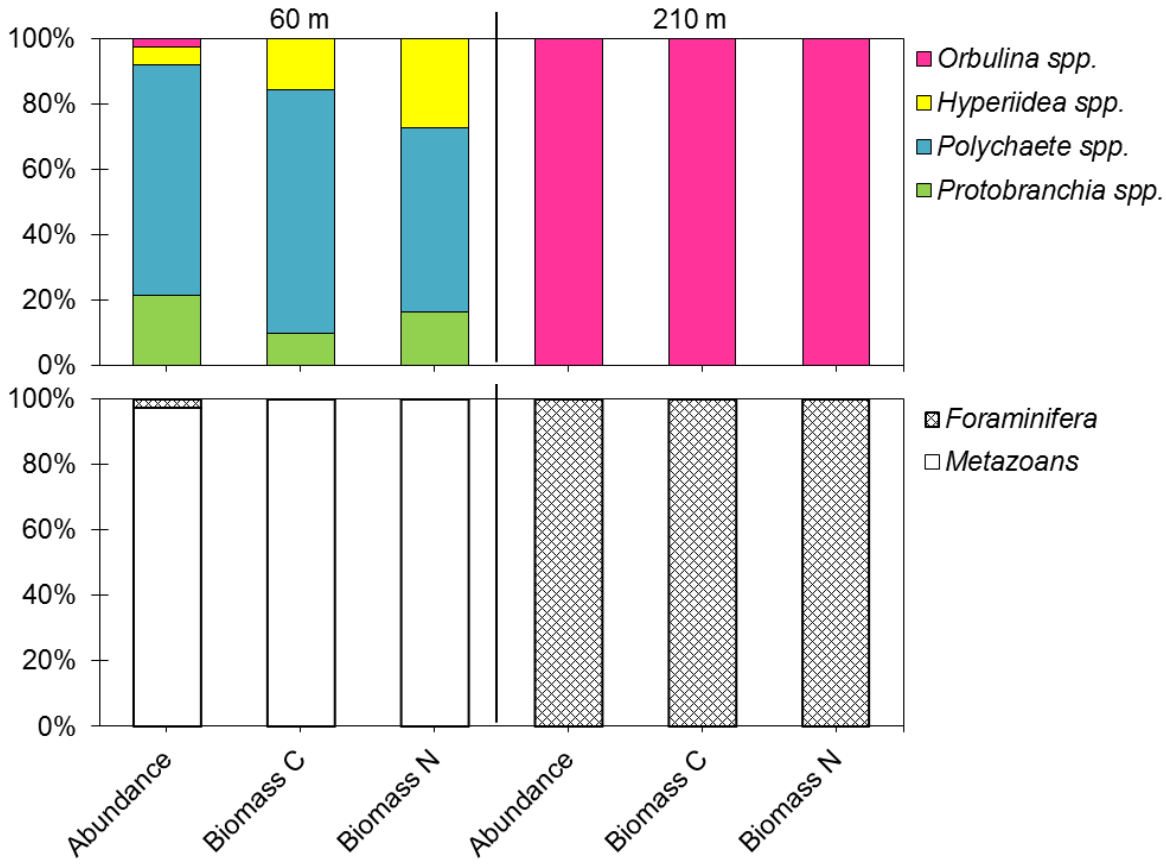


Figure 72. Average faunal community composition across the Baltic Sea sites, (averaged across experimental conditions, n=4).

5.5.2.1. Vertical Distribution Of Fauna

At all sites in both the Arabian and Baltic Sea, metazoan macrofauna abundance and biomass decreased rapidly with sediment depth, whereas foraminifera abundance and biomass did not. This suggests while the polychaete community was concentrated at the sediment-water interface, foraminifera were living at depth. It has been suggested that the uppermost layers of marine sediments are more important when studying macrofauna, with 40–50 % of all macrofauna existing in the top 1 cm and 80 % in the top 5 cm (Flach and Heip, 1996; Witte, 2000). In this study, fauna were only identified to 3 cm depth, due to sampling constraints.

5.5.3. Faunal Uptake Of OM

The incubation experiments revealed rapid uptake of the added OM by foraminifera and macrofauna. After 5 days, elevated ^{13}C and ^{15}N signatures were detected under all treatments, at all sites in both the Arabian and Baltic Sea.

Although the average recovery of added label (7.5 ± 3.5 %) from the Arabian Sea faunal biomass may seem minor (Table 18), these recoveries are comparable with previous experiments in the region (Woulds et al., 2007; 15 ± 9 %, including bacterially-processed and respired label). The highest recovery of added label was at 814 m (14.1 %, high oxygen experiment) and the lowest values were observed at 1156 m, (1.6 %, low oxygen experiment). The contribution of the faunal pools to the total OM processing will be discussed in Chapter 6.

At all sites where foraminifera dominated the faunal community (as represented by carbon biomass), foraminifera also accounted for the majority of the faunal label uptake (55–100 %). At 60 m in the Baltic Sea, metazoan macrofauna accounted for 100 % of label uptake, as only a single foraminifera test was identified.

Carbon uptake by metazoans in our study was up to 3 times larger than that observed at 800 m at a nearby Indian margin site (Hunter et al., 2012: 5.5 mg C m^{-2} and 0.36 mg N m^{-2} after 4 days). The differences between studies are likely due to variations in local faunal community structure and possibly OM concentration as discussed below. Benthic heterogeneity cannot be ignored, and may be responsible for discrepancies between studies.

No simple relationship was observed between faunal uptake and site depth, and results suggest that variations in uptake may be due to a combination of oxygen availability, background OM characteristics, faunal communities and temperature.

5.5.3.1. Controls On Faunal Uptake

Oxygen

While the presence of oxygen at 60 m (100 μM) in the Baltic Sea correlates with greater faunal carbon uptake than at the sulphidic 210 m. However, cross margin trends in faunal uptake in the Arabian Sea do not correlate with ambient oxygen conditions. This suggests that oxygen availability is not the sole driver of carbon uptake by benthic fauna, and other factors are discussed in later sections. The lack of metazoans at 210 m is suggested to be an oxygen-driven absence, by both retarding faunal activity and decreasing the faunal biomass.

However, changes in faunal uptake were observed in the oxygen manipulation experiments, indicating that relatively subtle shifts in oxygen concentrations do impact benthic faunal carbon uptake. Artificial reduction of oxygen concentrations at the oxygenated (100 μM) 60 m Baltic Sea site and the hypoxic (22.4 μM) 1156 m Arabian Sea site led to reductions in faunal carbon uptake. Despite the expectation that oxygen availability would more greatly affect metazoan macrofauna, it was the foraminifera that showed the greatest reduction in carbon uptake (Levin et al., 2000). It is suggested that this reduction in carbon uptake by foraminifera is due to the loss of several taxa in the low oxygen experiments (*Lenticulina* spp*., Pullenia* spp*.,* and *Bolivina* spp*.,* which also showed sensitivity to oxygen concentrations at both 500 m and 814 m. The greatest within-site variation of faunal class dominance was observed at the OMZ-boundary, 814 m. Under ambient oxygen conditions, carbon uptake was split between foraminifera (55 %) and metazoan macrofauna (45 %). When oxygen concentrations were lowered, metazoan macrofauna contribution to uptake also decreased (7 %) and a smaller decrease was seen under elevated oxygen conditions (24 %).

A notable increase in total carbon uptake by all fauna was observed at 814 m in the Arabian Sea under elevated oxygen concentrations, as shown by an increase in labelling of both faunal groups. Increased oxygen availability at this site therefore allowed both metazoans and foraminifera to function more efficiently/make greater use of the added OM. However the increased oxygen availability applied to the community at 210 m in the Baltic Sea did not yield greater uptake rates. This may be due to the small biomass and

limited community structure (100 % foraminifera), as foraminifera are better suited to low oxygen concentrations and thus may not benefit greatly from increased availability of oxygen (e.g. Levin et al., 2000; Levin, 2003; Gooday et al., 2000).

Although an oxygen threshold has been suggested for Arabian Sea sediments (Woulds et al., 2007) there is not sufficient evidence in this study to apply a threshold here. It may be complicated by the fact that any threshold is likely to be taxon-specific (Levin et al., 2000). The results in this study suggest that the availability of oxygen plays a role in the faunal processing of OM, but that other factors must also be responsible.

Background OM quantity and quality

In the Arabian Sea, label uptake was highest at the site with greatest organic carbon content and least degraded OM (500 m) suggesting that the faunal community was primed for responding to the added OM pulse (Table 2). The difference in OM availability and quality between 500 m and 814 m, (both low O_2 availability; 0.5 and 1.8 μM respectively) may explain the decrease in faunal carbon uptake at the more-degraded, lower OM 814 m site. Furthermore, under ambient oxygen concentrations, total faunal uptake at 814 m and 1156 m was not different, despite differences in local oxygen availability. This may be due to the similarity of local OM availability and quality at the sites (Table 2), and is consistent with previous studies which have also observed a greater influence of OM availability than oxygen on the response of faunal communities an OM pulse (e.g. Woulds et al., 2007; Levin et al., 2000).

In the Baltic Sea, faunal uptake of added OM was lower at the OM rich 210 m site (14.2 %OC) than at the lower OM 60 m site (3.5 %OC), despite 210 m having a higher quality and concentration of sedimentary OM (Table 2). Therefore, faunal community and oxygen availability play a greater role in controlling faunal carbon uptake in the region, rather than OM quantity or quality.

Community structure

While a generally positive correlation was observed between fauna group biomass and uptake (Figure 64), this relationship did not hold at the OMZ-boundary site (814 m).

Foraminifera dominated carbon uptake at all sites, which was unsurprising given that they are better able to tolerate hypoxia than larger metazoan macrofauna (Josefson and Widbom, 1988; Moodley et al., 1997) and are common in faunal communities in oxygen-

deficient settings, including the Arabian Sea OMZ (Sen Gupta and Machain-Castillo, 1993; Levin et al., 2002; Larkin and Gooday, 2009).

The dominance of foraminifera in carbon uptake at 500 m is due to foraminiferal dominance of the biomass, suggesting that more abundant taxa play a larger role in OM processing. This is supported by previous observations that uptake of ^{13}C-labelled algae by faunal groups occurs in direct proportion to group biomass in a variety of marine settings: e.g. estuarine environments (Middelburg et al., 2000), shelf-sediments(Buhring et al., 2006a; Kamp and Witte, 2005), and in the deep-sea (Woulds et al., 2007).

The lack of correlation between faunal biomass, abundance and uptake at 814 m is through to be due to the peak in metazoan macrofauna abundance on the margin. Larger organism have larger guts and are more motile (both horizontally and vertically) than foraminifera and are therefore capable of ingesting greater volumes of sediment, i.e. label, in a. short amount of time (Fauchald and Jumars, 1979; Levin et al., 1997; Nomaki et al., 2005; Miller et al., 1998).

In the Baltic Sea, faunal class dominance was caused by the oxygen-driven absence of metazoans at 210 m. Thus, the absence or presence of a faunal group determined the relative importance of other taxa. This is in line with findings from isotope-labelling experiments across the Pakistan Margin OMZ. In that study, where metazoan macrofauna were absent, foraminifera dominated faunal carbon uptake (Woulds et al., 2007).

Previous isotope-labelling experiments have assessed the difference in and importance of uptake by different faunal groups e.g. metazoan macrofauna vs. foraminifera vs. metazoan meiofauna. However, there are a wide range of results and findings, across a multitude of environments and timescales, which makes it difficult to deconvolve the processes behind faunal group dominance in seafloor OM cycling. In this study foraminifera exert dominance over metazoan macrofauna at all Arabian Sea sites, both in terms of biomass and uptake. Thus, dominance of uptake by faunal groups in the Arabian Sea is suggested to be biomass-dependent. This dominance is weakened at the OMZ-boundary (814 m), due to the increase in oxygen availability and the resultant larger metazoan community — consistent with the findings of Woulds et al. (2007) where macrofaunal domination was observed at the Pakistan Margin OMZ-edge at 940 m.

While some studies suggest that macrofaunal uptake is an important pathway in OM cycling at the seafloor (e.g. Rossi et al., 2009; Sweetman et al., 2009) others show that

meiofauna can be more important (e.g. Moodley et al., 2000; Woulds et al., 2007). For example, in-situ experiments in an intertidal estuarine environment by Rossi et al. (2009) found that between 10 and 50 % of labelled carbon was taken up by macrofauna. Similarly, in ex-situ incubations of deep (700 m) Norwegian fjord sediments, Sweetman et al. (2009) found metazoan macrofauna were responsible for 100 % of faunal carbon processing after 7 days, and then after 14 days foraminifera were accountable for up to 5 % of processing, despite being a minor component of the benthic biomass.

In contrast, Moodley et al. (2000) suggest that meiofauna can be relatively more important than the macrofaunal group. This dominance is thought to be related to benthic community structure, as biomass is often positively correlated with label uptake (Middelburg et al., 2000; Woulds et al., 2007). However, the dominance of one faunal group over another has also been attributed to local dissolved oxygen conditions, whereby one group may have greater tolerance to dramatic changes such as intermittent hypoxia (Woulds et al., 2007). Similarly, on Arctic beach incubations by Urban-Malinga and Moens (2006), meiofauna accounted for most of faunal carbon uptake as metazoan macrofauna were not present (due to the absence of oxygen), but bacteria dominated benthic metabolism. Meiofaunal domination may have been assisted by the lack of grazing by or competition from macrofauna. However, biomass does not always correlate positively with label uptake. For example, in a fjord environment, Witte et al. (2003a) found that macrofauna were largely responsible for faunal label-uptake despite being <5 % of the benthic biomass. This study provides an additional example where foraminiferal OM uptake was more important that metazoan uptake in the majority of cases, and in this case that dominance was driven by community composition.

One reason for the generally observed biomass-uptake relationship in these experiments may be that larger macrofauna are able to ingest greater quantities of labelled material do to their increased gut size. Alternatively, or simultaneously, the dominance of larger fauna in OM processing could be due to predation on smaller organisms, e.g. foraminifera, and thus a 'double-uptake' of labelled material. While benthic macrofauna are known to ingest foraminifera accidentally, as part of detrital feeding, some are thought to selectively feed on foraminifera (review by Gooday et al. (1992) and references therein). Specifically, scaphopods are selective predators thought to prey on specific benthic foraminifera (Bilyard, 1974; Davies, 1987) and have been observed with foraminifera within their guts (Moodley et al., 2002). Reports of predation by macrofauna on foraminifera typically come from deep-sea settings and have involved scaphopods along with polychaetes, isopods,

molluscs and crustaceans(Lipps, 1983). For example, isopod predation on foraminifera has been observed in polynya on the Greenland Shelf (Ahrens et al., 1997), in the Norwegian Sea at 1288 and 2104 m depth (Svavarsson et al., 1993) and by Gudmundsson et al. (2000) in the Iceland Sea.

In this study, we assume that metazoan macrofauna also fed on meiofauna which may also have ingested the label, given the weight of evidence from previous studies. However, this cannot be independently verified as due to the size of fauna, isotopic signatures were determined for whole organisms with no differentiation between the gut system and the body tissue. Furthermore, downcore transport of OM (i.e. bioturbation and burrowing) could not be measured in this study, but the presence of macrofauna in many settings has led to the rapid vertical transport of OM in sediments (e.g. Blair et al., 1996; Levin et al., 1997) which may explain the greater quantities of label recovered at 2–3 cm depth at 814 m.

Summary of controls

In summary, the results suggest that oxygen availability, community composition, and background OM quantity and quality (proxies for food supply) all play a role in determining the uptake of OM by seafloor fauna. Faunal uptake was greatest under artificially increased oxygen concentrations and at sites with greater background OM, higher quality OM and larger faunal biomass.

When ambient oxygen concentrations were maintained in the Arabian Sea, oxygen did not appear to play a major role in carbon uptake by fauna. Instead label uptake was highest at the site with the greatest background food supply (500 m) as shown by its large organic carbon content and least degraded OM (indicated by higher DI values). A correlation between uptake and OM availability and quality suggests that the faunal community at 500 m was primed for responding to the added OM pulse. It was not possible to establish an oxygen threshold level as proposed by Woulds et al. (2007), but the influence of altered oxygen concentrations was greatest at the OMZ boundary (814 m) as shown in the oxygen manipulation experiments. The overall uptake was dominated by foraminifera, which was driven by their dominance of the biomass.

The faunal uptake of carbon in the Baltic Sea is largely controlled by oxygen, and further influenced by the faunal community composition (which was itself strongly controlled by

oxygen availability). Macrofauna were shown to be an important processor of OM in shallow sediments, while carbon uptake was negligible at 210 m

5.5.4. Vertical Transport Of OM

The presence of macrofauna in many settings has led to the rapid vertical transport of OM in sediments (e.g. Blair et al., 1996; Levin et al., 1997). Downcore transport of OM (i.e. bioturbation and burrowing) was not quantified in this study. While some previous studies have found isotopically labelled organisms confined to the top 5 cm of the sediment column (Aberle and Witte, 2003; Sweetman et al., 2009) others have reported rapid downward transport of label to 10–15 cm depth (Blair et al., 1996; Levin et al., 1997; Witte et al., 2003a). However, as labelled fauna were only picked down to 3 cm in each experiment, the vertical transport of OM can only be tentatively addressed.

In general, more added label was recovered from fauna in the surface sediments than at depth (2–3 cm) at all sites, with the exception of the manipulated O_2 experiments at 814 m. The presence of fauna at the surface is due to their requirement for oxygen. Under elevated oxygen conditions, oxygen penetration depth into the sediment is greater, enabling fauna to remain active at depth, as seen at 814 m (Figure 69). It may be that active metazoans were able to sequester food and bury it at depth within the sediment, (i.e. out of reach from competitors). This is of particular advantage as the relationship between food input and vertical distribution of macrofauna is thought to be due to the episodic nature of food supply to the seafloor, meaning food is scarce for long periods of times (Jumars et al., 1990). However active subsurface fauna were not observed at 1156 m where the oxygen penetration depth would have been greater, given the increase in bottom water concentrations.

However this downward migration was not observed at any other site under elevated oxygen concentrations. Further, burrowing fauna have been seen to move upwards in response to decreased oxygen (Nilsson and Rosenberg, 1994), but this movement was not seen in this study. It may be that fauna in the region are already living close to the sediment surface due to the low availability of oxygen. In the Arabian Sea OMZ, most fauna are thought to be found within the surface layers of the sediment column (e.g. Hughes et al. 2009), consistent with the finding here of decreasing metazoan biomass downcore in all experiments. Thus it appears that low bottom water oxygen concentrations and limited oxygen penetration into the sediments led to the majority of fauna living close to the

surface at our sites (Breuer et al. 2009; Hughes et al. 2009; Levin et al. 2009; Woulds et al. 2009).

In the Baltic Sea specifically, labelled fauna were not present at all sediment depths in each experiment (Figure 70, Figure 69). Under ambient O_2 concentrations, greater amounts of label were recovered from fauna in the surface 0–1 cm than at depth (1–3 cm), at both sites. However, under manipulated O_2 concentrations, this trend reversed.

Due to the rapid decrease in label recovery with sediment depth and the relatively low metazoan abundance, it can be assumed that the added label at these sites is likely to have been confined to the top 5 cm. Sweetman et al. (2009) found that labelled-foraminifera were confined to the top 0–2 cm after a 14-day experiment in a Norwegian fjord (Korsfjorden, 700 m). However, in-situ labelling experiments by Witte et al. (2003a) in a deeper (1265 m) Norwegian fjord revealed rapid vertical subduction of label down to 10 cm within 3 days, though most of the labelled fauna were found in the surface sediments. Similarly, on the North Carolina continental slope (850 m), Levin et al. (1997) reported rapid transport of label to >10 cm. In general, most of labelled organisms are found close to the sediment-water interface, even if mixing does occur deeper into the sediments (Sweetman et al., 2009; Sweetman and Witte, 2008; Witte et al., 2003a).

A large caveat is that the fauna in the oxygen manipulation experiments may not be active at their natural depth habitats. Fauna may have migrated upwards, in response to the pulse of food, or for oxygen.

5.5.5. Decoupling Of Carbon And Nitrogen Signatures

Decoupling of overall carbon and nitrogen uptake was seen in all experiments in the Arabian Sea (Figure 67). C:N ratios were not calculated for the Baltic Sea due to the lack of foraminifera, and the poor N resolution in macrofauna. There was greater retention of carbon compared to nitrogen in the faunal pool, thus the resulting C:N ratios of the labelled material in fauna was higher than in the original added algae (4.04). Decoupling was most evident in the foraminifera species *Lenticulina* spp. and *Globorotalia menardii*, and in the polychaetes. *Lenticulina* spp. showed enhanced nitrogen uptake under increased oxygen conditions, whereas *Globorotalia menardii* showed little or no nitrogen uptake under any experimental conditions. Polychaetes generally showed enhanced carbon reteuntion under ambient oxygen conditions.

Previous carbon- and nitrogen-labelling studies have demonstrated the importance of C:N coupling in seafloor sediments. Evrard et al. (2010) observed a strong nitrogen preference by meiofaunal organisms in coastal sediments, the opposite of what is observed here. This may be the result of the difference in nitrogen availability between the coastal environment and the oxygen minimum zone of the Arabian Sea. However, Rossi et al. (2007) observed a shorter residence time of organic nitrogen compared to organic carbon in estuarine sediments. The relationship between carbon and nitrogen assimilation by macrofauna in the Arabian Sea OMZ has previously been identified by Hunter al. (2012) in their carbon and nitrogen tracing study. The authors found that macrofauna C:N assimilation ratios varied between taxa and most values ranged between 10 and 60, greater than the 4.04 C:N ratio of the added label. Some species (e.g. nematodes and polychaetes) displayed ratios up to 250, suggesting a strong preference for carbon uptake. In this study, C:N ratios generally ranged from 7–12, at least double that of the added phytodetritus (4.04), suggesting that carbon is preferentially retained in comparison to nitrogen. Under ambient oxygen conditions, polychaete C:N ratios (~40) were within the range observed by Hunter et al. (2012). Initial thoughts were that the presence of carbonate material in the samples could skew the C:N ratios, but all samples were treated with HCl to decarbonate. Hunter et al. (2012) hypothesise that anaerobic metabolism increases faunal demand for organic carbon, given that lactate accumulation in animal tissue has been observed in fauna under persistent oxygen stress (Seibel, 2011). Enhanced C:N ratios were found under reduced oxygen experiments at 1156 m, where the faunal community is accustomed to much higher bottom water oxygen concentrations. Therefore, given the already low ambient oxygen concentrations at 500 and 814 m, it is not surprising that this trend is not also observed there.

5.6. Conclusions

- Benthic faunal communities play a significant role in determining the short-term fate of organic matter in Arabian Sea (Indian Margin) sediments.
    - The role of benthic fauna in short-term organic matter cycling is strongly influenced by oxygen availability, community composition, and background OM quantity and quality (proxies for food supply).
    - In general, faunal uptake was greatest:
        - under artificially increased oxygen concentrations.
        - at sites with larger background sedimentary OM contents.
        - at sites with higher quality sedimentary OM.

        - at sites with a large faunal biomass.
    - Macrofauna responded positively to artificially elevated oxygen concentrations, becoming more active (as indicated by greater uptake rates).
- Benthic faunal communities play a smaller role in determining the short-term fate of organic matter in Baltic Sea (Gotland Basin) sediments, than in the Arabian Sea.
    - The role of benthic fauna in short-term organic matter cycling is strongly influenced by oxygen availability and community composition.
    - In general, faunal uptake was greatest :
        - under ambient oxygen concentrations.
        - at sites with a large faunal biomass.
    - In general, faunal uptake was reduced when:
        - oxygen concentrations were manipulated.
    - Macrofauna were shown to be an important processor of OM in shallow sediments (60 m.), while carbon uptake was negligible at 210 m.
- In both regions,
    - Uptake was dominated by the most abundant faunal group (foraminifera at all sites except 60m).
    - Uptake generally decreased with sediment depth (downcore). The exceptions were when oxygen concentrations were artificially depleted.

6. CARBON BUDGETS

6.1. Introduction

The isotope tracer experiments conducted in this study have so far only quantified the faunal uptake of added organic matter. To build a complete picture of organic matter cycling, specifically carbon, at the seafloor other pools should be investigated. Many previous studies have found that remineralisation by the benthic community is the dominant fate of organic carbon arriving at the seafloor (e.g. Woulds al., 2009;

On comparison of isotopically labelled pulse-chase experiments conducted across the Pakistan OMZ with the results of previous studies, Woulds et al. (2009) identified three categories of benthic carbon processing patterns, as explained by environmental and biological variations: "respiration dominated", "active faunal uptake" and "metazoan macrofaunal" carbon processing. Later, Woulds et al. (2016) added a fourth category, "bacterial uptake-dominated" to account studies where bacterial uptake of carbon exceeded that of usually-dominant respiration. Thus, in order to complete a full carbon budget at the seafloor, studies using ^{13}C labelling of food sources can to quantify OM assimilation by benthic bacteria and remineralisation by the faunal community. This approach has been used previously, and studies generally show a rapid response to added OM dominated by respiration, followed by a bacterial dominance of faunal processing (e.g. Woulds et al., 2009; Anderson et al., 2008; Pozzato et al 2013). The vast majority of studies have been conducted at ambient oxygen concentrations, and so this study will join the few studies have conducted oxygen manipulation experiments (e.g. Pozzato et al., 2013).

6.1.1. Aims And Hypotheses

Building on the faunal OM process patterns reported in the previous chapter, this study includes both the respiration and bacterial uptake of OM – completing the biological carbon budget. The aim was twofold:

- to investigate the response of biological carbon-processing in the Arabian and Baltic Sea to changes in bottom water oxygen concentrations.
- to categorise the regions according to the categories of benthic carbon processing patterns defined by Woulds et al. (2009; 2016).

Thus, the following hypotheses were addressed:

- Biological sedimentary organic matter processing is:
    - dominated by bacteria and foraminifera where oxygen is depleted and organic matter quality is low (e.g. in the OMZ core of the Arabian Sea, and at the deep anoxic sites of the Baltic Sea).
    - evenly shared between macrofauna, foraminifera and bacteria where oxygen is not limited and organic matter quality is high (e.g. outside of the OMZ in the Arabian Sea, and at oxygenated sites in the Baltic Sea).
- Respiration-dominated uptake sites will include those from the lower slope, with low temperatures and low sedimentary OM:
    - 1156 m, Arabian Sea.
- Bacterial-uptake dominated sites will include those that are sandy and/or permeable, and with a large bacterial community:
    - 210 m, Baltic Sea.
- Active faunal-uptake sites will include those with higher faunal biomasses, greater sedimentary OM and higher quality OM:
    - 500 m, Arabian Sea.
- Metazoan-macrofaunal-uptake-dominated sites will include those with large metazoan macrofaunal communities, high OM availability and sufficient oxygen concentrations:
    - 814 m, Arabian Sea.
    - 60 m, Baltic Sea.
- Artificial oxygen depletion will move a site towards or into the respiration-dominated uptake category:
    - 814 m, Arabian Sea.
    - 1156 m, Arabian Sea.
    - 60 m, Baltic Sea.
- Artificial oxygen elevation will move a site towards or into the active faunal-dominated uptake category, providing there is a large faunal biomass and sufficient sedimentary OM:
    - 500 m, Arabian Sea.
    - 814 m, Arabian Sea.

6.2. Results

A summary of site conditions is shown in Table 2, full site details can be found in Chapter 3: Material and Methodology.

6.2.1. Benthic Biomass

As reported in chapter 5, faunal communities were divided into foraminifera and metazoan macrofauna. The metazoan macrofauna included polychaete species in Arabian Sea, while molluscs and amphipods were also present in the Baltic Sea. Foraminifera were more diverse, with up to 11 taxa identified.

Foraminifera were present at all sites in both study areas, although only one individual was seen at 60 m in the Baltic Sea. Metazoan macrofauna were present at all Arabian Sea sites, and only at the shallow (60 m) Baltic Sea site. Foraminifera showed the greatest domination of at benthic community under the lowest oxygen conditions, at the 500 m (0.5 μm O_2) and 210 m (0.5 μmO_2) sites. In the Arabian Sea, metazoan macrofauna, predominantly polychaete species, displayed the greatest abundance at the OMZ boundary (814 m) where both the organic matter (5 %) and dissolved oxygen concentrations (1.8 μM O_2) were adequate.

Due to experimental costs, bacterial biomass was only measured in the top 1 cm of sediment at all sites, and thus faunal community data is now reported using surficial (01 cm) data. Metazoan biomass was greatest at 814 m in the Arabian Sea, and at 60 m in the Baltic Sea. Foraminifera biomass was greatest at the OMZ core (500 m) and was only measured in small amounts in the Baltic Sea (210 m only).

6.2.1.1. Bacterial Biomass

In total, 39 different PLFAs were identified and for the ease of visual representation, only the 29 most enriched are shown henceforth.

The most abundant PLFAs in both study areas were 16:0, 18:1ω7, 14:0 and 16:1ω7c (Figure 73, Figure 74). Total PLFA concentrations reached 24.2 mg C m^{-2} in the Arabian Sea sediments, but were much higher in the Baltic Sea, reaching 947.1 mg C m^{-2}. PLFA concentrations were consistently larger under low-oxygen experimental conditions. At 500 m in the Arabian Sea, larger PLFA concentrations were also found under increased

oxygen concentrations. However, at 1156 m (Arabian Sea) and 210 m (Baltic Sea), increased oxygen concentrations corresponded to lower PLFA concentrations. Total concentrations of the bacterial biomarker PLFAs (i14:0, i15:0, ai15:0, i16:0 and 18:1ω7) were low at all sites: between 4.0 and 24.2 mg C m^{-2} in the Arabian Sea, and between 10.5 and 122.1 mg C m^{-2} in the Baltic Sea. Bacterial biomarker PLFA concentrations, differed between both sites and experimental treatments (Figure 75).

Bacterial biomass in the top 1 cm was quantified by summing the concentrations of five bacteria-specific PLFAs (i14:0, i15:0, ai15:0, i16:0, and 18:1ω7) and applying the correction detailed by (Middelburg et al., 2000). In the Arabian Sea, surface bacterial biomass decreased with increasing site depth (Figure 76, Table 20); from 1.24 ± 0.43 g m^{-2} at 500 m to 0.40 ± 0.03 g m^{-2} and 0.37 ± 0.14 g m^{-2} at 814 m and 1156 m respectively. In the Baltic Sea surface bacterial biomass ranged from 0.89 ± 0.31 g m^{-2} at 60 m to 7.14 ± 0.92 g m^{-2} at 210 m water depth (Figure 76).Bacterial biomass decreased with increasing ambient oxygen concentrations in both study areas. Similarly, at 60 m and 1156 m bacterial biomass was greater when oxygen conditions were reduced. At 500 m and 210 m bacterial biomass was greater under elevated oxygen concentrations. Conversely, bacterial biomass at 1156 m decreased when oxygen concentrations were increased. At 814 m, bacterial biomass did not differ between experimental treatments.

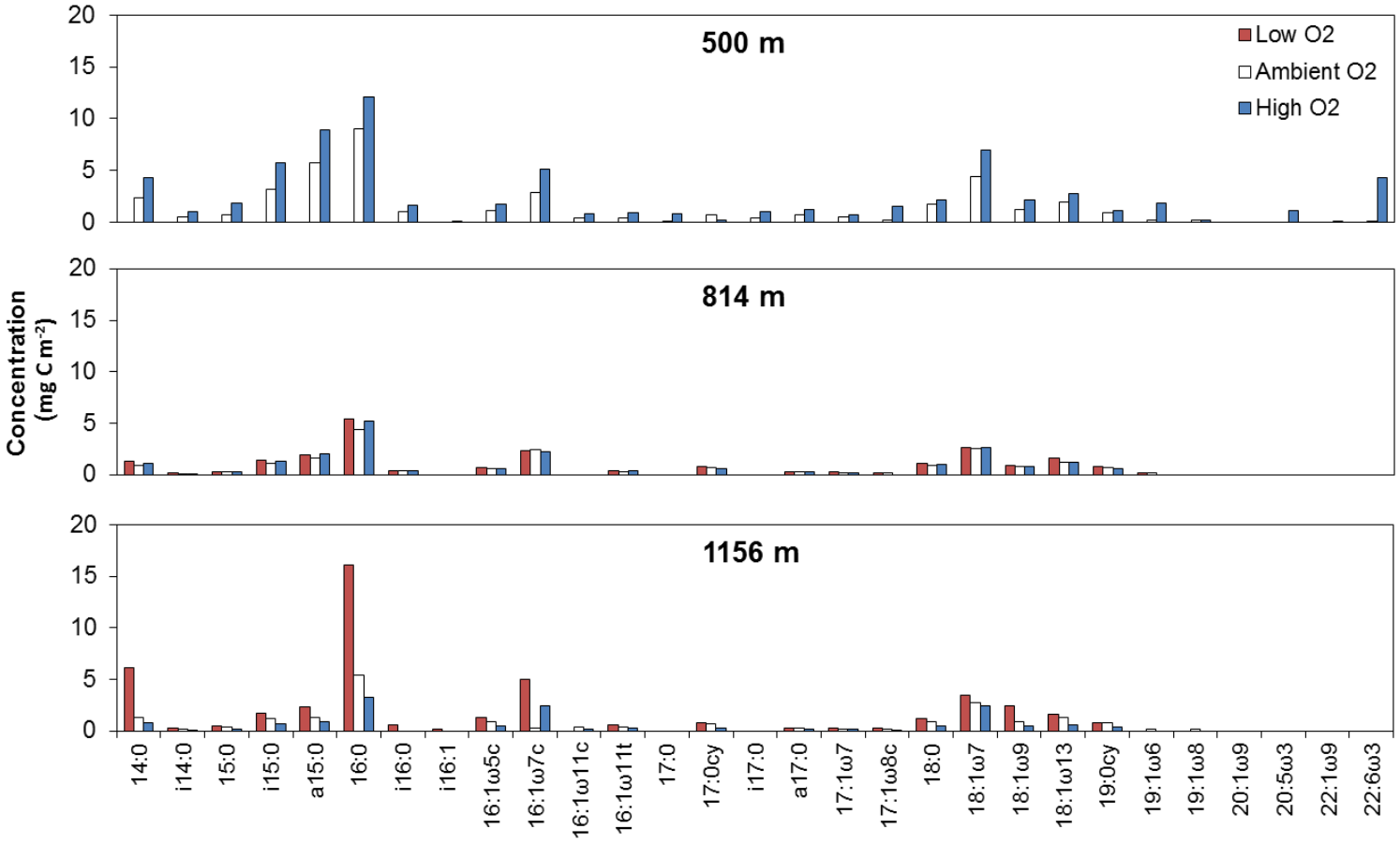


Figure 73. Concentrations of selected sedimentary PLFAs in surface sediments (0-1 cm) of sites in the Arabian Sea.

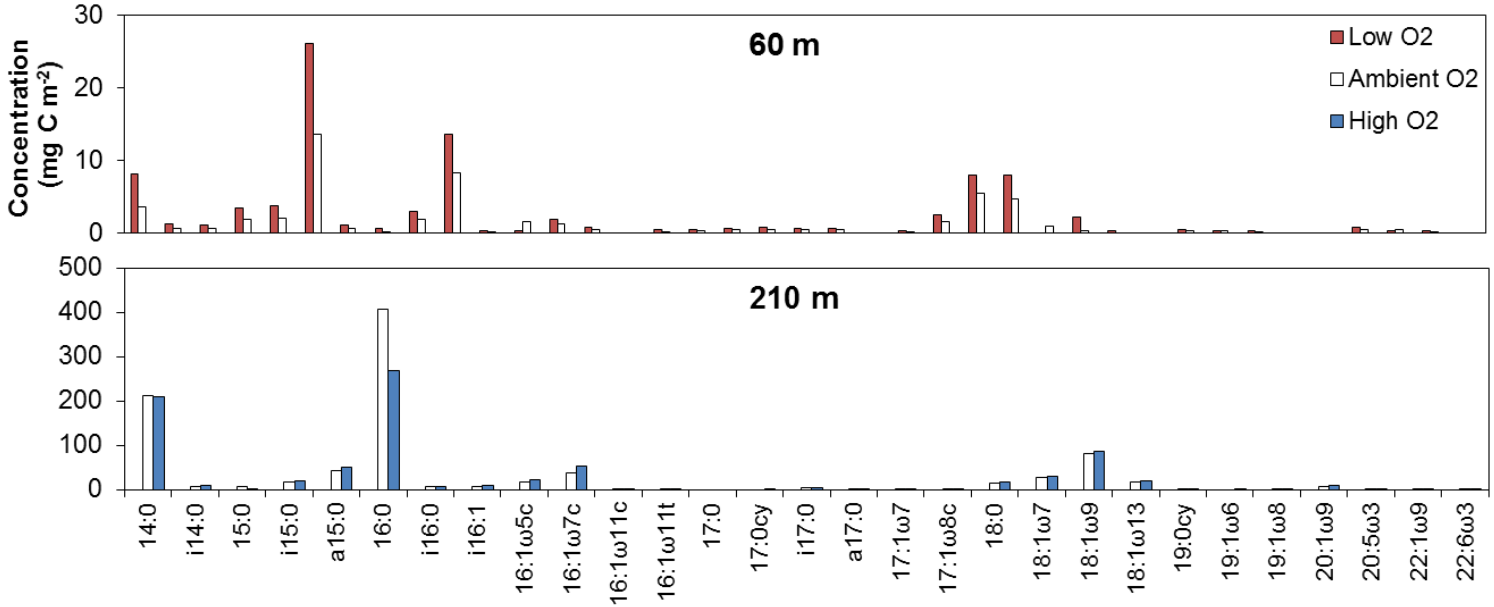


Figure 74. Concentrations of selected sedimentary PLFAs in the surface sediments (0-1 cm) of sites in the Baltic Sea (note difference in scale between sites).

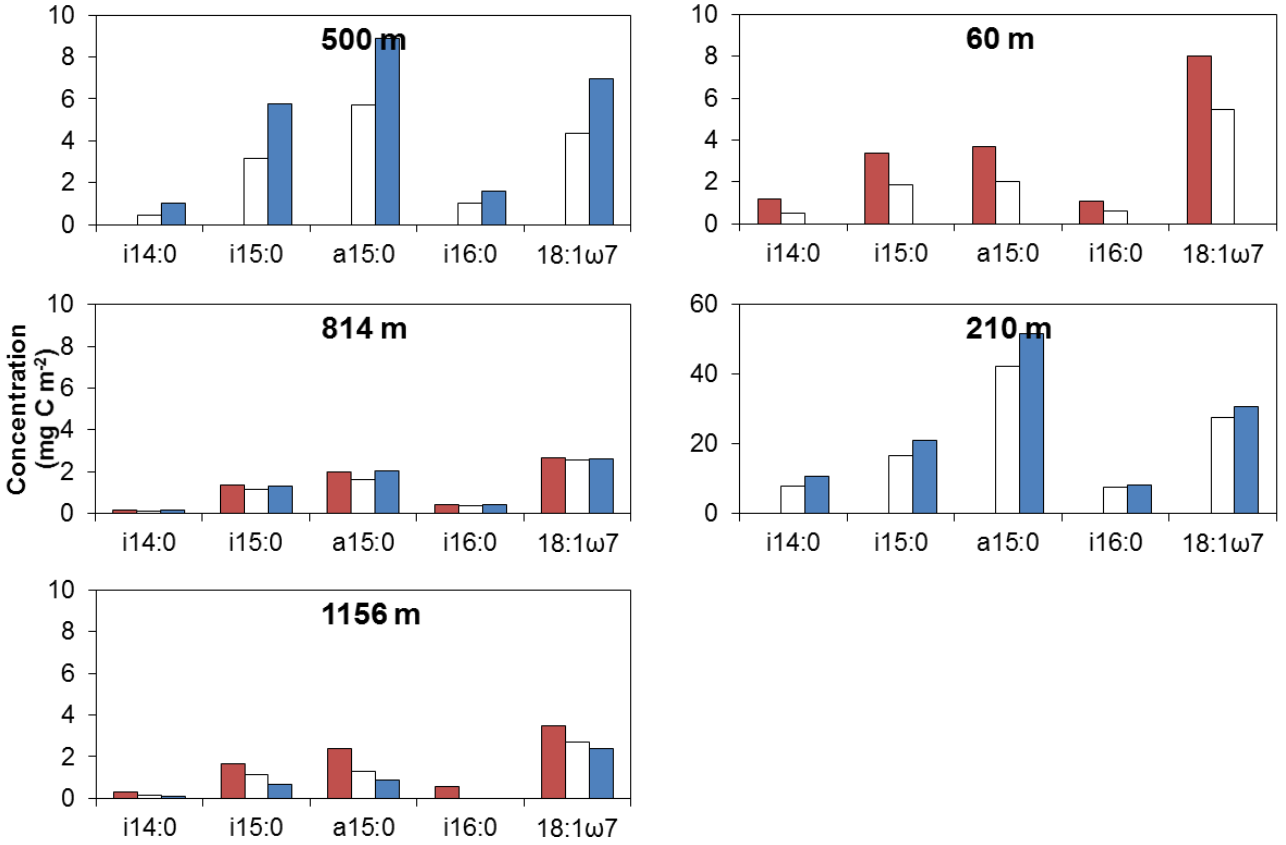


Figure 75. Concentration of bacteria-specific PLFAs in surface sediments (0-1 cm) at all sites, under different experimental conditions.

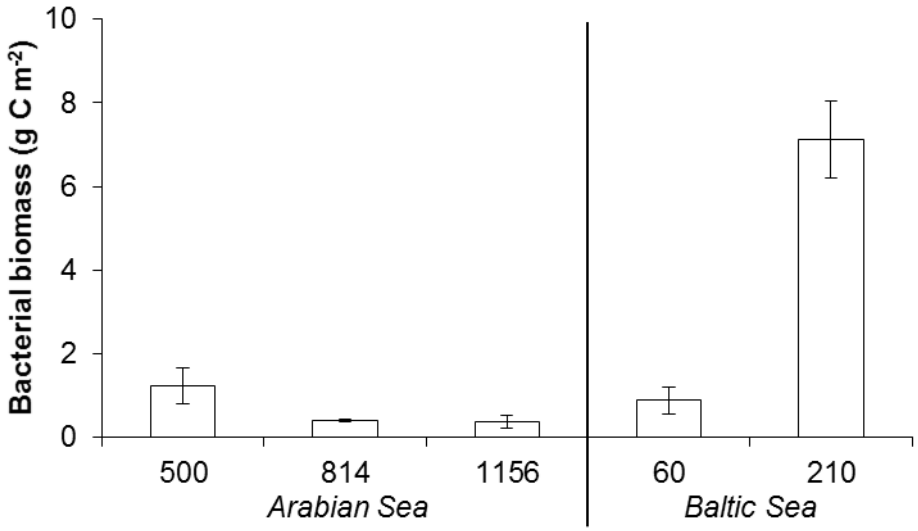


Figure 76. Bacterial biomass at all sites, top 1 cm of sediment (error bars represent ± 1 S.D., n≥2).

6.2.1.2. Total Benthic Community Biomass

Bacteria dominated the total benthic biomass at all sites, in both study areas (Figure 77). In the Arabian Sea, bacterial biomass domination was greatest at the oxygen depleted 500 m site (86.4 ± 4.1 %), and decreased with depth: 814 m (79.1 ± 1.2 %) and 1156 m (75.6 ± 6.6 %). Similarly in the Baltic Sea, bacteria made up nearly all of the biomass recovered: 94.7 ± 1.8 % at 60 m, and 99.8 % at 210 m. The same trend was seen in absolute biomass (mg C m^{-2}); decreasing bacterial biomass with water depth (Figure 78).

Conversely, foraminiferal dominance increased with site depth in the Arabian Sea: 13.3 ± 4.0 % at 500 m, to 15.8 ± 0.9 % at 814 m, and 22.9 ± 6.2 % at 1156 m. However, this pattern was not seen in absolute foraminiferal biomass, which was greatest at 500 m (Figure 78).

Table 20. Benthic biomass in the top 1 cm at all study sites (error bars represent ± 1 S.D., n≥2).

Site		Biomass (mg C m^{-2})			
Study area	**Depth** *m*	**Metazoans**	**Foraminifera**	**Bacteria**	**Total**
Arabian Sea	500	3.5 *(± 4.9)*	181 *(± 41)*	1241 *(± 428)*	1.43 *(± 0.43)*
	814	26.0 *(± 18.1)*	79.6 *(± 19.2)*	401 *(± 27.4)*	0.51 *(± 0.03)*
	1156	6.8 *(± 2.8)*	106 *(± 53)*	375 *(± 143)*	0.49 *(± 0.14)*
Baltic Sea	60	46.6 *(± 18.5)*	-	886 *(± 310)*	0.93 *(± 0.31)*
	210	-	14.4 *(± 9.1)*	7135 *(± 919)*	7.15 *(± 0.92)*

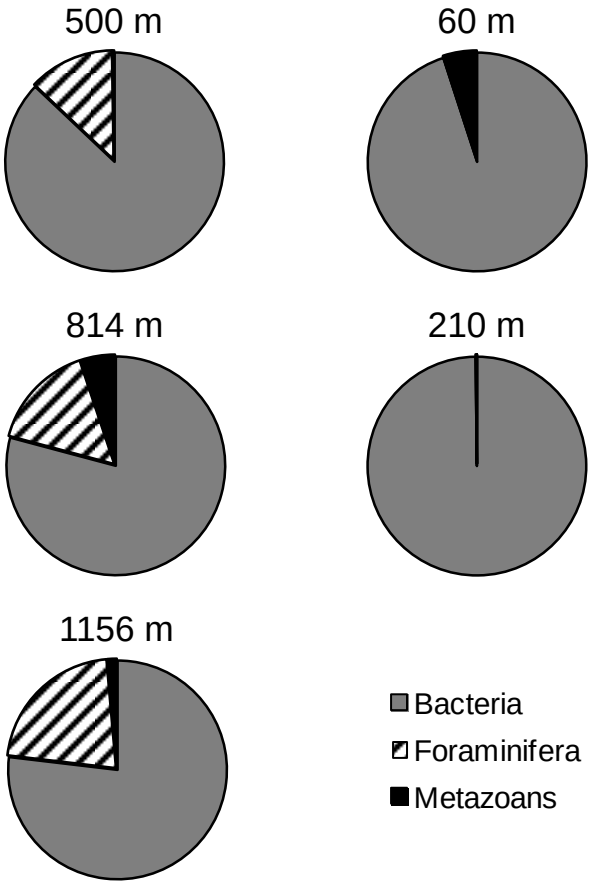


Figure 77. Whole benthic community composition at all sites in both study regions.

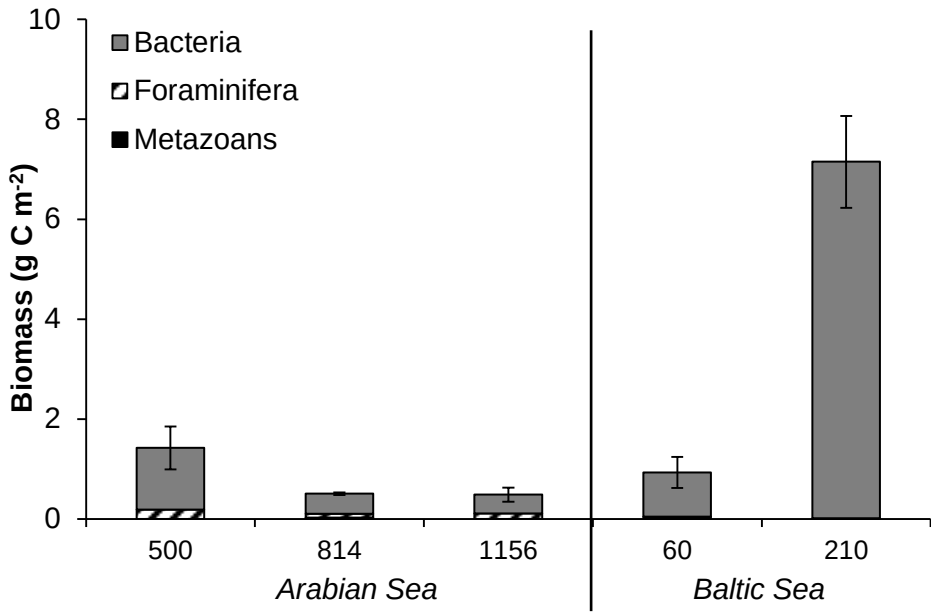


Figure 78. Absolute benthic biomass (C) composition at all sites in both regions

6.2.2. Biotic Carbon Uptake

6.2.2.1. Bacterial Carbon Uptake

Incorporation of ^{13}C into individual PLFAs reached 0.27 and 27 mg C m^{-2} in the Arabian and Baltic Seas respectively. Across the Arabian Sea, the most ^{13}C-labelled individual PLFAs were 16:0, 14:0, 16:1ω7c, and 22:1ω9. In general, PLFA-suite labelling patterns were similar at each site in the Arabian Sea, even though total concentration differed (Figure 79). In the Baltic Sea however, most label was incorporated into 16:0, 14:0, 16:1ω7c, 20:1ω9, and 19:1ω6 (Figure 80). Irrespective of site, greater isotopic labelling of individual PLFAs, (notably 16:0, 14:0, and 16:1ω7c) was observed under decreased oxygen concentrations.

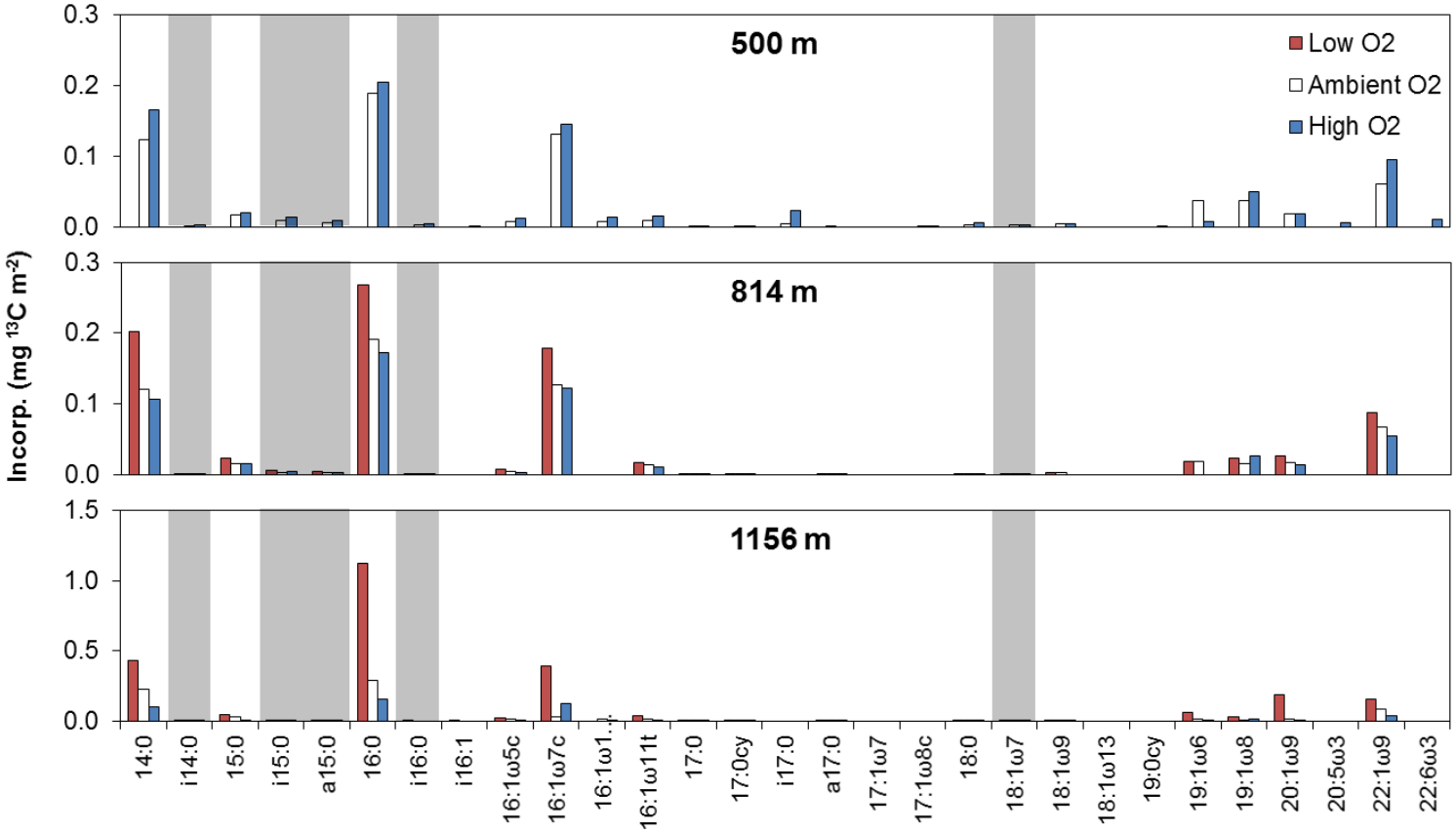


Figure 79. ^{13}C-labelled PLFAs in the surface sediments (top 1 cm) of the Arabian Sea (note difference in scale in 1156 m plot). Bacteria-specific PLFAs are shaded in grey.

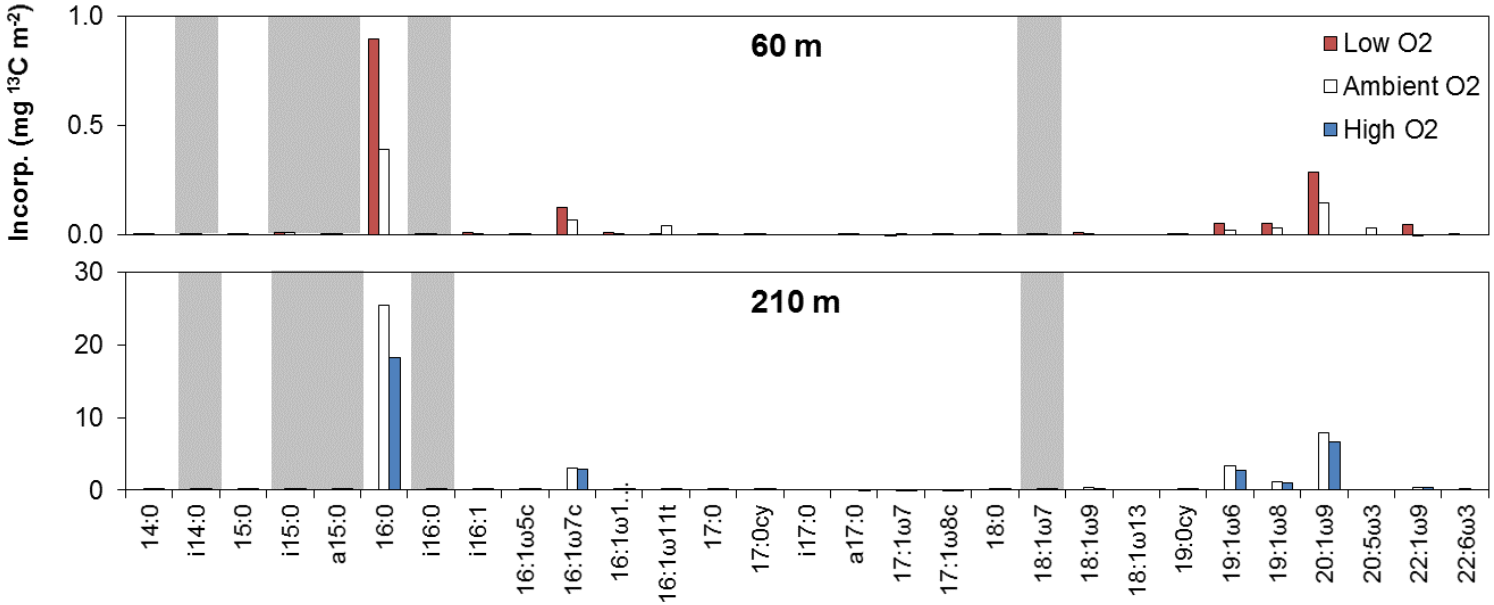


Figure 80. ^{13}C-labelled PLFAs in the surface sediments (top 1 cm) of the Baltic Sea (note difference in scales between sites). Bacteria-specific PLFAs are shaded in grey.

Bacteria-specific uptake of added label was calculated using the sum of incorporation into five bacteria-specific PLFAs (i14:0, i15:0, ai15:0, i16:0, and 18:1ω7) and applying the correction detailed by (Middelburg et al., 2000). Uptake of added ^{13}C-labelled material after 5 days was evident at all sites under both ambient and manipulated oxygen concentrations. Bacterial incorporation of added label under ambient oxygen conditions was greatest at 210 m in the Baltic Sea (8.46 mg C m^{-2}) (Figure 81). The smallest bacterial carbon uptake under ambient oxygen concentrations also occurred in the Baltic Sea, at 60 m depth (0.29 mg C m^{-2}).

Under ambient oxygen concentrations in the Arabian Sea, bacterial carbon uptake was greatest within the OMZ (500 m,1.24 mg C m^{-2}) and decreased with increasing water depth; 0.57 mg C m^{-2} (814 m) and 0.48 mg C m^{-2} (1156 m).Elevated oxygen concentrations led to a corresponding increase in carbon uptake at 500 m, (+45 %), at 814 m (+48 %) and at 11566 m (+28 %).When oxygen concentrations were artificially reduced, carbon uptake by bacteria increased at 814 m (+45 %) and tripled at 1156 m (+209 %). As with the Arabian Sea sites, bacterial carbon was greatest at the site with the lowest bottom water oxygen concentrations(210 m, 8.46 mg C m^{-2}), and order of magnitude greater than those at the shallow oxygenated site (60 m, 0.42 mg C m^{-2}). At 60 m artificially lowered oxygen concentrations corresponded to an increase in carbon uptake by bacteria (32 %). At 210 m elevated oxygen concentrations led to a small decrease(8 %) in carbon uptake.

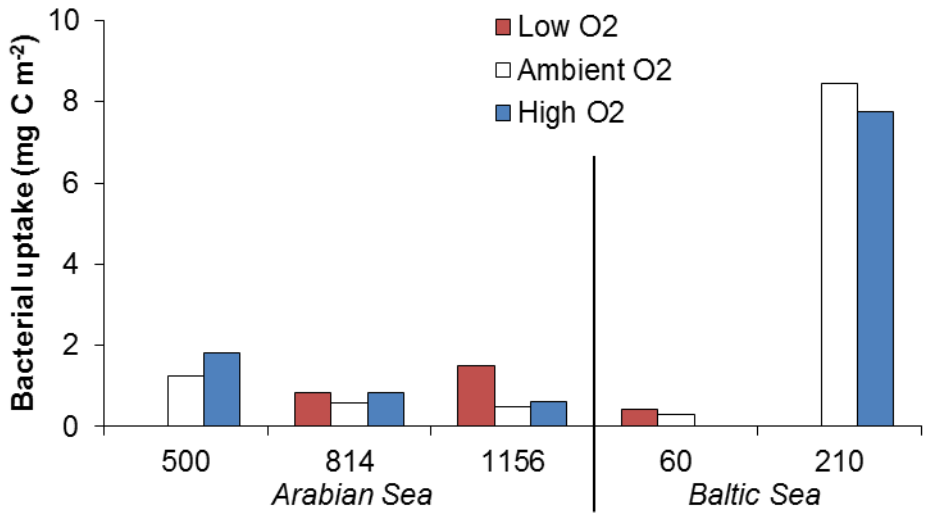


Figure 81. Bacterial carbon uptake (top 1 cm) under different experimental oxygen conditions, at all sites in both study regions (n = 1).

6.2.2.2. Total Benthic Carbon Uptake

Under all experimental conditions at all Arabian Sea sites, bacterial enrichment was lower than both foraminiferal and metazoan uptake (where measured), accounted for 0.3–13.9 % of total benthic uptake (Table 21, Figure 82, Figure 83). In all but one incubation, foraminifera dominated carbon uptake, accounting for between 39.7 and 96.2 % of benthic carbon incorporation. Under ambient oxygen conditions at 814 m, metazoan macrofauna were responsible for 57.8 % of carbon uptake.

In the Baltic Sea, the shallow oxygenated site (60 m) was dominated by metazoan carbon uptake, and the deep anoxic site (210 m) was dominated by bacterial uptake.

Only at 814 m did oxygen manipulation change the dominant pool responsible for carbon processing, where both elevated and lowered oxygen concentrations led to a shift to foraminifera-dominated uptake. Under low oxygen conditions this can be attributed to the decrease in metazoan processed tracer, and under elevated conditions it is due to a four-fold increase in carbon uptake by foraminifera. However there were subtle changes in the degree of dominance by biotic group at other sites. At 1156, elevated oxygen concentrations led to an increase in the both proportion and absolute amount of carbon processed by metazoan macrofauna. Under reduced oxygen conditions, the contribution of both metazoans and bacteria to carbon uptake increased, due to a decrease in absolute foraminiferal carbon uptake and a three-fold increase in bacterial tracer uptake.

Table 21. Total benthic carbon uptake in the surface sediments (0–1 cm) at all study sites in both regions (n=2).

Site		**Experiment oxygen condition**	**Uptake (mg C m^{-2})**			
Area	**Depth** *m*		**Metazoans**	**Foraminifera**	**Bacteria**	**Total**
Arabian Sea	500	Ambient	-	31.2 *(± 6.2)*	1.24	32.4 *(± 6.2)*
		High	0.1 *(± 0.2)*	31.9 *(± 4.8)*	1.80	33.8 *(± 5.0)*
	814	Low	1.9 *(± 1.5)*	6.6 *(± 2.0)*	0.83	9.3 *(± 3.5)*
		Ambient	13.4 *(± 5.9)*	9.2 *(± 3.5)*	0.57	23.2 *(± 9.4)*
		High	17.9 *(± 5.3)*	40.7 *(± 15.6)*	0.85	59.5 *(± 20.9)*
	1156	Low	2.5 *(± 3.6)*	6.7 *(± 4.2)*	1.49	10.7 *(± 6.8)*
		Ambient	3.1 *(± 3.4)*	20.9 *(± 0.3)*	0.48	24.5 *(± 3.7)*
		High	9.6 *(± 8.9)*	20.8 *(± 7.3)*	0.62	31.0 *(± 16.2)*
Baltic Sea	60	Low	3.7 *(± 1.0)*	-	0.42	4.1 *(± 1.0)*
		Ambient	13.0 *(± 2.6)*	-	0.29	13.3 *(± 2.6)*
	210	Ambient	-	0.4 *(± 0.06)*	8.46	8.9 *(± 0.1)*
		High	-	0.07 *(± 0.07)*	7.75	7.8 *(± 0.1)*

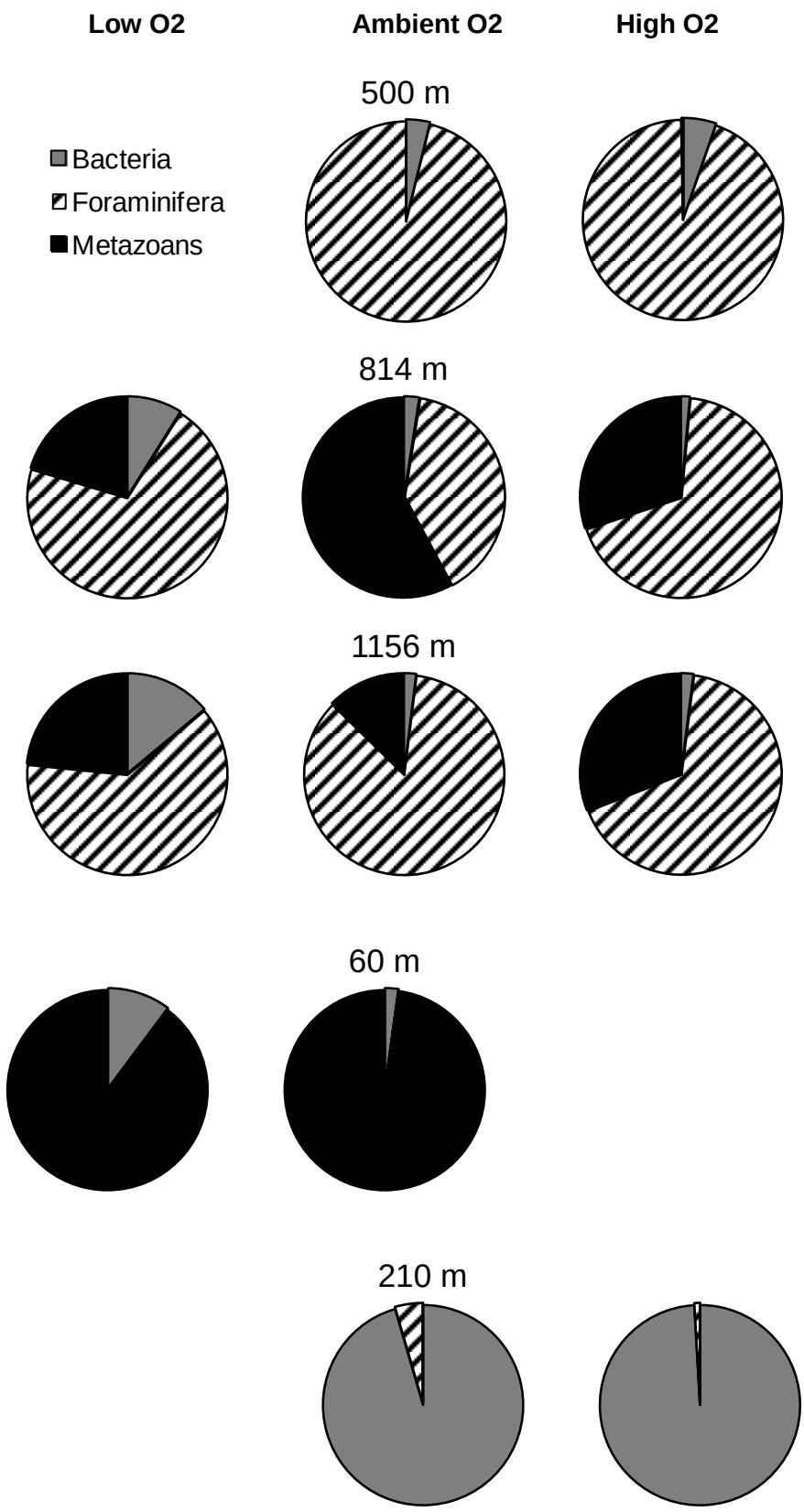


Figure 82. Percentage carbon uptake by different biological pools at all sites across the Arabian and Baltic Seas.

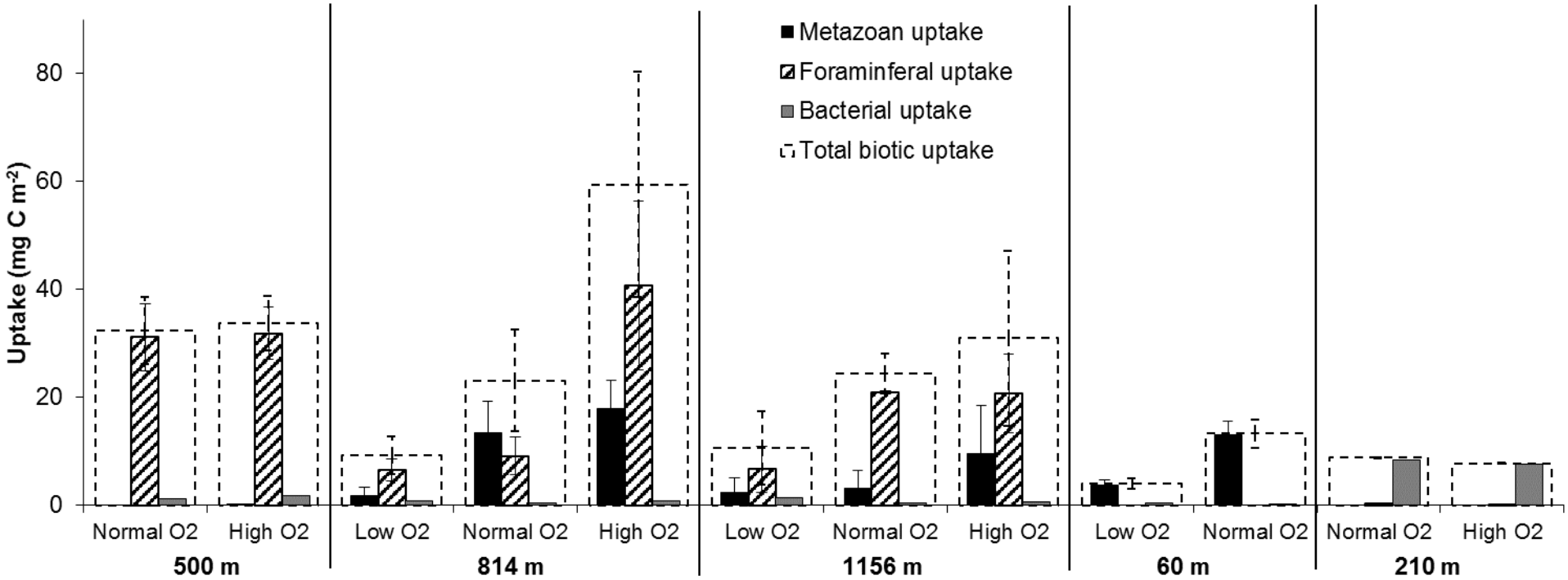


Figure 83. Total biotic uptake of carbon by each biological group, across all sites under different oxygen manipulations (error bars represent range, n=2).

6.2.2.3. Biomass Specific Uptake

Biomass-specific uptake for each biotic group was calculated by correcting the uptake of carbon for the carbon biomass of the pool (mg C uptake / mg C biomass) in the surface sediment (0–1 cm depth).

At all depths in both study areas, bacterial biomass-specific uptake was smaller than the biomass-specific uptake of both metazoans and foraminifera (Figure 84). At 500 m, the biomass corrected uptake by foraminifera was larger than metazoans. At 814 m and 1156 m depth, biomass-specific uptake by metazoans exceeded that of foraminifera, with the exception of the low oxygen manipulation experiment at 814 m. In the Baltic Sea, metazoan and foraminifera biomass-specific uptake were greatest at 60 m and 210 m respectively.

Biomass-specific uptake differed between experimental conditions at sites (Figure 84). Under manipulated oxygen conditions at 814 m, foraminiferal and metazoan biomass corrected uptake decreased, and little change was seen in the bacterial uptake. Conversely, elevated oxygen concentrations at 1156 m corresponded to an increase in both bacterial and metazoan biomass-specific uptake, while only a bacterial response was observed during decreased oxygen conditions. Foraminiferal responses did not differ between experimental treatments. However, an increased foraminiferal biomass-specific uptake occurred at 500 m under elevated oxygen concentrations, unlike the decreased seen at 814 m. In the Baltic Sea, metazoan biomass-specific uptake decreased under reduced dissolved oxygen conditions.

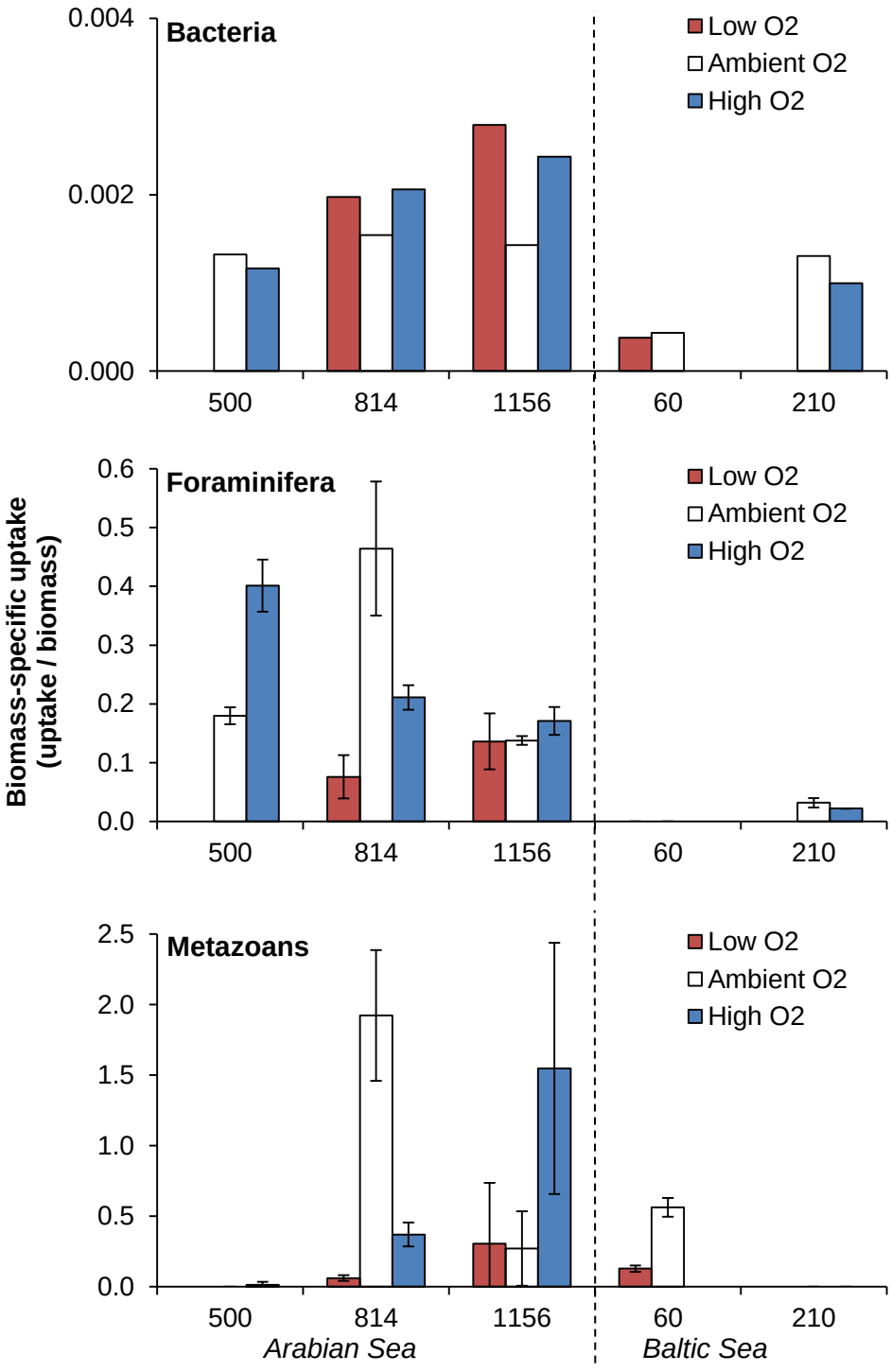


Figure 84. Biomass-specific carbon uptake in surface sediments (0–1 cm) by A) bacteria, B) foraminifera and C) metazoan macrofauna ,under different experimental oxygen conditions, at all sites. Note different scales (error bars represent range, n≥2).

6.2.3. Respiration

6.2.3.1. Arabian Sea Respiration

Respiration of added organic matter was not measured directly, but by the accumulation of labelled DIC in the porewaters and the calculated flux of DIC from the sediments.

Interstitial DIC concentrations decreased rapidly down-core in all experiments, at all sites, to background concentrations within the top 10 cm of sediment (Figure 85). Surficial pore-water DIC concentrations were greatest at the 500 m site, within the oxygen minimum zone (0.5 μM O_2), almost an order of magnitude greater than DIC production at the 814 m and 1156 m sites.

Calculated respiration rates in the Arabian Sea differed between both sites and experimental treatment (Table 22, Figure 89). Under ambient oxygen conditions, respiration of added label was greatest at 1156 m (0.70 ± 0.13 mg C m^{-2} h^{-1}). At this site, both artificially lowered and elevated oxygen concentrations resulted in decreased respiration rates; 0.55 (± 0.14) and0.53 (± 0.32) mg C m^{-2} h^{-1} respectively. Respiration rates were lowest at 814 m (0.46 ± 0.07 mg C m^{-2} h^{-1}) which also displayed reduced respiration under both artificially lowered and elevated oxygen concentrations; 0.38 (± 0.12) and0.24 (± 0.06) mg C m^{-2} h^{-1} respectively. In contrast, increased oxygen concentrations corresponded to greater respiration at 500 m; 0.69 (± 0.16) mg C m^{-2} h^{-1} under ambient conditions and 1.09 (± 0.08) mg C m^{-2} h^{-1} under elevated oxygen conditions.

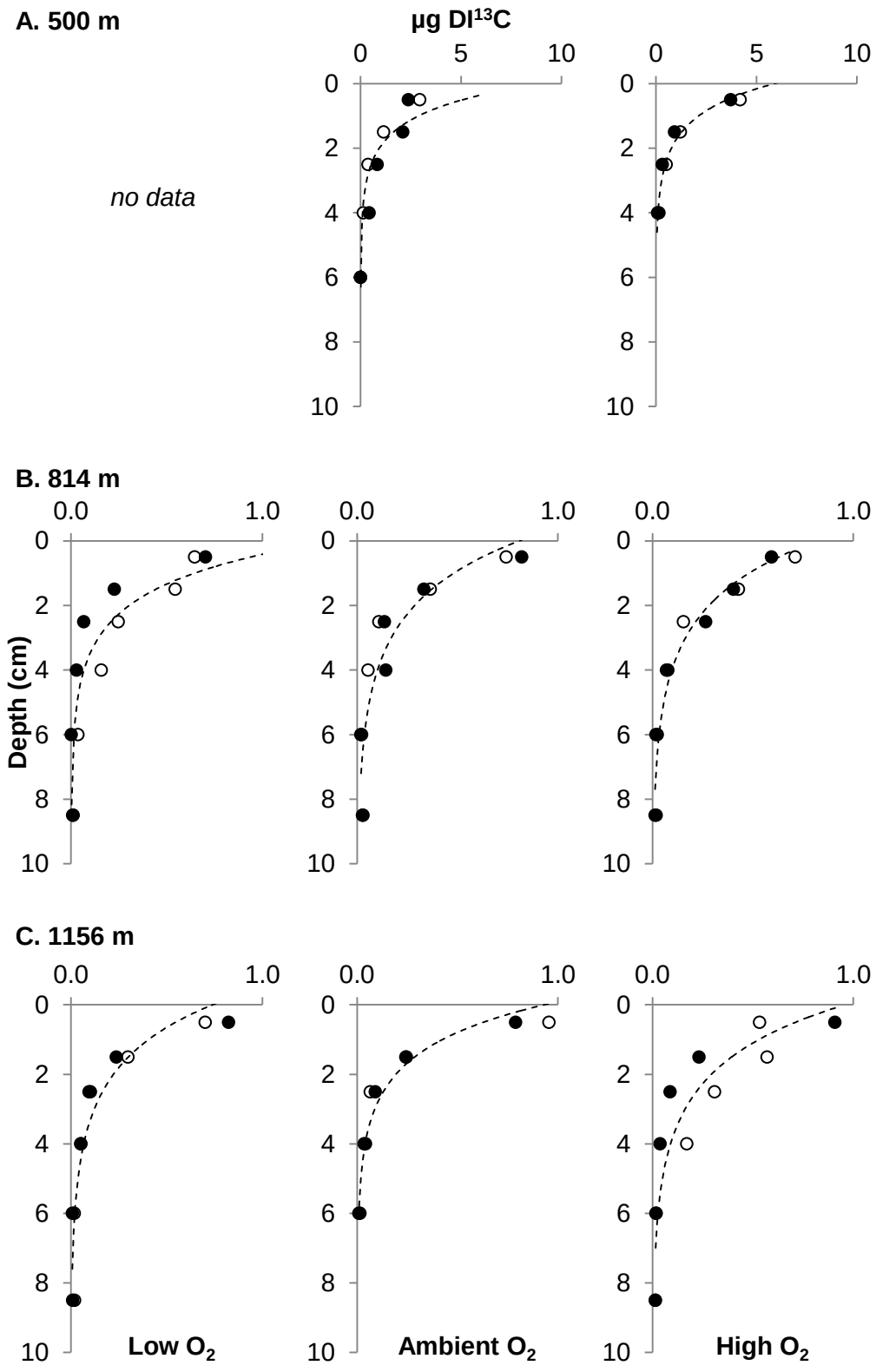


Figure 85. DI^{13}C concentrations in Arabian Sea sediment porewaters. Open and closed circles indicate replicate cores. Dotted line indicates average.

Table 22.Average respiration rates during shipboard incubation experiments in the Arabian Sea (n=2)

Depth	Oxygen	Respiration
m		*mg C $m^{-2}h^{-1}$*
500	Ambient	0.69 (± 0.16)
	High	1.09 (± 0.08)
814	Low	0.38 (± 0.12)
	Ambient	0.46 (± 0.07)
	High	0.24 (± 0.06)
1156	Low	0.55 (± 0.14)
	Ambient	0.70 (± 0.13)
	High	0.53 (± 0.32)

6.2.3.2. Baltic Sea Respiration

Respiration of added organic matter was measured directly both in-situ by use of a lander, and ex-situ by the accumulation of ^{13}C-abelled DIC in the overlying waters of sediment incubations.

6.2.3.2.1. In-situ respiration

Initial respiration of added organic matter was highest at the 210 m site (0.222 ± 0.003 mg C m^{-2} h^{-1}), followed by the 75 m (0.194 ± 0.012 mg C m^{-2} $hour^{-1}$) and 60 m (0.129 ± 0.009 mg C m^{-2} h^{-1}) sites (Table 23, Figure 86).

At two sites (75 m, 210 m) the lander chambers were opened and allowed to flush with bottom waters before closing for a second incubation period (Figure 87). At the 75 m site, following a five hour opening, post-opening respiration was half that of pre-opening (0.050 ± 0.006 mg C m^{-2} h^{-1}). At the 210 m site, following a single hour opening, post-opening respiration was similar to that of pre-opening (0.277 mg C m^{-2} h^{-1}, no valid replicate).

*Table 23. Summary of average respiration rates observed during in-situ lander experiments in the Gotland Basin, Baltic Sea (n=2). *Stirring mechanism failed in chamber B at 210 m.*

Depth	Pre-opening		Opening	Post-opening	
m	**Respiration** *mg C m^{-2} h^{-1}*	**Duration** *h*	**Duration** *h*	**Respiration** *mg C m^{-2} h^{-1}*	**Duration** *h*
60	0.194 (± 0.012)	24	-		
75	0.129 (± 0.009)	23	5	0.050 (± 0.006)	18
210	0.222 (± 0.003)	22	1	0.277 (*n = 1)	17

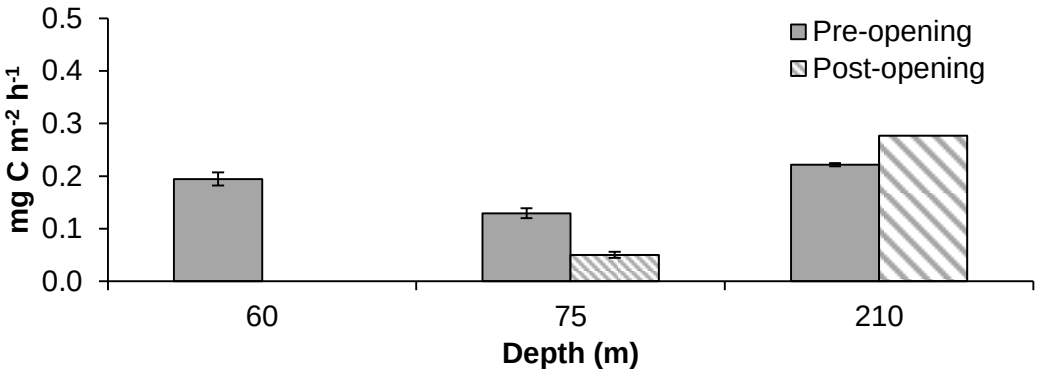


Figure 86. Respiration rates of added organic matter during in-situ lander experiments in the Gotland Basin, Baltic Sea (opening lengths: 75 m, 5 hours; 210 m 1 hour) Error bars represent range, n=2.

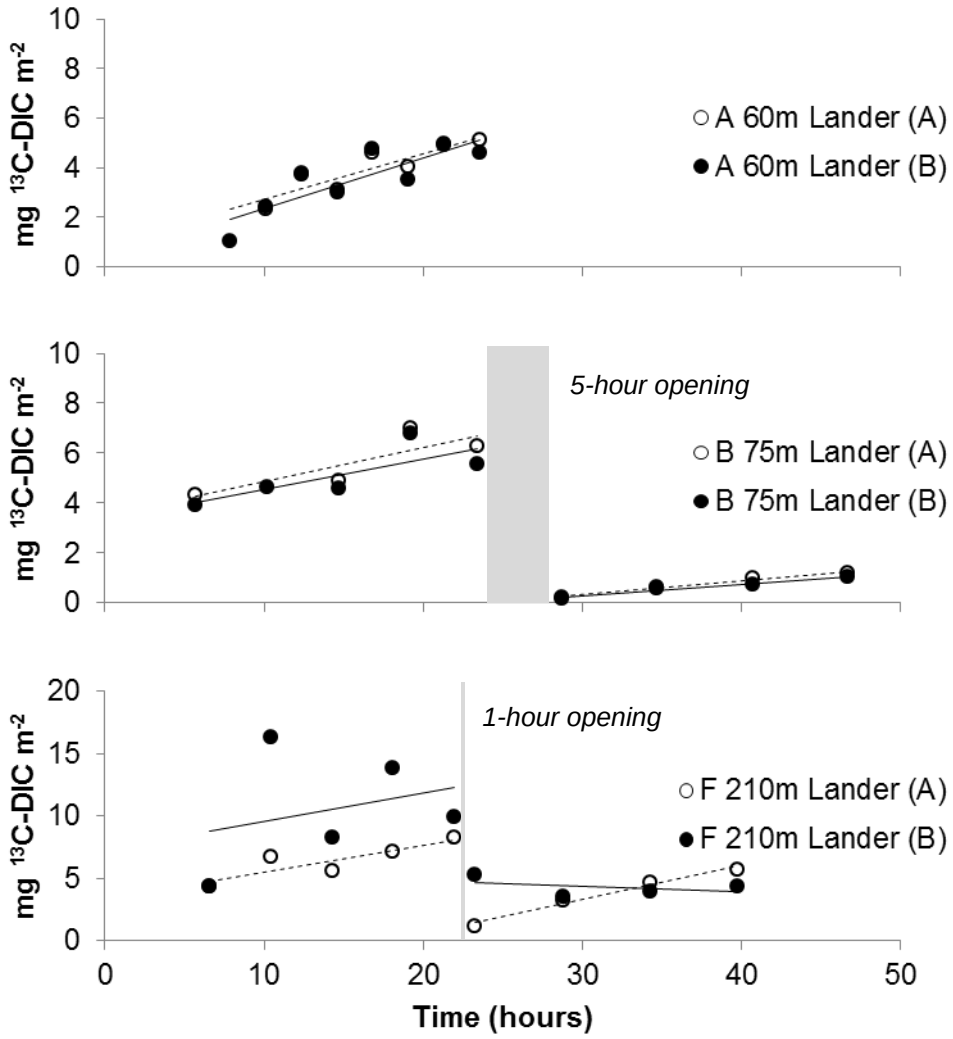


Figure 87. DIC production during in-situ lander experiments in the Gotland Basin, Baltic Sea. Post-opening rates taken after chambers were flushed with ambient bottom water (five hours at 75 m, one hour at 210 m).

6.2.3.2.2. Ex-situ respiration

Under ambient oxygen conditions, respiration was greater at the oxygenated 60 m site (0.228–0.414 mg C m^{-2} h^{-1}) than at the deeper anoxic 210 m site (0.085–0.122 mg C m^{-2} h^{-1}) (Table 24, Figure 88, Figure 91).

At the oxygenated 60 m site, respiration rates following two-day incubations were double those following five-day incubations: 0.414 ± 0.038, and 0.228 ± 0.032 mg C m^{-2} h^{-1} respectively. In contrast, experiment duration did not seem to influence respiration rates

at the anoxic site (210 m) in the same way. Five-day incubations resulted in greater respiration rates than two-day experiments: 0.122 ± 0.007, and 0.085 ± 0.003 mg C m^{-2} h^{-1} respectively.

When oxygen concentrations were artificially depleted at the shallow site (60 m) respiration rates more than halved (0.083 ± 0.040 mg C m^{-2} h^{-1}). However, when oxygen concentrations were artificially elevated at the deep site (210 m), respiration rates did not significantly change (0.102 ± 0.018 mg C m^{-2} h^{-1}).

Table 24. Summary of average respiration rates observed following shipboard incubation experiments of sediments from the Gotland Basin, Baltic Sea (error bars represent range, n=2).

Depth	Oxygen	Days	Respiration
m			*mg C m^{-2} h^{-1}*
60	Ambient	2	0.414 (± 0.038)
	Ambient	5	0.228 (± 0.032)
	Low	5	0.083 (± 0.040)
210	Ambient	2	0.085 (± 0.003)
	Ambient	5	0.122 (± 0.007)
	High	5	0.102 (± 0.018)

6.2.3.3. Respiration Summary

Average respiration rates of added OM were greater in the Arabian Sea than in the Baltic Sea (Figure 89). At all sites except 210 m, manipulated oxygen concentrations corresponded to changes in respiration rates.

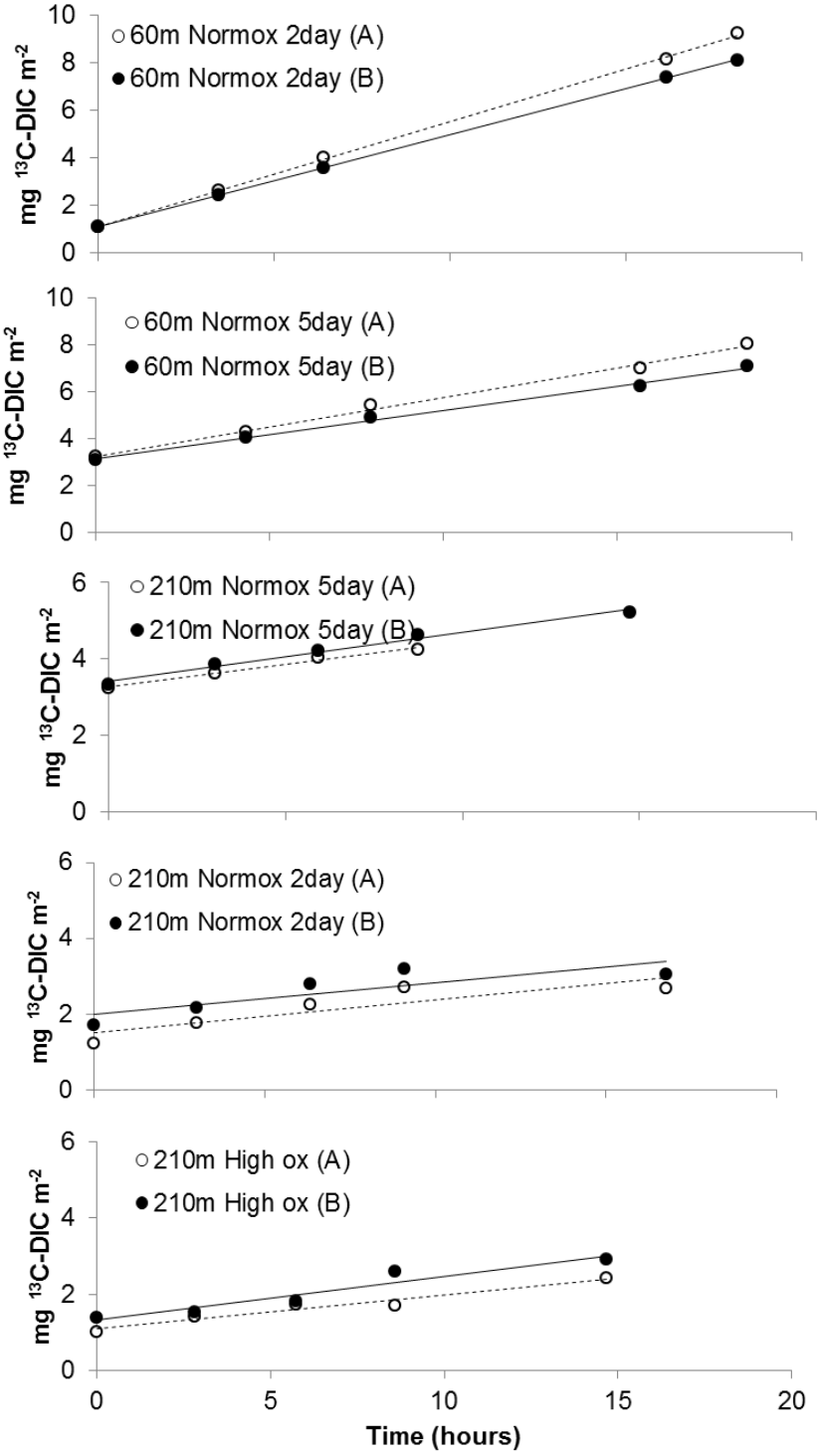


Figure 88. Respiration of added organic matter followingshipboard incubations of seafloor sediments in the Baltic Sea.

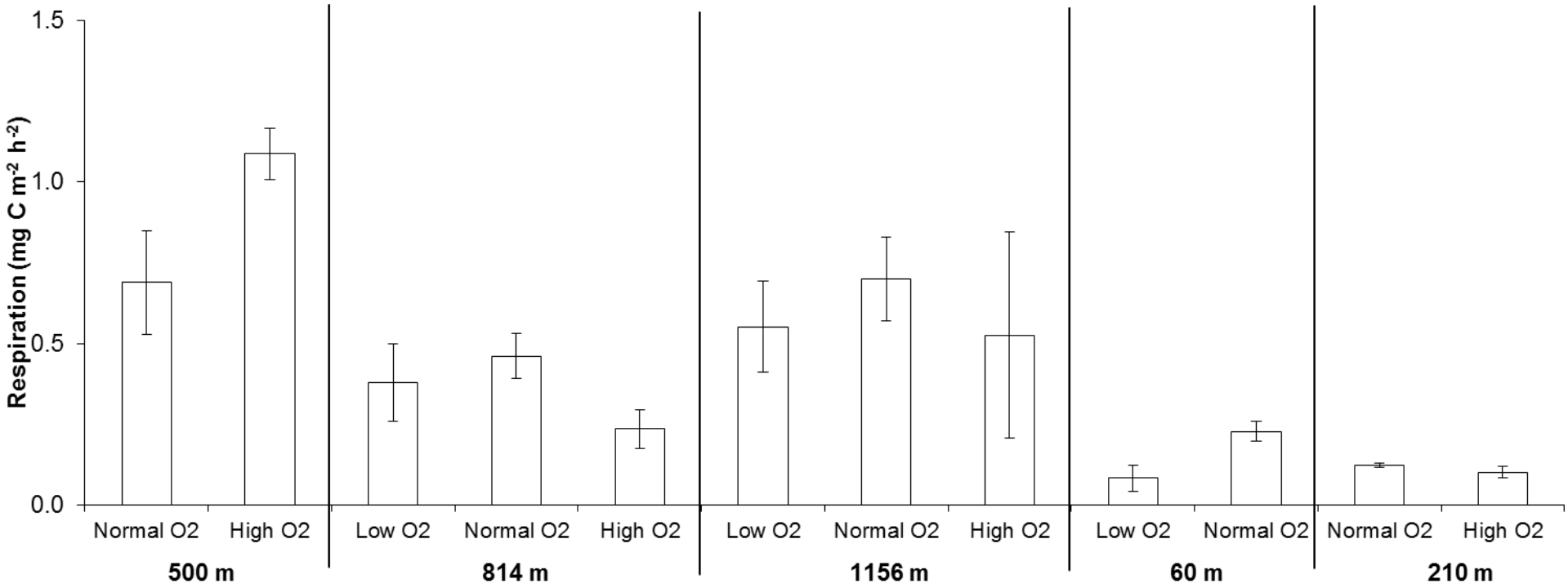


Figure 89. Average respiration rates under oxygen manipulation across both study sites (error bars represent range, n=2.).

6.2.4. Total Carbon Processing

A summary of the fate of added OM is shown in Table 25, Figure 90 and Figure 91.

Under ambient oxygen conditions, respiration was the dominant fate of added OM (69–79 %), but this not hold for all experimental cores.

At all sites, the domination of respiration increased when oxygen concentrations were reduced: increasing by 14 % at 814 m, 9 % at 1156 m and 4 % at 60 m.

At all sites except 500 m, the domination respiration as the fate of added OM reduced under elevated oxygen conditions, decreasing by 37 % at 814 m, 17 % at 1156 m and 1 % at 210 m. At 500 m respiration accounted for 69 % under ambient conditions, but increased to 80 % when oxygen concentrations were elevated.

At 814 m, faunal uptake correlated positively with oxygen concentration, with metazoan macrofauna and foraminifera accounting for 20 % and 46 % of the processed OM respectively.

Table 25. Carbon uptake into different biological pools at all sites, under ambient and manipulated oxygen conditions (n=2)

Site	Depth	Oxygen	Respiration	Bacterial uptake	Foraminferal uptake	Metazoan uptake	Total
	m		*mg C m^{-2} h^{-1}*				*mg C m^{-2} h^{-1}*
Arabian Sea	500	Ambient	0.69 *(± 0.16)*	0.012	0.29 *(± 0.06)*	-	0.99 *(± 0.22)*
		High	1.09 *(± 0.08)*	0.015	0.26 *(± 0.04)*	0.001 *(± 0.002)*	1.37 *(± 0.12)*
	814	Low	0.38 *(± 0.12)*	0.007	0.054 *(± 0.016)*	0.016 *(± 0.012)*	0.46 *(± 0.15)*
		Ambient	0.46 *(± 0.07)*	0.005	0.083 *(± 0.032)*	0.12 *(± 0.05)*	0.67 *(± 0.16)*
		High	0.24 *(± 0.06)*	0.007	0.34 *(± 0.13)*	0.15 *(± 0.04)*	0.73 *(± 0.23)*
	1156	Low	0.55 *(± 0.14)*	0.010	0.046 *(± 0.029)*	0.017 *(± 0.018)*	0.63 *(± 0.19)*
		Ambient	0.70 *(± 0.13)*	0.004	0.16 *(± 0.002)*	0.023 *(± 0.025)*	0.88 *(± 0.16)*
		High	0.53 *(± 0.32)*	0.004	0.14 *(± 0.05)*	0.066 *(± 0.061)*	0.74 *(± 0.43)*
Baltic Sea	60	Low	0.083 *(± 0.04)*	0.003	-	0.027 *(± 0.007)*	0.11 *(± 0.05)*
		Ambient	0.23 *(± 0.03)*	0.002	-	0.095 *(± 0.019)*	0.33 *(± 0.05)*
	210	Ambient	0.12 *(± 0.007)*	0.074	0.003 *(± 0.001)*	-	0.20 *(± 0.01)*
		High	0.10 *(± 0.02)*	0.067	0.001 *(± 0.001)*	-	0.17 *(± 0.02)*

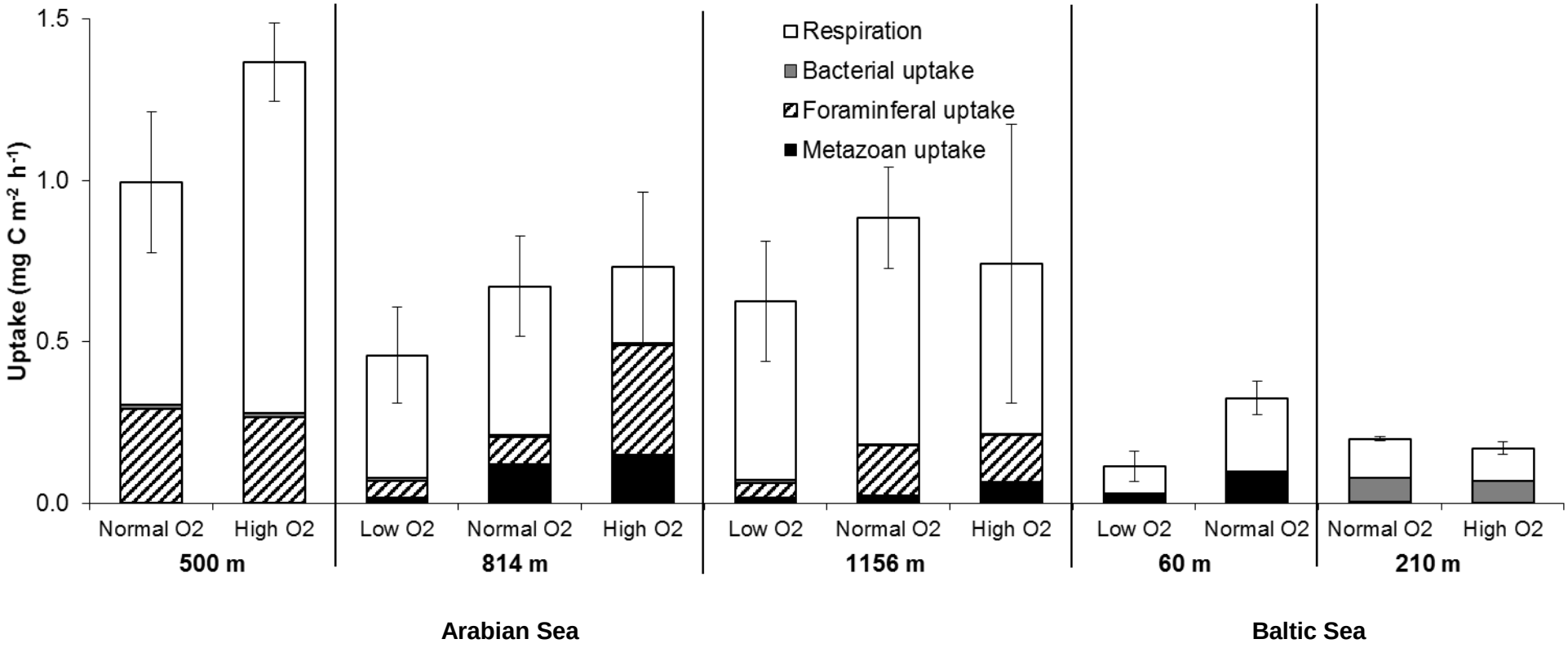


Figure 90. Uptake into the measured biologic carbon pools across both the Baltic Sea and the Arabian Sea sites (error bars represent range, n=2)

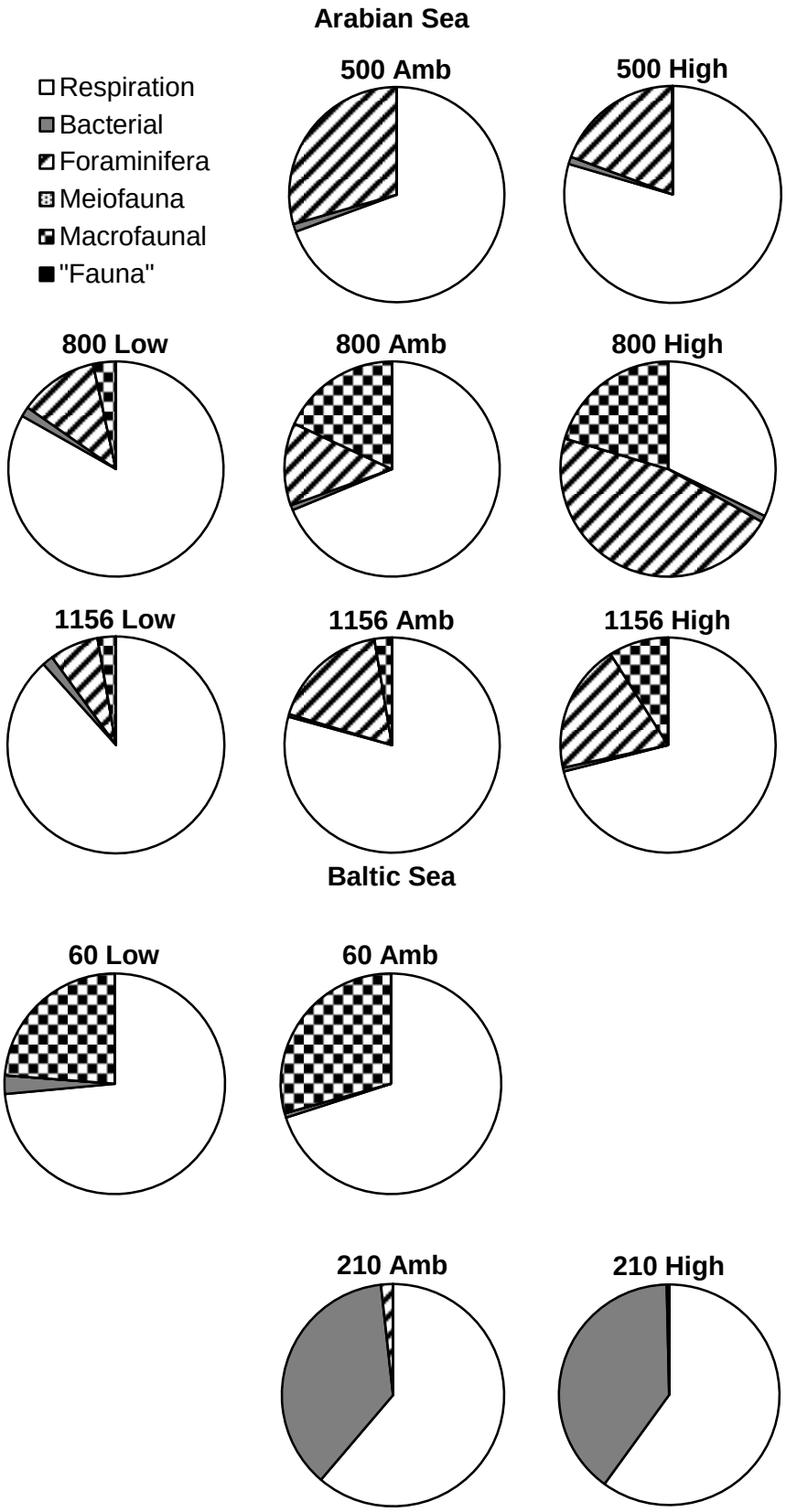


Figure 91. Pie charts showing the relative uptake of added carbon into biological carbon pools, under ambient and manipulated oxygen conditions at all sites in both the Arabian and Baltic Seas.

6.3. Discussion

6.3.1. Limitations

Using the flux of DIC from the sediments as a measure of respiration makes the assumption that the balance of dissolution or precipitation of carbonaceous sediment is zero. Thus, the DIC produced in the experiments is assumed to be solely due to metabolic activities.

In the Baltic Sea, respiration rates were measured both in-situ by use of landers and ex-situ following sediment incubations. At the 60 m oxygenated site, in-situ respiration rates were broadly similar to those calculated from five-day shipboard incubations of sediments. However, in-situ respiration at the 210 m site did not match those rates observed following incubation of sediment for either two or five days. This raises questions regarding the validity of shipboard incubations to measure respiration of organic matter, as sediments may be contaminated with oxygen during core-recovery. However, similarity between A- and B-core was noted in both in-situ and ex-situ experiment approaches in the Baltic Sea experiments.

The use of pore-waters to calculate benthic solute fluxes in the Arabian Sea is subject to several potential inaccuracies. Firstly, the calculations used here assumes steady state conditions, but in reality pore-waters may be subject to variability on daily to seasonal timescales . Secondly, the one-dimensional model is an oversimplification of the benthic environment, excluding the influence of benthic fauna, and ignoring processes such as irrigation, thus the fluxes here are likely to be underestimates. It has been shown that bioturbation and faunal irrigation of sediments can significantly alter benthic flux dynamics, especially in shallow continental margin sediments (Aller, 1983; Pelegri et al., 1994; Wang and Van Cappellen, 1996; Glud et al., 1994). Thus, benthic flux calculations are most often used at sites greater than 1000 m water depth, where the role of benthic fauna is small (e.g. Zabel et al., 1998; Hensen et al., 1998). However, in low oxygen environments (e.g. OMZs) the reduced oxygen concentrations inhibit extensive sedimentary faunal activity (Jannink et al., 1998; Van der Weijden et al., 1999; Smith et al., 2000) and so use of pore-waters for benthic solute flux modelling is acceptable. The third limitation, is the potential for pore-water artifacts to have been introduced during the sampling, recovery and processing of sediment cores.

It is recognised that the fluxes presented here may have been affected by one or more of these inaccuracies, since both bioturbation and irrigation are neglected in the simple model.

Similar one-dimensional diffusive flux models have been used to estimate a range of benthic fluxes in similar environments (Holcombe et al., 2001; Law et al., 2009; Schenau and De Lange, 2001; Winkler, 1888). Law et al. (2009) used both a simple model and the more detailed PROFILE model (Berg et al., 1998) on the Pakistan margin and found them to be in broad agreement, highlighting the suitability of simple-models for basic flux modelling.

The OM dose at each site in both areas was consistent in order to make comparisons between sites and stations, but the differential responses could then be due to the diverse C addition relative to naturally available OM. However, previous studies have found that results are not primarily driven by OM dose (e.g. Pozzato et al., 2013). Only a small amount of the added OM was processed in the experiments (5 days), implying that the carbon addition was substantial and that the benthic communities were not food-deprived.

6.3.2. Fate Of Added Carbon

The results presented here clearly demonstrate that added carbon was processed in the surface sediments at all sites within 5 days. The recovery of added OM to each experiment was in line with previous studies (e.g. Woulds et al., 2007; Moodley et al., 2005; Pozzato et al., 2013). In the Arabian Sea, 8.5–25.4 % of the added label was recovered. The recovery rate in the Baltic Sea was lower: between 2.4 and 6.8 %. In all but one experiment (814 m, elevated oxygen), respiration was the dominant fate of the added OM (Table 26). The distribution of the added OM between C pools differed between both site and treatment.

Table 26. Fate of added carbon in all experiments across both the Arabian and Baltic Seas.

Site	Depth	Oxygen	Respiration	Bacterial uptake	Foraminferal uptake	Metazoan uptake	Total % recovered label
	m		*% of total added*				
Arabian Sea	500	Ambient	11.3	0.2	4.8	-	16.3
		High	20.2	0.3	4.9	0.0	25.4
	814	Low	7.1	0.1	1.0	0.3	8.5
		Ambient	7.8	0.1	1.4	2.1	11.4
		High	4.3	0.1	6.3	2.8	13.5
	1156	Low	12.5	0.2	1.0	0.4	14.1
		Ambient	14.4	0.1	3.2	0.5	18.2
		High	11.7	0.1	3.2	1.5	16.5
Baltic Sea	60	Low	1.8	0.1	-	0.6	2.4
		Ambient	4.8	0.0	-	2.0	6.8
	210	Ambient	2.2	1.3	0.1	-	3.5
		High	1.8	1.2	0.0	-	3.0

Table 27. Compiled biological carbon-processing results from previous studies.

Site	Site conditions				Experimental		
	Depth	OC	O_2	Temp	Method	Duration	Dose
	m	*%*	*uM*	*°C*		*h*	*mg C m^{-2}*
Arabian Sea	140	1.46	92	22	Ex-situ	68	749
	140	1.43	4.9	18		44	632
	140	1.43	4.9	18		118	620
	300	2.36	4.5	15		61	633
	300	2.36	4.5	15		127	667
	300	2.56	4.9	15		58	628
	300	2.56	4.9	15		155	636
	940	3.31	5.8	9		112	659
	940	3.4	7.6	9.3		113	637
	1200	3.27	15	7.2		114	637
	1850	1.4	79	3.5		48	653
	1850	1.4	79	3.5		117	974
	1850	1.2	76	3.7		86	1805
Benguela Upwelling System	605	6.46	222.3	5.5	In-situ	18	1500
	1019	3.9	199.2	3.8		36	
	1335	7.4	237.6	3.3		36	
Wadden Sea	1.5	0.21	5	15	Ex-situ	96	377
Gdansk	1.5	0.05	oxic	20	Ex-situ	72	377
Faero-Shetland	1080	0.2	306	-0.7	Ex-situ	72	500
						144	
E.Med	1079	0.5	209	13.5	Ex-situ	144	500
NW.Spain	2170	0.14	256	3.6	Lander	35	434
Schelde Est.	0.1	0.26	oxic	18	Lab	24	432
N.Sea	37	0.2	oxic	16	Lab	24	432
N.Agean	102	0.12	oxic	14	Lab	24	432
	698	0.08	oxic	14	Lab	24	432
E.Med	1552	0.07	oxic	14	Lab	24	432
	3859	0.07	oxic	14	Lab	24	432
NE.Atlan 2170	2170	0.13	oxic	4	Lab	24	432

Biomass			OM processed				Label recovered	Reference
Bact	Foram	Macro	Resp	Bact	Foram	Macro		
g C m^{-2}			*mg C m^{-2} h^{-1}*				*%*	
1.1	0.13	0.11	2.83	0.17	0.13	0.62	35.4	Andersson et al. (2008) & Woulds et al. (2007)
1.1	0.13	0.11	2.07	0.32	0.39	0.21	20.6	
1.1	0.13	0.11	1.16	0.11	0.26	0.08	31.7	
1	0.1		0.36	0.04	0.08		4.6	
1	0.1		0.28	0.05	0.05		6.7	
1	0.1		0.53	0.32	0.09	0	6.1	
1	0.1		0.48	0.27	0.12		15.8	
0.7	0.07	0.91	0.47	0.02	0.01	0.43	18.4	
0.7	0.07	0.91	0.49	0.18	0.01	0.6	24.7	
	0.04	0.06	0.27	0.01	0.01	0	5.1	
0.3	0.38	0.11	0.06		0.16	0.01	2.3	
0.3	0.38	0.11	0.43	0.01	0.05	0.01	6.3	
0.3	0.38	0.11	2.46	0.02	0.1	0.04	12.1	
			1.74	0.08		0.01	2.2	Aspetsberger et al. (2007)
			0.36	0.1		0.04	1.2	
			0.94	0.1		0	2.5	
3.8	0.01	0.48	0.03	0		0	0.9	Evrard et al. (2010)
0.41		0.56	0.05	0.01		0	1.2	
4		0.74	0.05	0.21		0.01	3.9	Gontikaki et al. (2011)
4		0.74	0.3	0.12		0.01	12.6	
0.01			0.33	0.02			10	Gontikaki et al. (2012)
1.57	0.02	0.04	0.07	0.03	0.05	0.01	1.3	Moodley et al. (2002)
1.26			2.55	0.48		0.69	20.6	Moodley et al. (2005)
2.31			3.03	0.37		0.21	20	
0.52			2.9	0.16		0.03	17.1	
0.37			3.11	0.17		0.01	18.3	
0.25			2.75	0.08		0	15.7	
0.31			2.5	0.11		0	14.5	
0.31			0.3	0.03		0.01	1.8	

Table 27 continued...

Site	Site conditions				Experimental		
	Depth	OC	O_2	Temp	Method	Duration	Dose
	m	*%*	*uM*	*°C*		*h*	*mg C m^{-2}*
Porcupine Abyssal Plain	4800	0.4			Lander	60	1000
						192	
						552	
Sagami Bay	1449		46	2.3	Lander	48	1000
Arabian Sea	885	6.38	54	10	Ex-situ	168	400
	885	6.38	6	10	Ex-situ	168	400
	1791	1.03	125	4	Ex-situ	168	100
	1791	1.03	8	4	Ex-situ	168	100
Norwegian fjord	688		245	7	Ex-situ	48	1000
						168	1000
						336	
Sognefjord	1265		210	7	Lander	36	1000
						72	
German Bight	19		oxic	9	Ex-situ	12	310
						30	310
						132	310
Cretan Sea	1540		244	13	Lander	36	25
							250
Kongsfjorden	0.1	0.1	oxic	3	Ex-situ	144	600
	0.1	0.12	oxic	3	Ex-situ	144	600
Pearl Harbour (mangrove)	0.1	8.22	oxic	24	Ex-situ	48	1800
Pearl Harbour (post-removal)	0.1	3.05	oxic	24	Ex-situ	48	1800
Pearl Harbour (control)	0.1	0.52	oxic	24	Ex-situ	48	1800
Kaneohe Bay (post-removal)	0.1	0.91	oxic	24	Ex-situ	48	1800
Kaneohe Bay (control)	0.1	0.49	oxic	24	Ex-situ	48	1600
Schelde estuary	0.1	0.64	oxic		In-situ	96	1000
	0.1	0.06	oxic		In-situ	72	1000
Oosterschelde	0.5		oxic	10	Lab	6	950

Biomass			OM processed				Label recovered	Reference
Bact	**Foram**	**Macro**	**Resp**	**Bact**	**Foram**	**Macro**		
g C m^{-2}			*mg C m^{-2} h^{-1}*				*%*	
0.25	0.02	0.12	0.17			0.06	1.4	Witte et al. (2003) Aberle & Witte (2003)
0.25	0.02	0.12	0.17	0.01	0	0.01	3.6	
0.25	0.02	0.12	0.24	0.01	0.02	0	14.5	
	0.3				0.12	0.03	0.7	Nomaki et al. (2005)
1.07		2.53	0.31	0.02		0.11	18.7	Pozzato et al (2013)
1.07		2.53	0.32	0.01		0.41	32	
1.28		3.26	0.03	0.01		0	5.9	
1.28		3.26	0.04	0		0.01	8.6	
	0.08	1.62				0	0	Sweetman & Witte (2008) & Sweetman et al. (2009)
	0.07	1.62				0	0	
	0.08	1.62				0	0.1	
8.5		0.25	0.58	0.06		0.16	2.9	Witte et al (2003)
8.5		0.25	0.49	0.15		0.1	5.3	
20.4			0.08	0.48		0.02	2.2	Buhring et al (2006)
20.4			0.12	0.21		0.07	3.9	
20.4			0.06	0.04		0.02	5.2	
0.4		0.06	0.04	0.04			12.4	
0.4		0.06	1.49	0.1			22.8	
			3.5				84.5	Urban-Malinga & Moens (2006)
			2.92				70.4	
18.15		0.71	5.46	0.56		0.04	16.1	Sweetman et al (2010)
5		3.39	5.35	0.43		1.63	19.7	
6		0.34	3.84	0.19		0.31	11.6	
9		1.44	5.3	1.28		0.9	19.9	
3.5		0.88	6.13	0.2		0.52	20.5	
15		9.6		0.12		0.05	1.6	Moens et al (2002)
		10.2				0.11		Herman et al (2000)
5.79	1.23		7.76	3.17	3.96			Moodley et al (2000)

6.3.3. Respiration Of Added Carbon

In this study, respiration accounted for 1.8 to 20.2 % of the total added label. The greatest recovery rates were seen at 500 m (20.2 % recovered) and at 1156 m, where 11.7–14.4 % of added label respired. Respiration is not only the long-term fate of unburied OM (e.g. Rowe et al., 1991), but it is often the dominant sink in short term (hours to days) isotopic labelling studies (e.g. Moodley et al., 2005; Moodley et al., 2002; Woulds et al., 2007; Witte et al., 2003)

The respiration of added OM seen here is consistent with previous findings (e.g. Gontikaki et al., 2011; Moodley et al., 2005; Anderson et al., 2009). Respiration has been observed as the dominant fate of OM processing in a multitude of environments: e.g. N. Atlantic (45 %, Moodley et al., 2002), Norwegian fjord (68 %, Witte et al., 2003). Moodley et al. (2005) incubated sediments with labelled algae across a large range of temperatures and water depths, from coastal estuarine sites to the deep-sea, and found that approximately 15 % of added label was respired within 24 hours. Similarly, 25 % of added label respired within 5 days at 140 m on Pakistan margin (Anderson et al.., 2009). Gontikaki et al. (2011) observed that while bacteria dominated the processing of added carbon (77 %) within 3 days, respiration increased exponentially with time and accounted for 69 % of processed carbon after 6 days,

The respiration rates were averaged over the whole experiment duration and were within the range published for other sites . Previous results from the literature show that respiration rates decrease with both low temperature and increased water depth, which are in turn correlated (Figure 92), but a strong effect of temperature was not observed in this study. The effect of temperature on short-term OM processing was studied by Moodley et al. (2005) who found that a decrease in temperature led to reduced respiration rates (Westrich and Berner, 1988). Sediments from shallow coastal site were incubated under both ambient and reduced temperatures (16 to 6 degrees), which caused the respiration rate to fall.

OM decay is widely found to be reduced or slowed when oxygen is low or absent (e.g. Canfield, 1980) and there is evidence of bottom water concentrations holding some influence over respiration rates in the literature (Figure 93). At 500 m and 814 m, artificially elevated oxygen concentrations led to increased respiration of added OM. However, decreased oxygen concentrations at 814 m, 1156 m and 60 m also led to a

corresponding increase in respiration rates. In this study neither oxygen, nor temperature showed a pronounced effect on respiration rates, but there was some correlation with water depth (Figure 94), indicating that other factors must be responsible. The absence of a relationship between respiration and temperature is probably due to an overprinting of the effect by oxygen. Furthermore, the decreased respiration rates which occurred in response to artificially elevated oxygen concentrations imply that other factors become more important when the biological system is placed under stress.

Given that bacteria often form up to 95 % of the benthic biomass, it is assumed that they also perform the majority of benthic respiration(e.g. Moodley et al., 2002; Gontikaki et al., 2011; Witte et al., 2003). Using allometric relationships for respiration rates and benthic biomass, Heip et al. (2001) calculated respiration rates for the separate benthic classes (megafauna, macrofauna and meiofauna) on the Goban Spur, NE Atlantic. The authors found that macrofauna accounted for 50 % of benthic carbon respiration on the shelf and upper slope, but at depth, respiration was dominated by bacteria (~80 %). Given the lack of relationship with water depth, oxygen and temperature, the respiration rates in this study may be controlled by the size and activity of the bacterial communities. However, respiration rates showed no correlation with bacterial biomass. Instead, respiration rates in both study areas were positively correlated ($R^2 = 0.70$) with total foraminiferal biomass (where present). This is not hugely surprising, given that the present study sites are not particularly deep, and indicates that foraminifera may be responsible for a large proportion of the measured respiration.

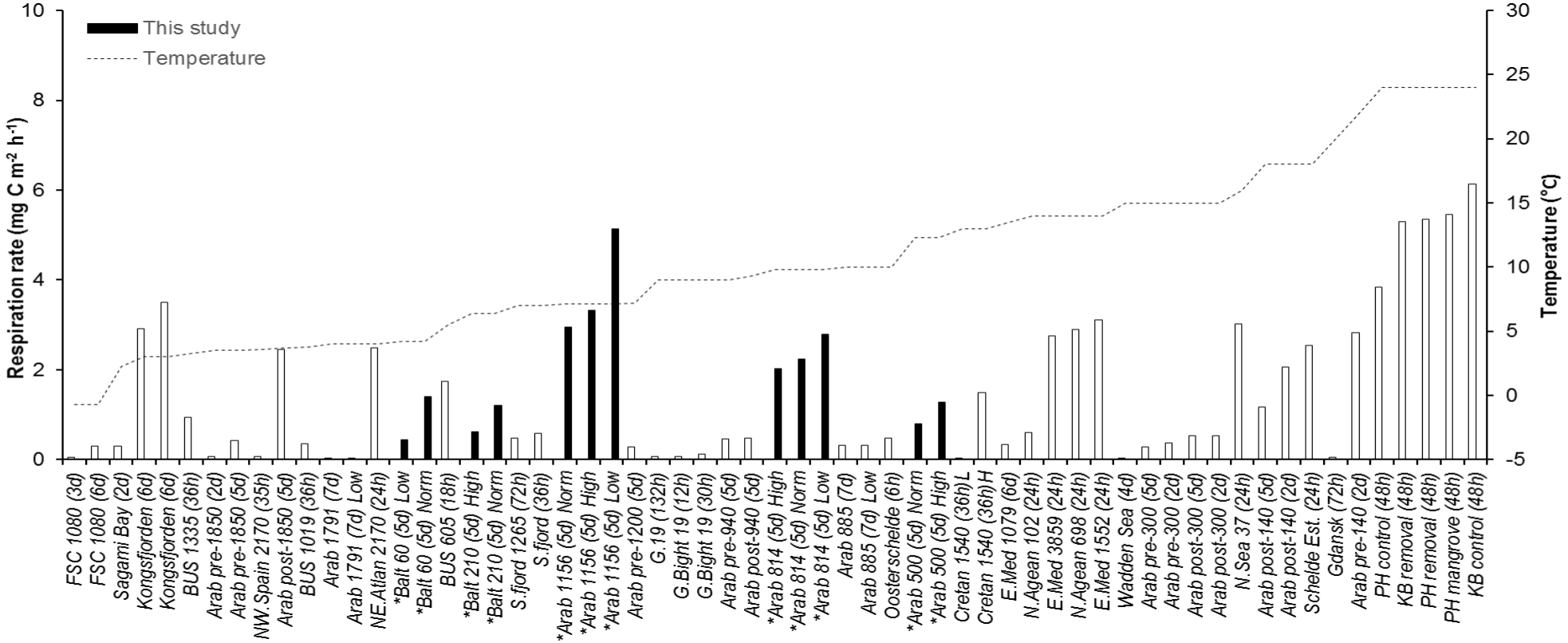


Figure 92. Respiration rates from previous isotope tracing experiments and this study. Sites are ordered by increasing temperature from left to right. Sites from previous literature are described in Table 27.

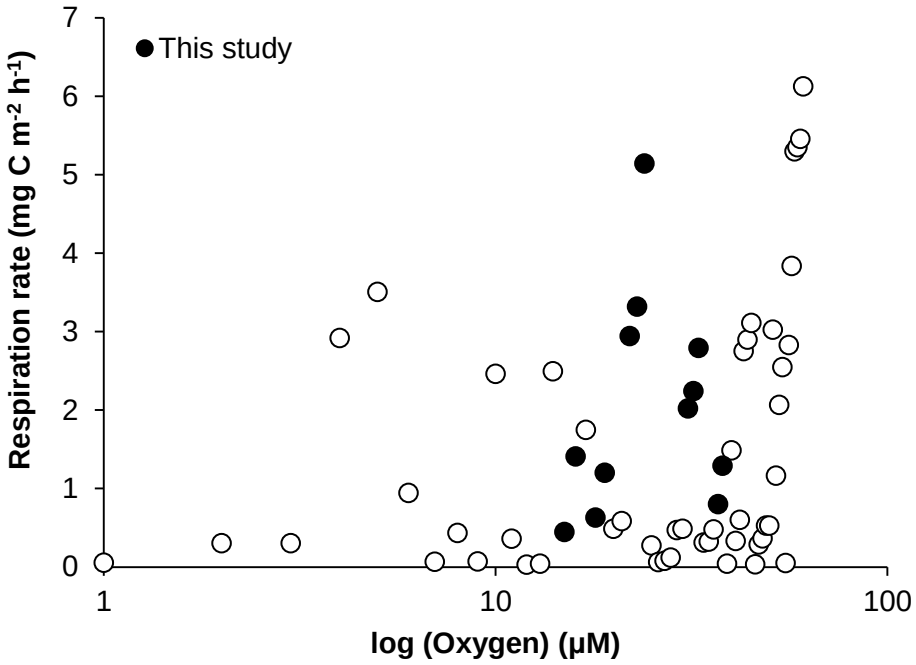


Figure 93. Respiration rates as a function of bottom water oxygen concentration, open circles represent data from previous literature. Sites described in Table 27.

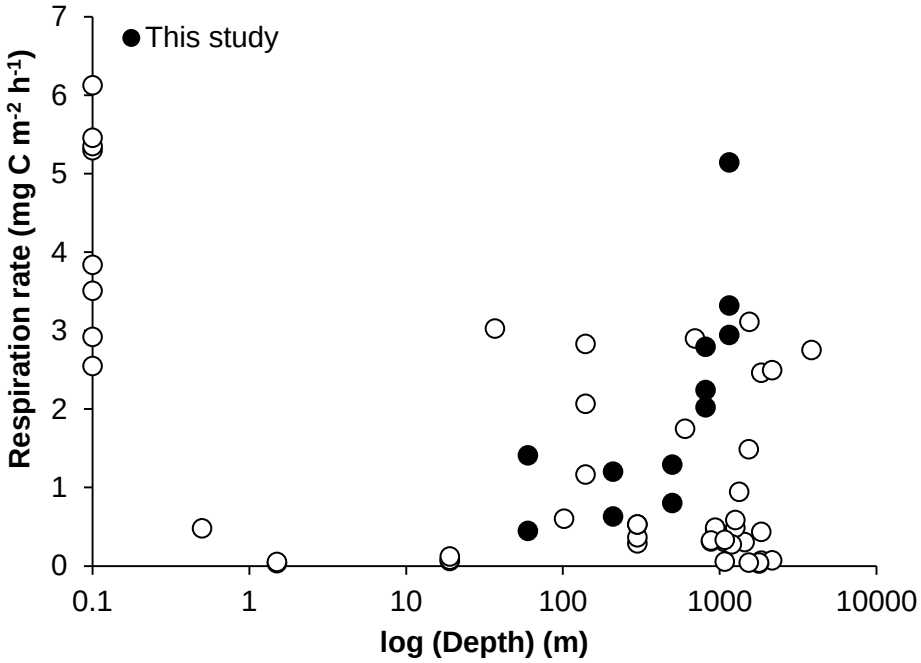


Figure 94. Respiration rates plotted as a function of water depth, from previous literature (sites described in Table 27) and this study.

6.3.4. Bacterial Uptake

In this study, bacteria account for 56–100 % of the biomass standing stock and have been previously shown to be key players in the processing of added OM (e.g. Moodley et al., 2002; Gontikaki et al., 2011; Witte et al., 2003). However, bacterial uptake was responsible for 0.5–3% of the OM processed in the Arabian Sea, and 37-40 % in the Baltic Sea (Figure 91). Bacterial assimilation was evident at all sites within the 5 day incubation, in line with previous findings (Table 27). The bacterial uptake rates at the Baltic Sea 60 m site were similar to those observed in shallow estuarine environments such as the Wadden Sea (Evrard et al., 2010), Kongsfjorden (Urban-Malinga & Moens, 2006), and the Schelde estuary (Herman et al., 2000). In contrast, the high bacterial uptake rates at 210 m were similar to those observed in the bacteria-rich Sognefjord (Witte et al., 2003), German Bight and Cretan Sea sediments (Buhring et al., 2006). The Arabian Sea bacterial uptake rates were comparable to others observed at similar depths in the region (Pozzato et al., 2013; Woulds et al., 2007), the Gulf of Gdansk (Evrard et al., 2012) and the Porcupine Abyssal Plain (Aberle and Witte, 2003). The latter sites all had similar bacterial biomasses, 0.5–1.5 g C m^{-2}, despite being at a broad range of water depths 1.5–4800. In this study, bacterial uptake was observed to be largely controlled by bacterial biomass (R^2 = 0.957) and correlated positively with sediment organic carbon content (R^2 = 0.97).Bacterial communities have previously shown a positive relationship with sedimentary organic carbon (e.g. Kunihiro et al., 2014; Moodley et al., 2005).

Assimilation of OM by bacteria is only one part of the role the bacterial community play in OM processing, and bacteria is often the dominant contributor to total community respiration. Given that bacteria dominate the biomass, it is expected that they are largely responsible for respiration of added OM. However, respiration did not display any correlation with bacterial biomass.

Although the anoxic 210 m site in the Baltic Sea had large bacterial biomass, it displayed relatively low biomass-specific uptake (Figure 84) which did not respond to changes in oxygen concentration. It appears that bacterial uptake is driven by the size of the active community, rather than by total biomass. The site with the smallest bacterial biomass (1156 m; 0.37 ± 0.14 g m^{-2}) displayed large biomass-specific carbon uptake, especially under artificially manipulated oxygen concentrations. Despite

having the largest bacterial biomass (7.14 ± 0.92 g m^{-2}), the 210 site showed relatively low biomass specific bacterial uptake (0.022 ± 0.003 mg C uptake per mg C biomass).

Hunter et al. (2012) observed a significant negative relationship between bacterial uptake and macrofauna biomass in the same region, and hypothesised that the faunal-bacteria interaction is a key influence on OM cycling but identified the need for targeted studies. It is thought that this is due to the competition for available food resources, and the likelihood that faunal also graze on the bacterial community (Hunter et al., 2012). A loose negative correlation was observed in this study, but no significant correlation was found in the wider literature (Figure 95). It is thought that macrofauna are able to feed more efficiently than bacteria on a large fresh addition of phytodetritus (van Nugteren et al., 2009), but a larger set of experimental manipulations over a longer time period are required to address this.

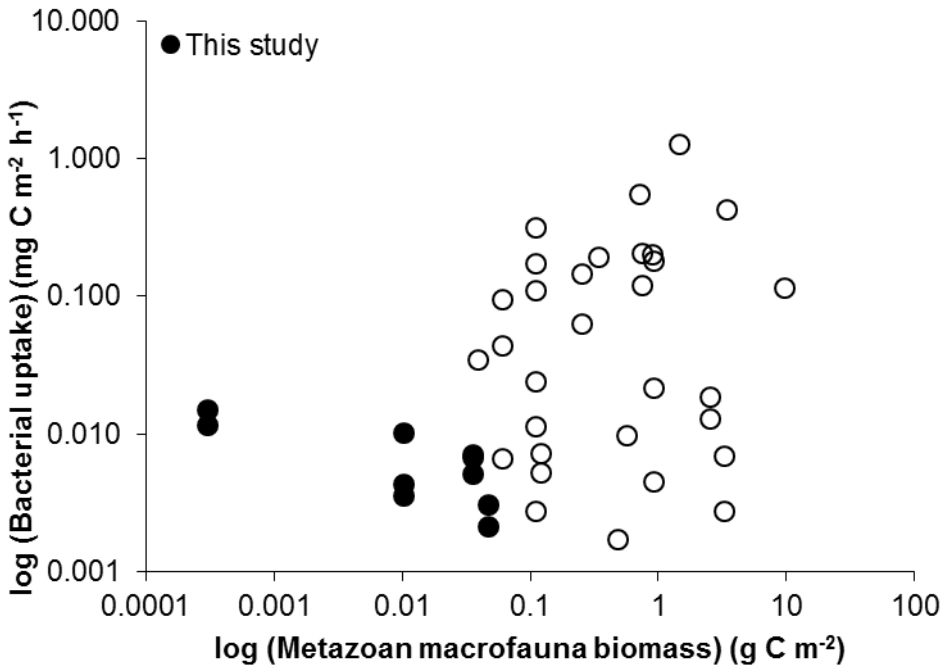


Figure 95. Bacterial uptake rate as a function of metazoan macrofauna biomass in this study and the wider literature (see Table 27).

6.3.5. Carbon Budgets

Woulds et al. (2009) proposed three categories to describe the pattern of biological carbon-processing patterns at the seafloor: “respiration-dominated”, “active faunal-uptake”, and “metazoan macrofaunal-dominated”. These categories only take into account the uptake of or respiration of carbon by the biological community. Later, Woulds et al. (2016) added a fourth category, “bacterial uptake-dominated” to account for studies where bacterial uptake of carbon exceeded that of usually-dominant respiration. The now-four categories allow the pattern of biological carbon budgets to be linked to site conditions and enable an improved qualitative and quantitative comparison of isotope tracing experiments.

6.3.5.1. Respiration-Dominated

Respiration-dominated sites are where >75 % of the total OM processing occurs as respiration. Such sites are typically found on the lower continental shelf or at abyssal depths, with low temperatures and low sedimentary OM contents (Figure 96). These conditions usually lead to a small benthic community, especially of metazoan macrofauna due to the low food availability at deeper water depths (Rowe et al., 1991). However, there are several exceptions to this typical characterisation including shallow water sites such as the Gulf of Gdansk (1.5 m, Evrard et al., 2012), the Wadden Sea (1.5 m, Evrard et al., 2010), North Sea (37 m) and the North Aegean Sea (102 m, Moodley et al., 2005). But like the other deeper sites that fall into the respiration-dominated category, these sites have low or absent faunal communities and low sedimentary OM contents (0.05–0.21 %OC). Notable examples of this category are below-OMZ sites in the Arabian Sea (1200–1850 m, Woulds et al., 2007), the Eastern Mediteranean (1152–3859 m, Moodley et al,., 2005) and the Porcupine Absyssal Plain (4800 m, Witte et al., 2003). Notable exceptions within the respiration-category are the undisturbed Pearl harbour mangrove sites (Sweetman et al., 2010), which have much higher organic carbon contents (~8%) but very low faunal communities.

In this study, only the 1156 m site is categorised as respiration-dominated under ambient oxygen conditions likely due to its low faunal biomass despite a high sedimentary OM content (4.6 % OC). When oxygen concentrations were lowered at 1156 m, respiration dominated further, accounting for 89 % of all OM processing. The decreased oxygen concentrations was associated with a lower faunal biomass and a

50 % reduction in faunal carbon uptake. At both 60 and 814 m, artificially lowered oxygen concentrations resulted a shift from metazoan macrofauna-dominated OM processing under ambient conditions to respiration-dominated processing. Conversely, increased oxygen concentrations at 500 m resulted in a shift from active faunal- to respiration-dominated processing. It may be that oxygen-induced stress gave the bacterial community an advantage over fauna, and so processing shifted away from faunal uptake towards bacterial processing. However, bacterial uptake did not change between experiment manipulations, but it is suggested that the increase in respiration was driven by increased bacterial respiration.

6.3.5.2. Bacterial Uptake-Dominated

As proposed by Woulds et al. (2016), bacterial uptake is the dominant fate of biologically processed carbon, accounting for between 35 and 70 %. While respiration is no longer the dominant sink, it is still important, and may represent 25–40 % of the carbon budget. Faunal uptake is smaller, responsible for 5–20 % of the total OM processing. As a new category, bacterial uptake dominated sites have not been extensively recorded and have thus far only been observed in sandy sediments. It is suggested that permeable sediments can support large bacterial communities and may favour bacterial uptake, as advective porewater processes are known to enhance microbial processes such as remineralisation (Huettel et al., 2014; Boudreau et al., 2001; Rusch et al., 2003; Ehrenhauss et al., 2004). Key examples of this category are Faero-Shetland Channel (1080 m. Gontikaki et al., 2011), the German Bight after 12 and 30 hours (19 m, Buhring et al., 2006), and the Ythan Sand flat (1–2 m, Woulds et al., 2016). The Faero-Shetland Channel is deeper than the other examples, and was not sandy, but the authors observed this bacterial domination after three days before biological carbon processing switched to respiration-dominated after 6 days. However, none of the sites studied here fell into the bacterial update-dominated category, most likely due to the lack of sandy and/or permeable sediments.

6.3.5.3. Active Faunal-Uptake

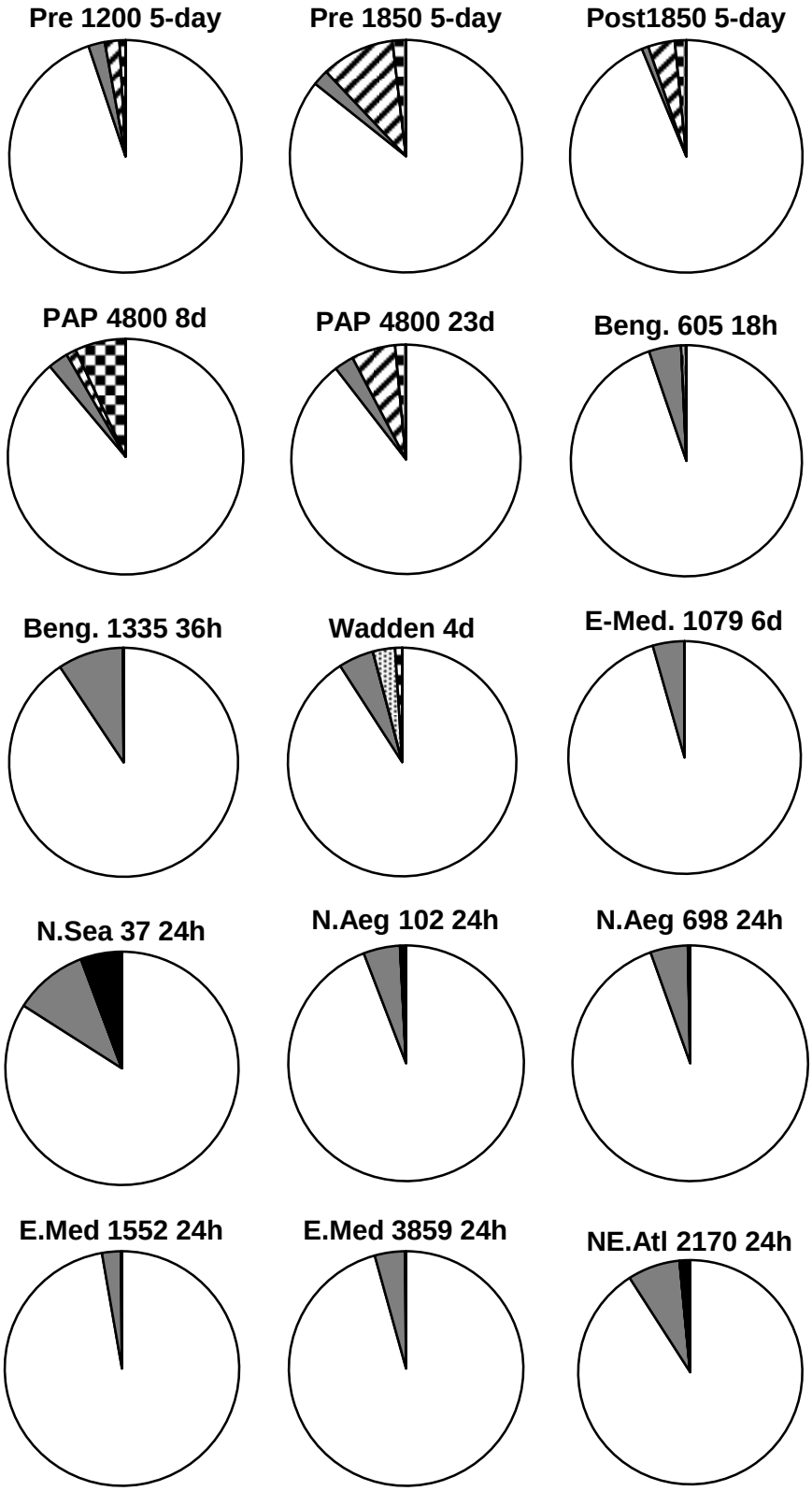
This category is applied to sites where respiration is <75 % and faunal (i.e. foraminifera and metazoan macrofauna) uptake accounts for >10 % of the total carbon budget. These sites are typically shallow, near shore or in estuarine environments where high surface productivity and large sedimentary rates foster OM-rich sediments

(Canfield, 1994) which in turn can host larger benthic communities (Rowe et al., 1991; Soetaert and Heip, 1989). The combination of greater faunal biomass and high quality OM has been shown to boost OM processing rates if oxygen concentrations are sufficient to support the benthic community (Woulds et al., 2007). Key examples of this category include upper slope Pakistan margin sites (140–300 m, Woulds et al., 2007), the Schelde Estauary (0.1 m, Moodley et al., 2005), and Ooesterschelde (0.5 m, Moodley et al., 2000). However it is important to note that deeper sites are also included in this category such as the Sognefjord sites (1265 m, Witte et al., 2003) where metazoan macrofaunaluptake is unexpectedly large most likely due to high oxygen concentrations (210 μm). This category can be sub-divided into foraminifera dominated and metazoan macrofauna dominated faunal-uptake, depending on the key faunal player (Figure 98). 60 m, 500 m, and 814 m under ambient oxygen conditions are all sites that are active-faunal dominated. The 60 m site is typical of the category, with aerated bottom waters (100 μm), relatively high sedimentary OC (3.5 %) and substantial metazoan macrofauna community. The 814 m site is not hugely surprising, given it has sufficient oxygen concentrations to support a macrofaunal community and even higher sedimentary OM (9.8 %). The 500 m site is somewhat of an exception, given that it does not support a metazoan community but does contain an active foraminiferal community which were responsible for 29 % of the carbon processing. This is thought to be due to OM rich sediments (12.3 %) and a foraminiferal community adapted to living under very low oxygen concentrations. When oxygen concentrations were artificially raised, the 1156 m carbon budget shifted from respiration dominated to active faunal-dominated, due to an increased processing capacity of the foraminiferal community. This suggests that oxygen is a controlling factor in the determination of OM pathways at this site.

6.3.5.4. Metazoan Macrofaunal-Dominated

Metazoan macrofaunal-dominated sites are unusual in the fact that metazoans are responsible for greater than 40 % of total carbon processing. The few sites that have been categorised as such include OMZ-boundary sites on the Pakistan Margin, where high sedimentary organic contents and sufficient oxygen concentrations support a remarkably high biomass macrofaunal community (Woulds et al., 2007). The communities are thought to be due to the "edge effect" (Mullins, 1985). No sites in this study fell into this category.

Previous studies



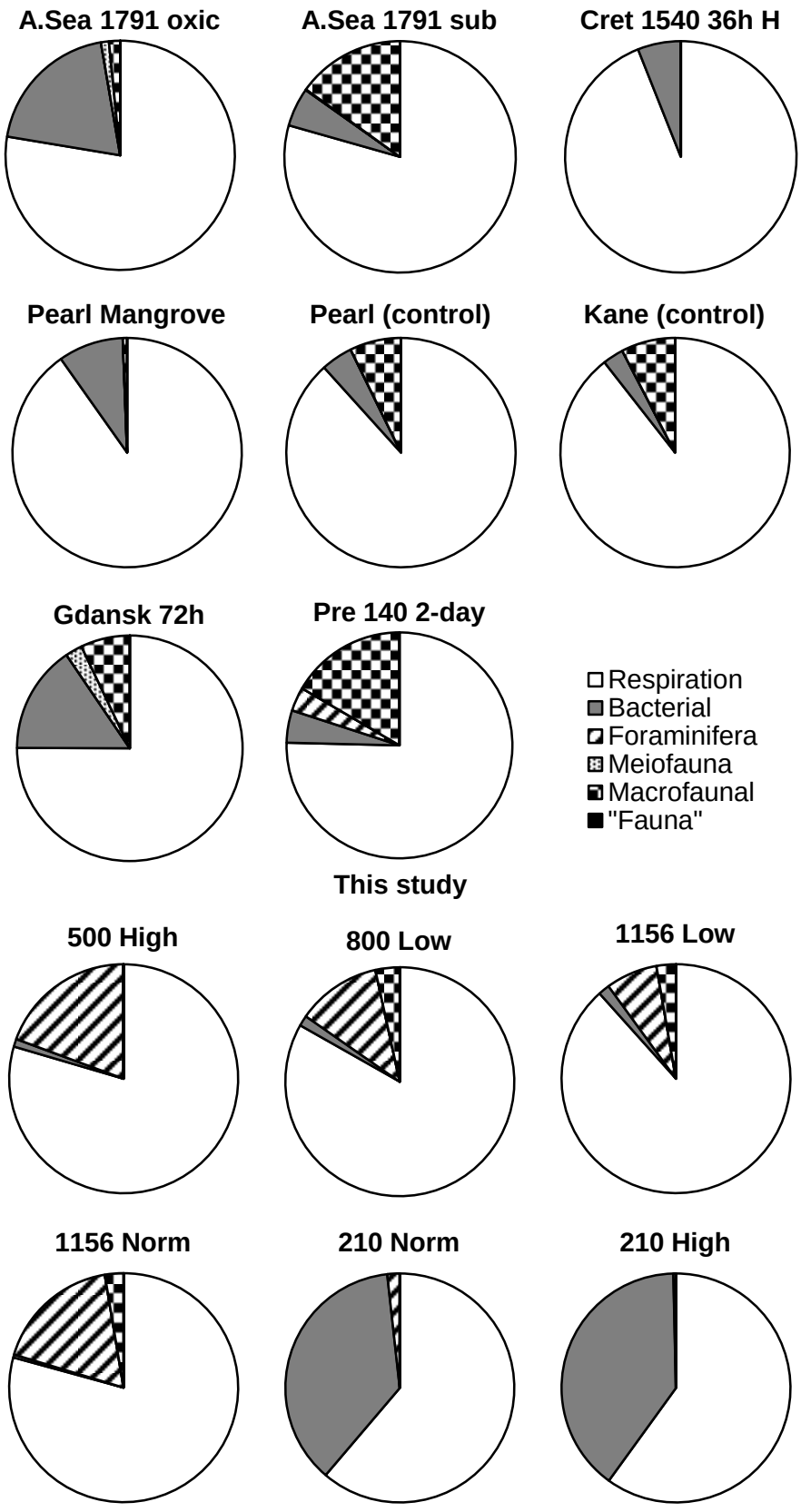


Figure 96. Respiration-dominated sites, site details given in Table 27.

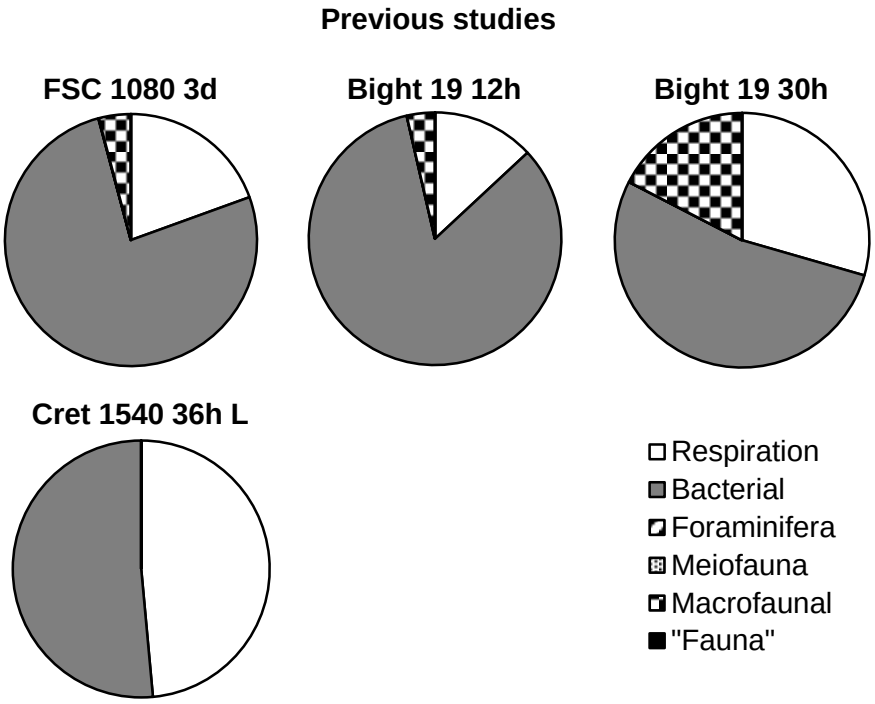
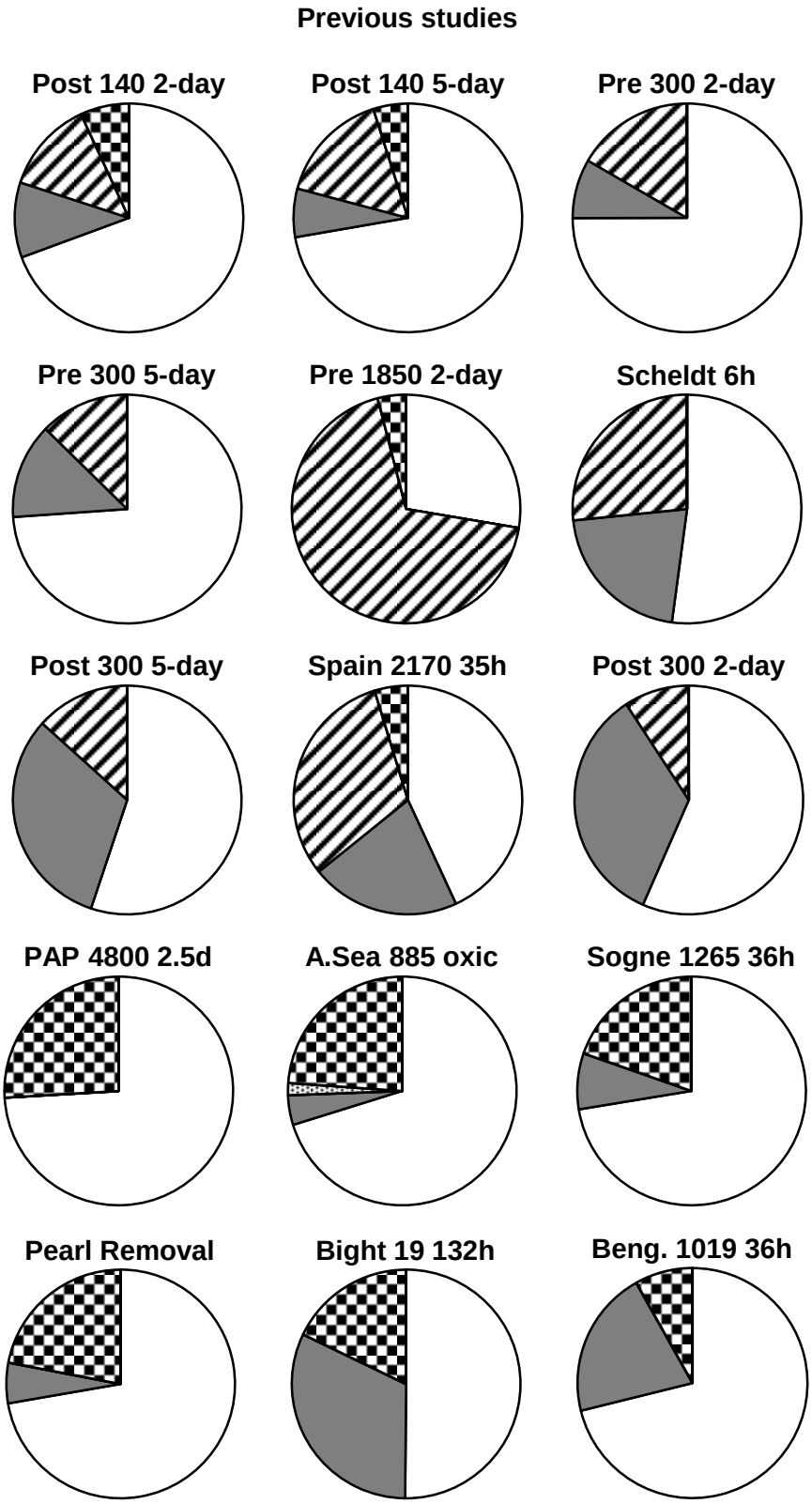


Figure 97. Bacteria-dominated sites, site details for those from the literature are given in Table 27.


Previous studies
Post 140 2-day
Post 140 5-day
Pre 300 2-day
Pre 300 5-day
Pre 1850 2-day
Scheldt 6h
Post 300 5-day
Spain 2170 35h
Post 300 2-day
PAP 4800 2.5d
A.Sea 885 oxic
Sogne 1265 36h
Pearl Removal
Bight 19 132h
Beng. 1019 36h

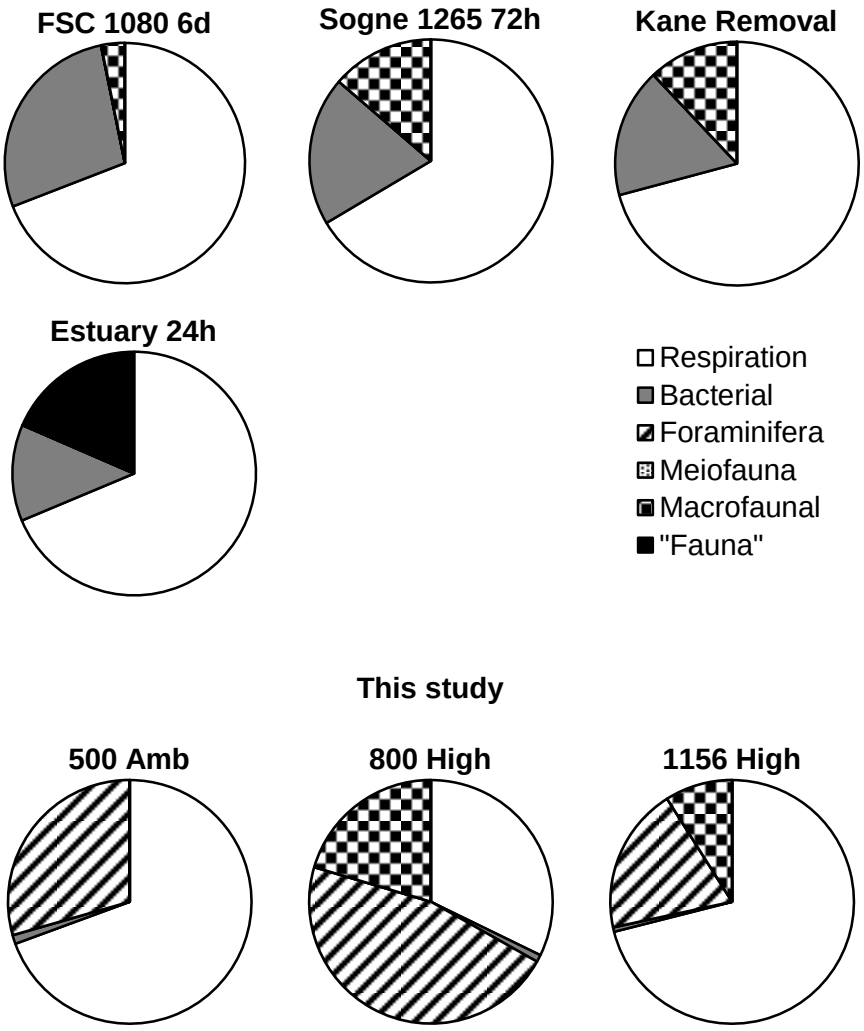


Figure 98. Active faunal-uptake sites, site details for those from the literature are given in Table 27.

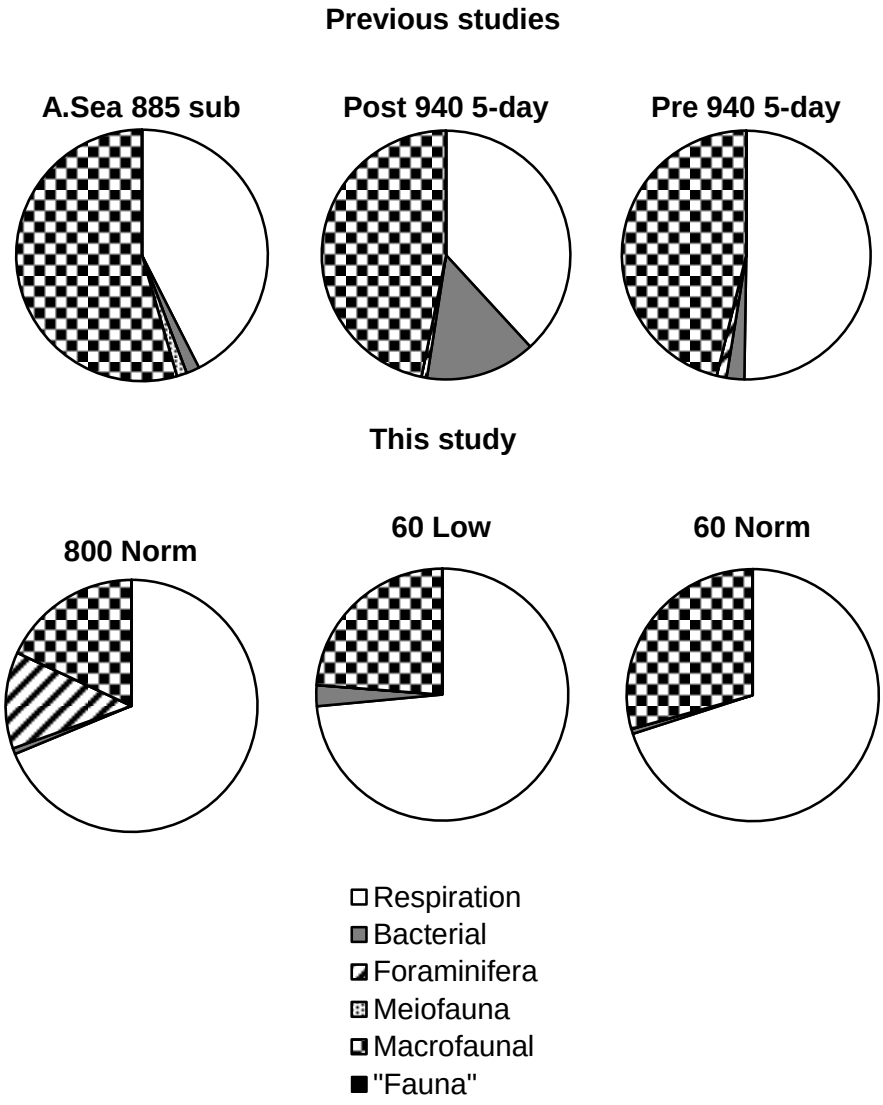


Figure 99. Metazoan-macrofauna-dominated site, site details for those from the literature are given in Table 27.

6.4. Conclusions

- In the Arabian Sea, sedimentary organic matter processing is dominated by respiration, except at 814 m under elevated oxygen conditions where foraminifera dominate.
- In the Baltic Sea, sedimentary organic matter processing is dominated by respiration at all sites.
- Benthic fauna and flora (i.e. including bacteria) play an important role in the short term processing of OM that arrives at the seafloor in both the Arabian and Baltic Seas:
    - where uptake contributed 20.9–31.6 % of total processed OM in the Arabian Sea under ambient oxygen conditions.
    - where uptake contributed 29.4–40.0 % of total processed OM in the Baltic Sea under ambient oxygen conditions.
- Faunal uptake was directly linked to benthic biomass, and to oxygen availability
- Reduced oxygen concentrations were shown to reduce the uptake rates of metazoan macrofauna, but did not have an impact foraminiferal OM processing.
- Biological sedimentary organic matter processing is dominated by bacteria or foraminifera where oxygen is depleted and organic matter quality is low
    - 500 m Arabian Sea (ambient).
    - 210 m Baltic Sea (ambient).
- Biological sedimentary organic matter processing is evenly shared between macrofauna, foraminifera and bacteria where oxygen is not limited and organic matter quality is high
    - 814 m and 1156 m Arabian Sea (ambient).
    - 60 m Baltic Sea (ambient).
- Respiration-dominated uptake sites include those from the lower slope, with low temperatures (1156 m, ambient, Arabian Sea).
- Bacterial-uptake dominated sites did not include those that are sandy and/or permeable, and with a large bacterial community.
    - Instead, carbon processing at the expected bacterial-update dominated site (210 m Baltic Sea, ambient) was dominated by respiration.
- Active faunal-uptake sites included those with higher faunal biomasses, greater sedimentary OM and higher quality OM (500 m, Arabian Sea).

- Metazoan-macrofaunal-uptake-dominated sites will include those with large metazoan macrofaunal communities, high OM availability and sufficient oxygen concentrations (814 m, Arabian Sea and 60 m, Baltic Sea, both ambient).
- Artificial oxygen depletion moved some, but not all, sites towards or into the respiration-dominated uptake category:
    - 814 m, Arabian Sea.
    - 1156 m, Arabian Sea.
- Artificial oxygen elevation only moved one site towards or into the active faunal-dominated uptake category:
    - 1156 m, Arabian Sea.
- Oxygen availability was found to be the overriding control on organic matter preservation and short term cycling at the seafloor in both regions.

7. CONCLUSIONS

7.1. Summary Of Achievements

This study has used both pigment analyses and whole-community isotope tracer experiments to conduct an in-depth analysis of short-term biological OM cycling at the seafloor, in both the Arabian and Baltic Seas

Sedimentary pigment abundances and compositions were investigated across the natural biogeochemical gradients (e.g. oxygen, grainsize, organic inputs, faunal communities) in the Gotland Basin of the Baltic Sea. In previous studies, fine-grained sediments have been found to have higher concentrations of organic carbon due to the similar hydrodynamic transport properties of both organic and fine particles, and sorption of organic matter onto mineral surfaces (Hedges and Keil, 1995; Mayer, 1994). This study was the first attempt to assess whether this relationship holds for the pigment component of the organic matter pool in the Baltic Sea.

^{13}C-enriched OM was used as a tracer of labile OM to mimic seasonal pulses of OM to the seafloor. Identical isotope-labelling experiments were conducted in the two contrasting regions, across sites with a natural range of environmental characteristics including oxygen availability, OM quality, and benthic community structure. Shipboard incubation experiments allowed manipulation of bottom-water oxygen conditions in order to identify the key factors controlling biological processing of OM at the seafloor: the role of community structure, and the impact of oxygen concentrations. This allowed direct comparison of the role of benthic communities in the short-term processing of OM in marine sediments between the two regions. Isotopically-labelled carbon was traced into the biological pools (bacteria, foraminifera and metazoan macrofauna) and the water column (dissolved inorganic carbon). ^{13}C was also traced into individual phospholipid fatty acids, as part of characterising the bacterial uptake of added label. This is the first whole-community carbon-tracing study conducted in the deep Baltic Sea, the first to build a complete biological carbon budget, and also the first to assess the impact of oxygen manipulation on faunal carbon processing in the region.

Furthermore, a comprehensive review of the related literature was conducted – the first to pull together marine hypoxia, benthic ecology, organic matter cycling and research approaches.

7.2. Summary Of Conclusions

7.2.1. The distribution and degradation state of sedimentary pigments across the Gotland Basin of the Baltic Sea

- Chlorophyll-a concentrations observed in the Gotland Basin are an order of magnitude greater than those observed by Bianchi et al., (2002) in Baltic Seston sediments. Carotenoid concentrations at the anoxic sites are similar to those previously observed by Lotocka et al. (2004) in the Gotland Basin. In general, the concentrations are much higher than those observed in eastern Mediterranean sediments (Bianchi et al., 1996) but an order of magnitude lower than those reported on the Peru continental shelf (Repeta and Gagosian, 1987).
- Carotenoids and pheophorbide-a dominated the surface sediment pool of pigments at all sites, suggesting that pigment-containing organic matter is degraded. However, a large proportion of the phytoplankton bloom reaches the sediment intact, as indicated by the preservation of intact carotenoids – despite heavy grazing in the water column, as indicated by the accumulation of pheophorbide-a.
- Sedimentary pigments in the Gotland Basin are good indicators of sedimentary organic matter degradation state. This was highlighted by both correlation to DI, and the lack of systematic decay trend during the 10-day incubation experiments. Pigment decay was only observed at the anoxic 210 m site, where both the organic matter and pigment suites were freshest. Total pigment concentrations declined downcore at all sites, suggesting further decay upon reaching the seafloor, on a timescale greater than that observed during the 10-day decay experiments.
- Both total and individual pigment concentrations declined downcore at all sites, in agreement with previous studies (e.g. Abele-Oeschger, 1991; Lotocka et al., 2004; Woulds and Cowie, 2009).
- Pigment compositions reflect organic matter source and can be used as indicators of phytoplankton species. Algal-class specific biomarkers were identified and were found to accumulate in the sediments. The dominance of fucoxanthin and zeaxanthin within the carotenoids indicates that cyanobacteria and diatoms are important organic matter sources to the region, with additional contributions from golden, green and red algae.

- The greatest pigment concentrations were found at the deepest sites, where oxygen concentrations were minimal of anoxic, faunal communities were small, organic carbon was greatest, grain size was largest and organic matter was freshest.
- Contrary to the hypothesis tested here, fine-grained sediments did not have higher concentrations of intact pigments (fresher organic matter). There was not a strong relationship between sediment textural properties and total pigment preservation, and instead, there were strong positive correlations with % sand. However, this study was the still the first attempt to assess whether this relationship holds for the pigment component of the organic matter pool in the Baltic Sea.
- Oxygen availability appears to be the controlling factor on pigment degradation state, given its role in the wider degradation of OM and control on faunal communities. Total sedimentary pigments in this study showed negative relationships with bottom-water oxygen concentrations ($\rho = -0.80$). Total pigment concentrations were greatest at the anoxic and hypoxic sites, suggesting that the absence of oxygen is retarding pigment decomposition and/or enhancing total sedimentary pigment accumulation. The high accumulation of pigments at the anoxic sites may be due to a combination of decreased oxygen and rapid sedimentation of organic matter, but this cannot be confirmed. In summary, the relationships between oxygen concentration and pigment abundance were not as strong or as significant as expected.
- It is thought that the effect of oxygen as control on pigment distribution in Baltic Sea is masked by other factors, which may also be interlinked, such as water depth, faunal re-working, organic matter source and sediment texture. However there was limited evidence for water-depth influenced and faunal-mediated degradation, which may be due to the fact that both are interlinked with oxygen exposure and availability.

7.2.2. The role of benthic fauna and flora in the short-term processing of sedimentary OM

- Under ambient oxygen concentrations, sedimentary organic matter processing was dominated by respiration at all sites in both the Arabian and Baltic Sea. However, benthic biological communities play a significant role in determining the short-term fate of organic matter. Uptake by benthic flora and fauna (i.e. including bacteria), contributed to 20.9–31.6 % of total processed OM in the Arabian Sea, and 29.4–40.0 % in the Baltic Sea.

- Benthic faunal communities play a smaller role in determining the short-term fate of organic matter in Baltic Sea (Gotland Basin) sediments, than in the Arabian Sea.
- The role of the benthic community in short-term organic matter cycling is strongly influenced by oxygen availability, community composition, and background OM quantity and quality (proxies for food supply). In general, uptake was greatest, under higher oxygen concentrations and at sites with larger background sedimentary OM contents, higher quality sedimentary OM, and a larger community biomass.
- Although an oxygen threshold has been suggested for Arabian Sea sediments (Woulds et al., 2007) there is not sufficient evidence in this study to apply a threshold here. It may be complicated by the fact that any threshold is likely to be taxon-specific (Levin et al., 2000). The results in this study suggest that the availability of oxygen plays a pivotal role in the faunal processing of OM, but that other factors must also be influential.
- In both regions, bacteria dominated the sedimentary biomass, but did not play the largest role biological carbon uptake except at 210 m in the Baltic Sea. In the Arabian Sea, foraminifera dominated faunal processing in all experiments, except at ambient oxygen concentrations at 814 m, where metazoan macrofauna processed slight more added OM. In the Baltic Sea, macrofauna were shown to be an important processor of OM in shallow sediments (60 m.), while carbon uptake was dominated by bacteria at 210 m, under both ambient anoxic and artificially oxygenated conditions.
- The oxygen manipulation experiments revealed that the biological community responds differently to both artificially lowered and elevated oxygen concentrations. Reduced oxygen concentrations were shown to reduce the uptake rates of metazoan macrofauna, but did not have an impact foraminiferal OM processing.
- In summary:
    - Biological sedimentary organic matter processing is dominated by bacteria or foraminifera where oxygen is depleted and organic matter quality is low (e.g. in the OMZ core of the Arabian Sea, and at the deep anoxic sites of the Baltic Sea).
    - Biological sedimentary organic matter processing is evenly shared between macrofauna, foraminifera and bacteria where oxygen is not limited and organic matter quality is high (e.g. outside of the OMZ in the Arabian Sea, and at oxygenated sites in the Baltic Sea).
    - Bacterial-uptake dominated sites did not include those that are sandy and/or permeable, and with a large bacterial community. Instead, carbon

processing at the expected bacterial-update dominated site (210 m Baltic Sea, ambient) was dominated by respiration.

- Artificial oxygen depletion moved some, but not all, sites towards or into the respiration-dominated uptake category.
- Artificial oxygen elevation only moved one site towards or into the active faunal-dominated uptake category.
- Oxygen availability was found to be the overriding control on organic matter preservation and short term cycling at the seafloor in both regions.

7.3. Future studies

7.3.1. Pigment Studies

Given the limitations highlighted by the available extraction solvent while at sea, further work would entail an extensive re-extraction of archived freeze-dried sediments (where available) to fully ascertain the impact of ethanol extraction. This may yield information regarding the near-absence of pheophytin and confirm whether or not this is an artefact of

Knowledge of chlorophyll-a decay constants, sediment accumulation rates, and oxygen penetration depths at the sites would enable the calculation of oxygen exposure times. This would have allowed calculation of decay rates for pigments at all sites and provided a greater insight into the influences of faunal activity, oxygen availability, organic matter quality and source. solvent extraction methodology. Furthermore, downcore changes in grainsize were not available which may have yielded more information, particularly regarding sub-surface concentration peaks and the influence of sediment textural properties.

Additional future studies should investigate the pigment suites of the water column, to determine the degradation processes above the sediment-water interface and calculate the pigment content of organic matter arriving at the seafloor.

7.3.2. Faunal Processing Of OM

Future studies should be conducted in-situ where possible, given the recent advances in benthic lander technology. While the experiments here were conducted over 5 days, due to ship time, in-situ incubations would afford the ability to conduct experiments of longer duration. This would enable the linkage between short-term organic matter processing, as

documented here, to the longer-term processes of organic matter and decay. Oxygen is one of several potential controlling factors, and further manipulation experiments, incubated or in-situ, are needed to full deconvolve the various influences. Meiofauna were not included in this study, but future studies should endeavour to assess the whole community.

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