BENTHIC ORGANIC CARBON FLUXES IN THE SOUTHERN OCEAN: REGIONAL DIFFERENCES AND LINKS TO SURFACE PRIMARY PRODUCTION AND CARBON EXPORT.
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Benthic organic carbon fluxes
in the Southern Ocean:
Regional differences and links to
surface primary production and carbon export

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vorgelegt von
Oliver Sachs

Bremen
August 2007
Everything should be made as simple as possible.
But not simpler.

Albert Einstein (1879 – 1955)
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Zusammenfassung

Summary

Without doubt, global climate change is directly linked to the anthropogenic release of greenhouse gases such as carbon dioxide (CO$_2$) and methane (UN IPCC-Report 2007). Therefore, research efforts to comprehend the global carbon cycle have increased during the last years. In the context of the observed changes, it is of particular interest to decipher the role of the hydro-, bio- and atmospheres and how the different compartments of the earth system are affected by the increase of atmospheric CO$_2$. Due to its huge carbon inventory, the marine carbon cycle represents the most important component in this respect. Numerous findings suggest that the Southern Ocean plays a key role in terms of oceanic CO$_2$ uptake. However, an exact quantification of such fluxes of material is hard to achieve for large areas, not least on account of the inaccessibility of this remote region. In particular, there exist so far only few accurate data for benthic carbon fluxes. The latter can be derived from high resolution pore water oxygen profiles, as one possible method. However the ex situ flux determinations carried out on sediment cores, tend to suffer from temperature and pressure artefacts. Alternatively, oxygen microprofiles can be measured in situ, i.e. at the seafloor. Until now, no such data have been published for the Southern Ocean. During the Antarctic Expedition ANT XXI/4, within the framework of this thesis, in situ and ex situ oxygen profiles were measured and used to derive benthic organic carbon fluxes. Having both types of measurements from the same locations, it was possible to establish a depth-related correction function which was applied subsequently to revise published and additional unpublished carbon fluxes to the seafloor. This resulted in a consistent data base of benthic carbon inputs covering many important sub-regions of the Southern Ocean including the Amundsen and Bellingshausen Seas (southern Pacific), Scotia and Weddell Seas (southern South Atlantic) as well as the Crozet Basin (southern Indian Ocean). Including additional locations on the Antarctic Shelf, there are now 134 new and revised measurement locations, covering almost 180° of the Southern Ocean, for which benthic organic carbon fluxes and sedimentary oxygen penetration depth values are available.

Further, benthic carbon fluxes were empirically related to dominant diatom distributions in surface sediments as well as to long-term remotely sensed chlorophyll-$a$ estimates. The comparison of these results with benthic carbon fluxes of the entire Atlantic Ocean reveals significantly higher export efficiencies for the Southern Ocean than have previously been assumed, especially for the area of the opal belt.
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Section A: Concepts and outline
1 General introduction

The World Meteorological Organisation (WMO) and the United Nations Environment Programme (UNEP) founded the Intergovernmental Panel on Climate Change (IPCC) 1988 when global change became more and more obvious. The idea was that the IPCC should monitor and report in regular intervals the situation of the global climate, its effects for the society, and advice policy makers. The IPCC report 2007 clearly appoints the reasons for global climate change as follows: since 1750 the concentration of carbon dioxide (CO₂) raised from 280 ppm up to 379 ppm in 2005 (Solomon et al., 2007). This is an increase of 35 % compared to the first reliable measurements in 1750. The increment during the last decade is the largest since 50 years. The modern atmospheric CO₂ concentration is the highest value since 650.000 years. 78 % of this increase is attributed to the use of fossil fuels and 22 % is caused by the change of land use (e. g. uprooting).

These facts may illustrate the importance of carbon in the earth system. Where are the large carbon reservoirs on planet earth? Where are the sources and sinks of CO₂? What happens with the ‘missing carbon’, the part of anthropogenic generated and released carbon which is still missing in the global budget? Fig 1-1 gives an overview of the global carbon cycle and exhibits interactions between reservoirs and flux rates between different compartments.
Figure 1-1: Simplified global carbon cycle after Seiter (2004). The inventory of carbon (bold numbers) and the fluxes (italic numbers) are modified after Ittekkot et al. (2002) and Sarmiento & Gruber (2002). Arrows show carbon fluxes [Gt/year]. Anthropogenic changes with annual growth rates are indicated by red numbers. PP indicates the primary production of surface waters.

Besides water vapour, CO₂ is the main contributor to changes in atmospheric radiation; a minor part is generated by other greenhouse gasses. In contrast, variations in solar irradiance have a minor effect in global warming. In total, a warming of earths climate does exist. The aforementioned IPCC report documented that the surface temperature increased about +0.74°C over the last century (Solomon et al., 2007). Furthermore, the past 12 years were the warmest years since the beginning of temperature recordings. The temperature increase during the past 50 years was twice as high as the increase during the past 100 years and the climate sensitive Arctic region heated up twice as much as the global average. The IPCC report clearly attributes anthropogenic greenhouse gas emissions (mainly CO₂) to the climate development of the last 50 years.

Until now the oceans work as gigantic CO₂ sinks as they dissolve most of the carbon produced by combustion of fossil fuels. The IPCC report assumes that from all of the
anthropogenic $\text{CO}_2$ emissions since 1750 around 45 % stayed in the atmosphere and about 30 % was adsorbed by the world ocean (Solomon et al., 2007). This process on the one hand leads to saturation and on the other hand causes ocean acidification. Figure 1-1 shows the ocean sub-divided into a smaller reservoir of surface water and a larger pool of deep water. Both work as different compartments with a differing inventory and storage capacity in respect to carbon. A miner portion of the carbon reacting the ocean’s interior, settles on the surface sediments of the deep-sea. A sub fraction here from is subsequently remineralized whereas another part is buried in the sediments. Figure 1-2 illustrates this process known as the marine carbon cycle.

![Diagram of the marine carbon cycle](image)

**Figure 1-2:** Diagram of the marine carbon cycle. Phytoplankton converts inorganic carbon into organic biomass by photosynthesis. After dying or consumption by grazing the organic biomass sinks into the ocean’s interior. A distinct fraction of this freshly exported carbon of the euphotic zone is remineralized within the water column. Sediment traps are usually used to quantify this carbon flux to the deeper water column and to surface sediments. The use of free fall lander systems gives the opportunity to quantify the carbon flux which reaches the sea bed.

The marine carbon cycle is moved into the scientific focus during the last decades. Biological and physical processes in the surface ocean strongly control the air-sea carbon dioxide ($\text{CO}_2$) balance as a key factor of the earth’s climate system (Sarmiento & Le Quere, 1996). Marine carbon sequestration via the biological pump (Kumar et al.,...
The combination of these two processes in the Southern Ocean is attributed with the uptake of ~2 Pg of anthropogenic carbon dioxide per year (Siegenthaler & Sarmiento, 1993; Caldeira & Duffy, 2000) which is ~32% of the annual global anthropogenic carbon dioxide emissions during the 1990s (Houghton, 2003). The long-term efficacy of the biological pump depends on the depth of carbon export: Delivery of particulate organic carbon to the seafloor represents much longer isolation from the atmosphere (e.g. Boyd & Trull, 2007) than carbon recycling within the upper ocean. CO₂ fixation by phytoplankton via photosynthesis combined with the subsequent cycle of grazing, export to the deep, sedimentation, and remineralization represents one of the major CO₂ sinks in this respect. The Southern Ocean (SO) is recognized as one of the world’s most important regions (DiTullio et al., 2000; Ribbe, 2004). However, amounts and mechanisms of organic matter export to the deep-sea are still poorly constrained (Asper et al., 1992; Jahnke, 1996; Schlitzer, 2002).

Vast areas of the world ocean are characterized by deep-sea environments. Contrasting their areal importance, our knowledge of biogeochemical processes as well as of the deep-sea fauna is still limited, in particular for the climate-sensitive Polar Regions. Apart from ecological considerations, deep-sea sediments exhibit a globally important carbon sink. Several large programmes and projects such as JGOFS (Joint Global Ocean Flux Study), OMEX (Ocean Margin Exchange), BIGSET (Biogeochemical Fluxes of Matter and Energy in the Deep Sea), BIO-C-FLUX (Biological Carbon Flux in the Benthic Boundary Layer of the Deep Sea), 6C (Carbon Cycle, Carbonate Chemistry, Climate Change), or Carbo-Ocean addressed the marine carbon cycle during the last decades and at present. Nonetheless, due to their limited accessibility, polar deep-sea environments are still underrepresented in respect to benthic organic carbon fluxes and the linkage of benthic species distribution and small scale geochemical settings. At oligotrophic and deep-sea sites, the organic carbon rain rate to the sea floor (C₀rg flux), can be deduced in good approximation from measurements of the sedimentary oxygen demand.

The total oxygen uptake (TOU) normally exceeds and is to be distinguished from the diffusive oxygen uptake (DOU). Whereas TOU includes the contribution of epi and
macro fauna to the net respiration rate of a given sediment section (e.g. Graf et al., 1995; Rowe et al., 1997), DOU exhibits its basic turnover primarily caused by microbial activities. Both TOU and DOU can be determined ex situ, i.e., by shipboard sediment core incubation and laboratory measurements of pore water oxygen microprofiles, respectively. Alternatively these parameters can be determined in situ, i.e. at the sea floor using deep-sea benthic chamber and microporifer landers, respectively (Tengberg et al., 1995). In order to circumvent sampling artefacts as well as depressurization and temperature effects during core recovery, measurements should preferentially be performed in situ.

The use of micro sensors for flux determination was introduced already some 25 years ago (Revsbech et al., 1980; Revsbech & Jørgensen, 1986; Reimers et al., 1986). Although, since their in situ deployment is not trivial, data coverage is still modest for temperate regions (Fig. 1-3).

Figure 1-3: Worldwide in situ $C_{\text{org}}$ flux (DOU) determinations for water depths of more than 100 m water depth till 2003 (Reimers et al., 1984; Reimers, 1987; Archer et al., 1989; Bender et al., 1989; Jahnke et al., 1989; Berelson et al., 1990; Archer & Devol, 1992; Reimers et al., 1992; Devol & Christensen, 1993; Glud et al., 1994; Hales et al., 1994; Jahnke et al., 1994; Cai et al., 1995; Hales & Emerson, 1996, 1997; Glud et al., 1998; Lohse et al., 1998; Glud et al., 1999; Luff et al., 2000; Sauter et al., 2001; Wenzhöfer et al., 2001a+b; Epping et al., 2002; Giordani et al., 2002; Wenzhöfer & Glud, 2002 and additional database queries of PANGAEA (http://www.pangaea.de/).
For the deep high latitude Southern Ocean (SO), there are to our knowledge no *in situ* flux measurements beside our own investigations. There exist laboratory-based *ex situ* flux data for the deep SO (Schlüter, 1991; De Wit et al., 1997; Hulth et al., 1997; Smetacek et al. 1997; Rabouille et al., 1998), which, in comparison with *in situ* data, tend to considerably over-determine benthic fluxes mainly due to pressure and temperature artefacts occurring during sediment recovery (Glud et al., 1994, 1999, Sauter et al., 2001).

Within the framework of this thesis, a set of *in situ* and *ex situ* determined benthic fluxes was obtained during Cruise ANT XXI/4 (R/V "Polarstern") in 2004. The results were compared with satellite-observed chl-a distributions of spring and summer blooms in the Polar Front region. Benthic fluxes were determined at sites below an artificially induced diatom bloom (European Iron Fertilization Experiment, EIFEX, Strass et al., 2005; Assmy et al., 2006), and in areas of naturally high and low surface productivity (Sauter et al., 2001).

Sauter et al. (2001) showed that the correction of *ex situ* determined benthic fluxes in northern Polar Regions is possible, since decompression effects are linearly related to water depth whereas temperature effects are less important in polar regions. Proceeding from this approach, the new dataset of the SO was used to derive a revised correction function for existing flux determinations in the southern high latitudes. With additional, so far unpublished oxygen microprofiles, a fundamental dataset obtained at 134 sites was compiled. According to the newly established correction function, *ex situ* measurements were corrected (Fig. 1-4).
Proceeding from this data basis, fluxes and sedimentary oxygen penetration depth values (OPD) were compared with long term satellite observations (SeaWiFS, Sea viewing Wide Field-of-view Sensor projekt, NASA). For a detailed description of long-term carbon sequestration by the ocean, parameters such as export production, rain ratios, particle sinking rates and water depth has to be taken into account. The amount of material exported to the deep is the result of complex interaction of processes including primary production, aggregation, grazing as well as planktic and microbial communities present in the surface ocean.

Amongst other factors, variability in the relative density of planktonic cells depends on phytoplankton species and their physiological state. Thus, the mechanisms of particle sedimentation are still not fully understood (Asper et al., 1992; Jahnke, 1996; Schlitzer, 2002).

**Figure 1-4:** Worldwide *in situ* DOU determinations for water depths of more than 100 m water depth with the new determined and processed dataset in the Southern Ocean.
Figure 1-5 illustrates some of these mechanisms in the context of the Southern Ocean. The mean chlorophyll-a concentration (chl-a) observed over 10 years, shown in the left-hand satellite-derived image, is highest in shelf regions and frontal systems. On the top right of figure 1-5 the variability in chl-a (root square mean variability, rms) is particularly high over the shelf, with relatively low variability at the Antarctic front systems (e.g. Subantarctic Front, Antarctic Polar Front) suggesting steady production. Primary production and chl-a distribution counter draws to the sediment compartment. Different regions with individual diatom distributions are reflected in characteristic provinces of sedimentary diatom debris which were be mapped e.g. by Crosta et al. (1997), Zielinski & Gersonde (1997), Armand et al. (2005), and Crosta et al. (2005). One aim of this thesis is the comparison of surface sediments in this respect, which leads to regionally different oxygen gradients and oxygen penetration depths (bottom of fig. 1-5).

As a final step, benthic fluxes were compared statistically with the 10 year SeaWiFS observation and according to the sea surface production regime of the respect Southern Ocean region. The statistical examination revealed that data interpretation is difficult if the dataset is restricted to the high latitude Southern Ocean. This is attributed to high local, seasonal and annual variabilities in the surface chl-a distribution.

Most of the sites investigated here are located in the Atlantic Sector of the Southern Ocean. Only the comparison of these results with published in situ $C_{org}$ fluxes obtained from other sites of the Atlantic Ocean, lights-up the picture: Within this context, the importance of the Southern Ocean’s contribution to CO$_2$ drawdown can be assessed. Thus, these results can be considered a contribution to a refined comprehension of the global carbon cycle.
Figure 1-5: Schematic overview of the pathways of organic matter production, export, sedimentation, and benthic remineralization. This thesis investigates possible empiric relationships of sea surface production and benthic fluxes by applying a statistical approach.
References


2 Outline of the manuscripts

This thesis comprises original texts, figures, and tables of three submitted manuscripts. All of which have been submitted to international peer-reviewed journals (Nature, Deep-Sea Research I, Global Biogeochemical Cycles). Following the review-process, their final published form might slightly differ from the chapters presented in this work.

The work was carried out at the Alfred Wegener Institute for Polar and Marine Research in Bremerhaven and at the University of Bremen and was co-funded by the Deutsche Forschungsgemeinschaft within the Priority Program SPP 1158 (SA1030/1-1 – 1-4).

Three manuscripts represent the main part of the results compiled during the PhD and presented in three chapters of this thesis. All manuscripts are linked to each other. A brief outline of each manuscript is given below. They are all based on own investigations and were authored by myself as first author.

Chapter 3
Enhanced carbon export to deep-sea sediments underlying productivity hotspots in the Southern Ocean

Satellite images of the Antarctic Circumpolar Current reveal enhanced chlorophyll concentrations along the Polar Front. Oxygen uptake rates, a proxy for carbon flux, measured in situ in deep-sea sediments underlying the chlorophyll band weeks after its disappearance were threefold higher than in surrounding water. Similarly high values were recorded in sediments underlying the site of an iron fertilization experiment. We estimate that at least 10% of phytoplankton biomass artificially induced by iron addition reached the deep sea floor. Since carbon input to deep-sea sediments appears to triple with a doubling of surface biomass, artificial iron fertilization of the Southern Ocean from this point of view could sequester a significant fraction of current atmospheric CO₂ accumulation.
Chapter 4

**Benthic organic carbon flux and oxygen penetration reflect different plankton provinces in the Southern Ocean**


The manuscript addresses organic carbon fluxes to the sediment surface of different regions of the Southern Ocean derived from *in situ* and *ex situ* oxygen microprofiles. An empiric approach to correct *ex situ* measurements for their potential artefacts is presented. Furthermore, oxygen penetration depth values were investigated as a measure for benthic long term carbon input which was found to correlate with diatom species dominating specific regions of the Southern Ocean. Thus, benthic fluxes confirm the particularities of regionally dominant diatom species in respect to the efficiency of carbon export to the deep-sea.

Chapter 5

**Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean**

O. Sachs, J. N. Schwarz, E. J. Sauter, M. Schlüter, and M. Schodlok

This chapter focuses on datasets of benthic oxygen fluxes, satellite-derived primary production estimates and bathymetry which have been used to derive transfer functions for the export of carbon from the surface mixed layer to the sea floor. Biogeochemical provinces defined *a priori* using surface chlorophyll or sediment characteristics could not be distinguished by their transfer efficiencies. However, *a posteriori* definition of provinces based on the transfer efficiency showed a band of high export efficiency along the Southern Ocean opal belt and in the northern North Atlantic. Possible explanations for this are discussed.
Section B: Submitted manuscripts
3 Enhanced carbon export to deep-sea sediments underlying productivity hotspots in the Southern Ocean

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3.1 Abstract

The modern Southern Ocean plays a modest role in global air-sea exchange of carbon dioxide because its low, iron-limited phytoplankton production utilises only a fraction of nutrients provided by circumpolar upwelling of deep water 1-2. According to the Iron Hypothesis 3, phytoplankton growth rates and the accompanying draw-down of atmospheric CO2 during glacial cycles were significantly enhanced due to iron fertilization by 10-fold higher dust input levels in the Southern Ocean than today 4. Whereas local phytoplankton blooms occur naturally 5 and have been induced by artificial iron addition in in situ experiments 6, the fate of their biomass, which determines magnitude and duration of carbon sequestration in the deep ocean, is still under dispute 6-7. We studied the deep-sea floor underlying regions of low and high productivity, including the site of an iron fertilization experiment conducted a few weeks earlier, and found compelling evidence of fresh deposition of significant amounts of organic carbon emanating from surface blooms. Our in situ measurements of sedimentary carbon fluxes under recurrent high productivity hotspots along the Antarctic Polar Front are amongst the highest recorded from the ocean. In striking contrast, carbon deposition under adjoining low-productive waters was much lower. Our findings support the Iron Hypothesis and identify the Southern Ocean as a potential global-scale, long-term sink of atmospheric CO2.

3.2 Introduction

The current low productivity of the land-remote Southern Ocean, despite high nutrient concentrations of nitrate and phosphate, has been shown to be due to iron limitation of phytoplankton growth rates\(^8\). Unambiguous evidence has come from 5 experiments in which several tonnes of iron sulphate were added to patches of open ocean in different sectors and regions of the Antarctic Circumpolar Current (ACC)\(^9-12\). All experiments resulted in phytoplankton blooms and significant lowering of CO\(_2\) levels in the surface layer. However, the extent and duration of impact on atmospheric CO\(_2\) levels depends on the proportion of bloom biomass that sinks out of the surface layer relative to that recycled within it. For various reasons, the fate of experimentally induced biomass, but also that of natural blooms in the ACC, has been poorly documented so far\(^6\).

3.3 Results and discussion

Satellite images of surface chlorophyll concentrations, a proxy for productivity, indicate annually recurrent, narrow bands of chlorophyll concentrations >1 mg Chl m\(^{-3}\) along certain stretches of the Antarctic Polar Front (APF) that contrast with the lower (by half) values characteristic for the northern and southern branches of the ACC on either side\(^13\) (Fig. 3-1a). These chlorophyll hotspots disappear during the autumn with unknown fate (Fig. 3-1 b, c). At this stage we can only speculate on the provenance of the iron fuelling these restricted APF blooms but it is reasonable to assume that the fate of artificially induced blooms will be similar to those of natural ones. In order to estimate the amount of organic carbon deposited on the sea floor underlying the natural and artificial hotspots in comparison to less productive waters, we carried out in situ microsensor measurements of oxygen uptake by surface sediments from 4 sites in the Southern Ocean and retrieved undisturbed samples of the upper 20 cm sediments from 3 of them.

The first site was located in the centre (Station 598) of a stable, cyclonic eddy of about 100 km diameter located within a meander of the Antarctic Polar Front and in which an iron fertilization experiment (EIFEX) had been completed 2 week earlier\(^14\). The second, reference site (Station 600) underlay the south-western branch of the APF surrounding the eddy. Such mesoscale eddies in the ACC, clearly visible in satellite images of sea-
level height, are ideally suited for Lagrangian studies of temporal developments\textsuperscript{15}. They can extend from the surface to the sea floor and persist for several months, hence provide ideal containers for following the fate of bloom biomass from the surface to the deep-sea and sea floor\textsuperscript{16}. The other two sites were sampled \textasciitilde 3 weeks later and selected on the basis of surface chlorophyll concentrations during the previous months. Station 703 was located in the broad belt of impoverished water of the southern ACC whereas Station 705 was pinpointed under the annually recurrent, \textasciitilde 130 km broad band of high chlorophyll along the APF southwest of Africa that had disappeared \textasciitilde 6 weeks earlier (Fig. 3-1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-1.png}
\caption{Surface chlorophyll-\textit{a} concentrations across the ACC for 3 separate weeks in the 6-week period between 10\textsuperscript{th} of February and 20\textsuperscript{th} of March 2004. Due to the vagaries of cloud cover, each image is integrated from multiple passes of the SeaWiFS satellite over a week. The phytoplankton bloom along the meandering Polar Front crosses the centre of the image and is more diffuse to the west during the first week. The signal fades in subsequent weeks indicating demise of the bloom. The SeaWiFS (NASA) images were recorded several weeks prior to the \textit{in situ} flux measurements at the numbered sites marked with white dots.}
\end{figure}

A distinct fluffy layer of freshly deposited plankton cells and organic detritus distinct from the sediment surface was observed in the sediment core taken from site 600 (Fig. 3-2). At Site 705, the surface sediment consisted of an extremely soft layer which was both inhomogeneous and bioclastic, indicative of prolonged high sedimentation and accumulation rates. Freshly deposited material was identified on the surface but it did not appear as a discrete layer. In contrast, the sediment core retrieved from site 703 lacked any signs of freshly deposited material.
Figure 3-2: Evidence of freshly deposited material at Site 600 (a-c). a, Sediment core retrieved from the periphery of the eddy in which the iron-fertilization experiment (EIFEX) was performed showing a 5 mm thick layer of freshly deposited remains of a phytoplankton bloom, (arrow: foraminifer Bathysiphon cf. flavidus) lying on the sediment surface. b, Chl-α fluorescence of an intact dinoflagellate cell (arrow) indicates fresh phytoplankton material at ~3600 m depth (epifluorescence micrograph with Chl-α filter), scale bar, 50 µm. c, DAPI fluorescence indicates high bacterial activity on a colonised cell of the diatom Corethron pellnatum from the fluff layer, scale bar, 50 µm.

In situ microsensor measurements indicated high sedimentary oxygen uptake at the surface of all three stations underlying areas of chlorophyll concentrations >1 mg Chl m⁻³. (Sites 598, 600, and 705). Benthic organic carbon fluxes between 9.4 and 13.1 mg C m⁻² d⁻¹ derived from these in situ oxygen micro-profiles (Fig. 3-3) are in the range of typical values for the high-productive, up-welling areas off West Africa, whereas the flux measured at Site 703 underlying impoverished water (3.3 mg C m⁻² d⁻¹) was similar to values determined in the deep open Atlantic. The fresh sedimentation of labile organic material was particularly evident at Sites 598 and 600 where a discontinuity in the oxygen in situ microprofiles at about 5 mm sediment depth, i.e. at the sediment-fluff interface, reflected non-steady state conditions (red arrows in Fig. 3-3a, b). Notably, this change in the oxygen gradient coincides with a rapid drop in porosity (derived by the in situ measured formation factor, blue graph in Fig. 3-3a, b) below the fluff layer. As shown by the green bars in Fig. 3-3, fresh sedimentation is further supported by high oxygen consumption rates (2.1 and 1.3 µmol cm⁻³ d⁻¹) at the sediment surface of Stations 598 and 600 respectively as compared to much lower values in the sediment below (0.005 and 0.004 µmol cm⁻³ d⁻¹). In contrast, much lower activity in the surface layer (0.4 µmol cm⁻³ d⁻¹) but similar values to sites 598 and 600 in the sediment below (0.002 µmol cm⁻³ d⁻¹) were found at Site 703 (Fig. 3-3c).
Figure 3-3: Oxygen microprofiles (black dots) measured in situ at the sites marked in Fig. 3-1. Oxygen consumption rates (green, note different scales) and benthic organic carbon fluxes (red numbers) were obtained by fitting the data with the model PROFILE19 (red fits). A significant change in sediment porosity (blue dots) delineates the transition between an overlying fluffy layer and the sediment surface at Sites 598 and 600 (blue arrows). This coincides with a discontinuity in the pore water oxygen profile (red arrows) and reflects very recent sedimentation of fresh material. Modelled oxygen consumption rates at Stations 598, 600 and 705 exhibit a drastic drop below the fluff layer in comparison with Station 703. Porosity and O₂ consumption rates in the underlying sediment are similar at Sites 598, 600 and 703, but indicate softer, organic rich sediments at Site 705.

We were unable to obtain a sediment core from Site 598 but the similarity in oxygen profiles between this Site and 600 strongly suggests the presence of freshly deposited fluff layers at both sites, which in the eddy centre (Site 598) will have emanated from the EIFEX bloom. The species composition of the EIFEX bloom was similar to that observed in surrounding water prior to fertilization. Freshness of the fluff layer in core 600 is indicated by elevated phaeopigment concentrations (~7000 ng g⁻¹ dry weight), the presence of chlorophyll-a fluorescence in phytoplankton cells with intact nuclei (Fig. 3-2b) and high bacterial activities in comparison to the sediment below the fluff layer (Fig. 3-2c). Further, intact, chains of diatom species that dominated the sinking flux recorded from the EIFEX bloom18 (Chaetoceros atlanticus, C. dichaeta, Corethron pennatum, Fragilariopsis kerguelensis), including frustules of weakly silicified species (such as Guinardia cylindrus) were present in the fluff at site 600.
The remarkably similar benthic carbon fluxes underlying the EIFEX eddy centre (Site 598) and its peripheral APF loop (Site 600), despite differences in surface chlorophyll concentrations, can be explained by the dynamics of the EIFEX patch. At the time of fertilization, measured chlorophyll concentrations along the APF loop were 1.2 mg chlorophyll m\(^{-3}\) which is about twofold higher than within the eddy but declined significantly in the period when the EIFEX bloom was growing. Maximum values in the centre of the bloom (2.8 mg Chl. m\(^{-3}\)) were fourfold higher than those in surrounding water within the eddy core (Fig. 3-4).

The bloom peaked on 8. March, 24 days after fertilization, and a strong flux event through the deep water column was recorded subsequently\(^{19}\). The area covered by the continuously spreading patch when the flux occurred was approximately 20-30\% of the area of the eddy core within which it was rotating (Fig. 3-4). Because the patch was located off-centre, it described perfect, almost overlapping ovals of 70 and 50 km dimension around the eddy centre during the 5-week long experiment. Hence, material sinking out of the rotating patch will have been “smeared” over an area of about 3 to 5-fold greater extent in the course of a full, 7-day revolution, apparently shorter than the

**Figure 3-4:** Close-up of the EIFEX eddy. a, Just before fertilization. b, At the height of the experimental bloom. c, In its declining phase. Chlorophyll concentrations are according to the scale bar in Fig. 1. The red oval in a denotes the approximate boundary of the eddy core at that time. Chlorophyll concentrations were initially higher around the eddy periphery than within its core where the experiment was carried out. The eddy centre shifted northward by 35 km in the period between a and b. The fertilized patch, which circled clockwise within the eddy at about weekly intervals, is visible southwest of the eddy centre denoted by site 598 in panel b and southeast of it in panel c. The red line in panel d marks the track of one float positioned 200 m below the patch shortly after the flux event. The track is representative for the other floats positioned deeper in the water column down to 1000 m depth.
flux event. In contrast, material sinking out of the peripheral APF frontal jet (Site 600) will have been deposited as a band beneath it and not “smeared” over a more extensive sediment area. Thus, although surface chlorophyll concentrations along the APF were lower than in the centre of the EIFEX patch, the amount of fluff deposited on the underlying sediments was about the same as within the eddy. In other words, without an EIFEX bloom a fluff layer would not have been deposited in the impoverished eddy core.

At Site 705, where the highest fluxes were measured (13.1 mg C m\(^{-2}\) d\(^{-1}\)), the smoothness of the oxygen depth profile (Fig. 3-3d) indicates a steady state system characterised by enhanced, long term influx of organic carbon. In contrast, the fluff layers at sites 598 and 600 appear not to be a recurrent feature. The shallow oxygen penetration depth (OPD) of \(\sim 10\) cm at Site 705 contrasts with Sites 598, 600 and 703 where oxygen concentrations extrapolated from the microprofiles penetrate at least \(>40\) cm into the sediment. These are, to our knowledge, the first published \textit{in situ} flux data for the SO. Previous \textit{ex situ} observations of low OPD values in sediment samples from the APF are in good agreement with our \textit{in situ} fluxes at Site 705\(^{20-21}\).

A conservative estimate of the amount of carbon deposited from the surface blooms can be derived from measured benthic carbon fluxes and consideration of the spatial kinetics of the patch. From the satellite images and measurements carried out around the EIFEX eddy prior to fertilization, we know that the fresh material at Sites 600 and 705 were deposited at about the same time and derived from blooms of roughly similar magnitude (1-2 mg chlorophyll m\(^{-3}\) in an 80-100 m deep mixed surface layer). This corresponds to a phytoplankton biomass of approximately 4 g carbon m\(^{-2}\), at a C:Chl ratio of 30 determined from the EIFEX bloom. Carbon fluxes at the sediment / water interface at all sites were approximately 10 mg m\(^{-2}\) d\(^{-1}\). Since measurements at site 600 were carried out two weeks and at site 705 five weeks after deposition of the fresh material we assume that the measured benthic carbon fluxes prevailed for at least 35 days which results in a flux estimate of 350 mg C for this time period. This is a minimum estimate as we do not know for how long these fluxes lasted. These calculations indicate that at least 10\% of organic carbon built up by the surface bloom was deposited as fluff on the deep sea floor.
3.4 Conclusions

Our data indicate that a significant portion of the biomass of natural and artificially induced blooms reaches the underlying deep-sea floor within weeks after disappearance from the surface. Rapid sinking of surface blooms and deposition as fluff on the sea floor has been described for the North Atlantic\textsuperscript{22} and is probably due to diatom cells and chains aggregating into fast-sinking flocks that trigger the mass sinking\textsuperscript{23}. The proportion of organic carbon produced in the surface layer that is deposited on the underlying deep-sea floor appears to triple with doubling of chlorophyll concentrations above about 0.5 mg Chl m\textsuperscript{-3}. The amount buried, reflected in depth of oxygen penetration, depends on degree of recurrence of surface blooms. Higher levels of dust input during glacials\textsuperscript{4} will have resulted in much higher productivity and hence more intense burial of organic carbon over much larger areas than today. This is corroborated by the high abundances of \textit{Chaetoceros} resting spores – an indicator of higher productivity – in glacial ACC sediments of the Atlantic sector as compared to today\textsuperscript{24}. It follows that an iron-fertilized ACC, whether naturally by dust or artificially by ferrous sulphate, is capable of sequestering a significant portion of atmospheric carbon dioxide in surface sediments for time scales exceeding those of deep-sea ventilation, i.e. well in excess of 1000 years.

3.5 Methods

3.5.1 Study site

During expedition ANT XXI/4 of R/V “Polarstern” (27.03.-06.05.2004\textsuperscript{25}) in situ measurements and sampling was performed at four locations close to the Antarctic Polar Front (Tab. 3-1).
3 Enhanced carbon export to deep-sea sediments underlying productivity hotspots in the Southern Ocean

Table 3-1: Station list

<table>
<thead>
<tr>
<th>Site Label</th>
<th>Date</th>
<th>Latitude (S)</th>
<th>Longitude (E)</th>
<th>Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>02.04.04</td>
<td>49° 18,50'</td>
<td>02° 11,68'</td>
<td>3942</td>
</tr>
<tr>
<td>PS65/600</td>
<td>03.04.04</td>
<td>49° 59,88'</td>
<td>02° 20,22'</td>
<td>3589</td>
</tr>
<tr>
<td>PS65/703</td>
<td>29.04.04</td>
<td>52° 35,12'</td>
<td>09° 00,19'</td>
<td>3330</td>
</tr>
<tr>
<td>PS65/705</td>
<td>30.04.04</td>
<td>49° 00,06'</td>
<td>12° 15,32'</td>
<td>4293</td>
</tr>
</tbody>
</table>

Site labels are abbreviated in the text (e.g. 598 for PS65/598).

3.5.2 Benthic carbon fluxes

Benthic carbon fluxes were derived from in situ oxygen microprofiles obtained by an autonomous deep-sea microprofiler (Unisense A/S, Denmark) deployed in combination with a free-fall lander system. The profiler was equipped with five oxygen sensors and a formation factor probe (resistivity sensor). Since the pore water oxygen gradient at the sediment surface is altered during recovery of sediment cores due to depressurization and temperature changes, fluxes measured at sediment cores (ex situ) tend to over-estimation\(^{26-27}\). Therefore, such micro profile measurements should be performed in situ. According to ref.\(^{28}\) Clark type oxygen sensors (Unisense A/S) with tip diameters of \(~25 \mu m\) and a stirring sensitivity <2%, pre-calibrated according to ref.\(^{27}\) were lowered through the sediment water interface into the sediment with a vertical resolution of 0.5 mm during 5-6 hours at the sea floor. Porosity data for accurate flux calculation were obtained according to ref.\(^{27}\) from in situ measured formation factor profiles. Diffusive oxygen fluxes were determined from the in situ measured data using the fit procedure and the software PROFILE\(^{29}\). Oxygen diffusion coefficients were calculated according to\(^{30}\) using the individual temperature, pressure and salinity conditions of each site. Profiles apparently affected by bio-irrigation and from broken sensors were discarded. The profiles acquired at Site 600 were affected by noise that we ascribe to the intrusion of salt water (\(~2 \text{ ml}\)) into the liquid-filled (3M FC77, Fluorinert\textsuperscript{TM}) housing of the step motor. In this case, only data inside the 70% confidence interval were included in the fit procedure. Flux values are given as the median of all profiles used at one site (two at each of the sites 598, 600, and 703; four at Site 705). Oxygen consumption rates were also calculated using PROFILE\(^{29}\).
3.5.3 Sediment sampling

For sediment sampling a multiple corer with a core diameter of 10 cm was deployed\textsuperscript{31}. Apparently undisturbed sediment cores were obtained at sites 600, 703, and 705. At Site 598 no sediment was retrieved despite repeated efforts. Upon recovery, sediment samples were immediately segmented into 1 cm slices in the shipboard cool laboratory. The top centimetre was cut into two slices of 5 mm. Sediment samples were shock frozen in liquid nitrogen and stored at -80 °C. If present, fluff was sampled separately by pipette, shock frozen and stored at -80°C. A portion of the fluff was preserved in hexamine-buffered formaline solution (2%) and stored at 4 °C.

3.5.4 Sediment investigations

Samples were examined by light and epifluorescence microscopy revealing chl-a in cells of phototrophic dinoflagellates, single cells and chains of diatoms with intact nuclei (made visible by 4',6-Diamidino-2-phenylindoldihydrochloride (DAPI) staining). High bacterial activities were observed by DAPI staining in formaline fixed fluff samples.

Fluff and sediment samples for light microscopy investigations were transferred into Utermöhл chambers and onto microscope slides. Samples were filtered over Black Nuclepore® membranes (Whatman, pore size 0.8 μm.) for epifluorescence microscopy.

Pigment analyses were performed by high performance liquid chromatography (HPLC). For analytical preparation, 1 cm\textsuperscript{3} of sediment was mixed with 50 μl of internal standard (canthaxanthin) and 1 ml of glass beads (1 mm diameter). This mixture was extracted 3 times with 2 ml acetone in a cell mill for 3 minutes. After centrifugation (10 minutes at 4000 U min\textsuperscript{-1} and 0 °C) the extracts were unified and concentrated on an Alltech C18\textsuperscript{TM} solid phase extract clean column. Pigments were eluted with 100% acetone and further concentrated under nitrogen atmosphere in the dark to a final volume of 0.3 ml. Finally, pigments were measured with a Waters™ HPLC system according to ref.\textsuperscript{12}.
3.5.5 APEX floats

Four autonomous profiling APEX (Autonomous Profiling EXplorer) floats were deployed below the fertilized patch at depths of 200 m, 300 m, 500 m and 1000 m before departure from the EIFEX experimental site. The floats ascend to the surface once every 2 days and transmit their data to satellite for about 10 hours before sinking back to their parking depth.

3.6 References


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**Author contributions** O.S. and E.J.S. carried out the field work, data evaluation, and manuscript preparation. M.S. contributed to the flux determination and manuscript preparation. O.S. performed pigment analyses together with I.P. and P.A. provided data from EIFEX. U.B. was chief scientist of the cruise and provided the chl-a satellite images. V.H.S. was responsible for physical measurements during EIFEX. V.S. led EIFEX and contributed substantially to preparation of the manuscript.

**Competing interests statement** The authors declare that they have no competing financial interests.

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Enhanced carbon export to deep-sea sediments underlying productivity hotspots in the Southern Ocean
4 Benthic organic carbon flux and oxygen penetration reflect different plankton provinces in the Southern Ocean

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Key words: benthic organic carbon fluxes, deep-sea sediments, Southern Ocean, microsensors, oxygen penetration depth

4.1 Abstract

Based on the comparison between benthic oxygen fluxes derived from oxygen microprofiles measured at sediment cores (ex situ) and by means of free falling lander systems (in situ), a correction function was set up that was applied on existing ex situ flux data in order to revise the database for the Southern Ocean. Organic carbon fluxes range from 0.5 to >35 mgC m\(^{-2}\) d\(^{-1}\). Oxygen microprofiles were measured at 134 sites in different sub-regions mainly of the Atlantic Sector of the Southern Ocean. Oxygen penetration depths and benthic organic carbon fluxes were derived from the profiles and investigated in respect to regional characteristics. In the Scotia Sea (~3000 m water depth) oxygen penetration depths of less than 15 cm were observed in deep-sea sediments. In contrast, the oxic zone extends to several decimetres in abyssal sediments of the Weddell Sea and south-eastern South Atlantic. The depth of oxygenation reflecting sedimentary long term organic matter influx was found to be correlated with diatom key species characterizing different regions of the surface ocean. From the partly very high fluxes derived from micro sensor data it can be concluded that episodic and seasonal sedimentation pulses are important for carbon supply to the sea floor even at great depths.


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4 Benthic organic carbon flux and oxygen penetration reflect different plankton provinces in the Southern Ocean

4.2 Introduction

The transfer of particulate organic carbon from the sea surface to the deep ocean and its remineralization and burial at the seafloor closely links the atmospheric CO$_2$ concentration to the marine carbon cycle. Carbon and nutrients remineralized or buried in surface sediments are removed from air-sea exchange of CO$_2$ or primary production for periods of 100s to 1000s of years.

Recent benthic organic carbon fluxes are mainly quantified by the *in situ* deployment of microprofilers and benthic chamber systems (e.g. Reimers et al., 1986; Reimers, 1987; Glud et al., 1994; Tengberg et al., 1995; Jahnke, 1996; Sauter et al., 2001; Wenzhöfer & Glud, 2002). *In situ* microprofilers allow for measuring O$_2$ profiles in surface sediments with a high vertical resolution up to sub-millimeter scale. From these microgradients, the sedimentary dissolved oxygen uptake (DOU) can be derived as a measure of organic carbon rain rates to the seafloor (hereafter referred to as C$_{org}$ flux), which is indicative of the flux of particulate organic carbon reaching the seafloor (e.g. Revsbech & Jørgensen, 1986; Reimers et al., 1986; Jahnke, 1996). Compared to such *in situ* measurements, fluxes derived by *ex situ* determinations on shipboard are often biased by sampling artifacts. For example, *ex situ* oxygen probes determined at deep-sea sediments (>1000 m) tend to be affected by decompression leading to an overestimation of the concentration gradients (Reimers et al., 1986). Due to these artefacts, such *ex situ* measurements provide reliable information about the oxic zone of the sediment and a semi-quantitative measure of the long term C$_{org}$ flux but no exact determination of the DOU.

Based on compilations of benthic flux studies, budgets of the amount of particulate organic matter transferred to the seafloor were derived for large ocean basins or even on a global scale (Jahnke, 1996; Schlüter et al., 2001; Wenzhöfer & Glud, 2002; Seiter et al., 2005). These investigations are linked to sediment particle trap studies (Wefer & Fischer, 1991; Lampitt & Antia, 1997; Honjo, 2004) providing values for C$_{org}$ fluxes in the water column and are relevant for the comparison of biological processes, flux budgets and model calculations.

Compared to the northern North Atlantic, upwelling regimes as off Namibia or regions in front of South America, still only little is known about benthic C$_{org}$ fluxes in the Southern Ocean (SO), a key region for the global marine carbon cycle (Kumar et al., 1995; Caldeira & Duffy, 2000; Sarmiento et al., 2004). Especially the region separating the
Antarctic and Subantarctic zone (ASZ), referred to as the biogeochemical divide (Martinov et al., 2006), and seems to have a crucial impact in respect to the present and past global CO₂ cycle. Considering the Atlantic sector of the Southern Ocean, only a limited number of studies investigated Cₑ(org) fluxes in the ASZ region via sediment particle traps (e.g. Wefer & Fischer, 1991; de Baar et al., 1995; Smetacek et al., 1997; Bathmann et al., 1997; Fischer et al., 2000, 2002) or radio nuclide tracers (Rutgers van der Loeff et al., 1997). Data on Cₑ(org) fluxes reaching the seafloor of the ASZ are based on a very limited number of O₂ microprofiles and sediment incubations (Schlüter, 1991; Hulth et al., 1997; Smetacek et al., 1997; De Witt et al., 1997; Rabouille et al., 1998; Schlüter et al., 2001). Accurate flux data derived from in situ oxygen microprofile measurements were not available for this area until now. Instead, only ex situ measurements were reported so far. Due to the lack of data, the Southern Ocean south of 60° was excluded from the global carbon budgets derived by Jahnke (1996) and Seiter et al. (2005).

In this paper we present new results including the first in situ oxygen measurements reported for the SO, derived from measurements of oxygen profiles in surface sediments and a compilation of more than 134 oxygen profiles (Rutgers van der Loeff, 1990a; Schlüter, 1990; Rutgers van der Loeff & Berger, 1991; Schlüter, 1991; Smetacek et al., 1997; de Wit et al., 1997; Rabouille et al., 1998; Sachs et al., subm.). This study of in situ and ex situ flux data is complemented by additional unpublished data sets obtained during previous field expeditions (1986-1990, 1992-1994, 2004) to the Mid Atlantic Ridge region (Holby, 1994), Amundsen and Bellingshausen Seas (Holby, 1996), the Antarctic Peninsula region, the Scotia and Weddell Seas and the east Antarctic shelf (Fig. 4-1).

Based on a comparison of in situ with ex situ oxygen profiles a correction function for ex situ data previously measured in Southern Ocean sediments was established. This allows us to estimate organic carbon fluxes reaching the seafloor for sites were ex situ measurements are available and obtain a retrospective data analysis correcting existing benthic oxygen and Cₑ(org) fluxes as well as oxygen penetration depth values (OPD, the oxygenated zone in sediment). In a second step regional differences of particulate organic matter fluxes were considered for the region south of 40° S. The combined dataset allows for considering the specific pattern, e.g. with respect to the biogenic silica cycle, of particulate organic matter fluxes reaching the seafloor. The compilation of these data significantly improves the data basis and our understanding of regional
differences of benthic fluxes in the Southern Ocean.

Figure 4-1: For the region from the Amundsen and Bellingshausen Seas (west of the Antarctic Peninsula) to the Crozet Basin (60° E) oxygen profile measurements of surface sediments were compiled. In total 134 sites were considered, x indicating in situ sites. This includes new measurements as well as previously published data (Tab. 4-1). The Antarctic Polar Front (white line) is given according to Orsi et al. (1995).

4.3 Materials and methods

In this study, data derived from measurement of oxygen profiles in surface sediments from different sources were compiled and considered: a) In situ and ex situ measurements were performed during the Polarstern Expedition ANT XXI/4 (Sachs et al., subm.) on a latitudinal transect across the Antarctic Polar Front system. b) Ex situ and two in situ datasets obtained during the Polarstern Expeditions (ANT V/4, ANT VI/2-3, ANT VIII/3 & 6, ANT X/5-6, ANT XI/3) to the Amundsen and Bellingshausen Seas (Pacific Sector) as well as the Atlantic sector of the Antarctic Circumpolar Current, the Scotia and Weddell Seas, the east Antarctic shelf and continental slope. These data previously considered with respect to the depth of the oxic habitat within the sediment (Rutgers van der Loeff, 1990a; Schlüter, 1990; Schlüter et al., 2001), were now used for flux determination and the revised investigation of the regional patterns of OPD values. In total 134 microprofiles were considered for OPD studies in different regions of the Southern Ocean whereas 96 were suited to derive $C_{org}$ flux values from (Tab. 4-1).
4.3.1 Measurements of *in situ* and *ex situ* oxygen microprofiles

*In situ* oxygen microprofiles were measured during Expeditions ANT X/6 (Holby, 1994, Fig. 4-2) and ANT XXI/4 (Sachs et al., subm.) by means of a deep-sea microprofiler. Mainly due to ice coverage and frequent rough weather conditions, these are the first *in situ* oxygen microprofile measurements published for the Southern Ocean.

Microprofilers were equipped with up to five pressure compensated Clark type oxygen sensors with a tip diameter of ~25 μm and a stirring sensitivity <2%. Sensors were pre-calibrated according to Sauter et al. (2001). During ~5-6 hours at the sea floor, sensors were lowered through the water-sediment interface into the sediment with a vertical resolution of 0.5 mm. A Niskin bottle mounted onto the lander frame and closing in concert with the lander’s releaser provided bottom water for sensor re-calibration. For porosity determination, the microprofilers were also equipped with a resistivity sensor (formation factor probe).

Oxygen diffusion coefficients were calculated according to Boudreau (1997) using the individual *in situ* temperature recorded by a current meter (Aanderaa, Norway) mounted onto the lander frame. Diffusive *in situ* oxygen fluxes were determined from the uppermost 3-4 mm of the pore water oxygen profiles using the software PROFILE (Berg et al., 1998). The fit curve (Fig. 4-2) of measured oxygen profiles were computed by the model PROFILE.
Porosities were derived for ex situ and in situ oxygen profiles by measurement of the formation factor Boudreau (1997). Where such information was not available, a “mean” porosity profile calculated from three in situ measured high resolution profiles was applied. The comparison of this porosity distribution with values determined ex situ at the same sites revealed a deviation of <1%.

Diffusive oxygen fluxes were converted into organic carbon rain rates on the basis of the modified Redfield Ratio (Anderson & Sarmiento, 1994) and under the assumption that in oligotrophic deep-sea sediments the major part of organic carbon is remineralized by oxic respiration.

For the compilation of ex situ fluxes only profiles which were measured in sediment samples recovered by a multiple corer (MUC, Barnett et al., 1984) were considered. Only cores with apparently undisturbed sediment surface and clear supernatant water column were selected and transferred to the ship’s cool laboratory (2-4°C). Shipboard pore water oxygen microprofiles were measured immediately using Clark type glass
microelectrodes similar to those applied for *in situ* measurements. In a few cases, especially when the oxygen penetration depth exceeded several decimetres, Clark type steel-needle probes were applied. Microelectrodes were calibrated prior to each measurement against the bottom water oxygen concentration determined by Winkler titration (Grasshoff et al., 1983) and oxygen-free seawater. The microelectrodes were mounted into a micromanipulator and profiles were measured with a vertical resolution of 0.1 to 2 mm. Oxygen measurements were conducted down to as much as 32 cm. At cores where the anoxic zone was not reached by the measurement, OPD was estimated by fitting a double exponential function to the oxygen profile.

Except the study of Sachs et al. (subm.), all of the published deep-sea studies of the SO represent *ex situ* measurements, which tend to considerably over-estimate benthic fluxes (e.g. Reimers et al., 1986; Glud et al., 1994 and 1999; Sauter et al., 2001). This is mainly due to pressure release and, if the sample comes from warm or temperate regions, temperature artifacts which may occur during sediment recovery. Whereas the oxygen gradient at the water-sediment interface is very sensitive against such artifacts, the thickness of the oxic zone within surface sediments (i.e. the oxygen penetration depth) is much more robust in this respect and offers an additional indication for benthic carbon fluxes (Rutgers van der Loeff, 1990a; Cai & Sayles, 1996; Schlüter et al., 2001).

In addition OPD values measured from box corer sub-samples were gathered in the years 1986, 1987 and 1988 from the Weddell Sea and Antarctic shelf region. No flux values were taken from such samples due to the potentially poor preservation of the sediment surface.

Specific observations were made at two particular sediment samples: (1) Sediments at site PS65/600-2 were covered by a consistent 5 mm thick fluff layer (Sachs et al., subm.). (2) At site PS1782 Rutgers van der Loeff (1990b) and Rutgers van der Loeff & Berger (1991) describe “extremely fluid sediment” from a high accumulation area in 5016 m depth. It should be mentioned here that in case of fluff present on top of the sediment, the flux correction is misleading since the bacterial activity and the diffusion is changing dramatically with sediment depth. Similarly, a correction cannot be given for “liquid” or “extremely fluid” sediments as suggested by *in situ* and *ex situ* investigations of Arctic deep-sea sediments (Molloy Hole, Fram Strait, 5400 m depth, Sauter and Sachs, unpublished). Due to the given specific sediment consistency, C$_{org}$ fluxes were not corrected for these particular SO sites. However, the OPD value was used in both cases.
4.4 Results and discussion

4.4.1 Relationship between \textit{ex situ} and \textit{in situ} flux measurements

Whereas the \textit{in situ} oxygen probes allow the direct computing of $C_{\text{org}}$ fluxes, \textit{ex situ} measurements might be biased by sampling artefacts (e.g. Reimers et al., 1986). As shown by Glud et al. (1994, 1999) or Sauter et al. (2001) the comparison of \textit{ex situ} and \textit{in situ} measurements obtained of the same site allows for assessing a specific relationship. This can be applied to correct $C_{\text{org}}$ fluxes of \textit{ex situ} determined profiles. Subsequently we investigated the suitability of this approach for the Southern Ocean. For this purpose the ratio of \textit{in situ} / \textit{ex situ} flux data based on new measurements and previous published data is considered. In Figure 4-3 the available global dataset of \textit{in situ} / \textit{ex situ} measurements obtained at the same sampling site are shown. The data are compiled from Glud et al. (1994), Glud et al. (1999), Sauter et al. (2001) and Wenzhöfer & Glud (2002). Due to unusual warming of the sediment samples (Wenzhöfer et al., 2001, n=4) and unusual sediment compaction (Sauter et al., 2001, n=1) a sub-set of these data were not considered in Figure 4-3.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ratio_doulab_douins_vs_depth.png}
\caption{Ratio $\text{DOU}_{\text{lab}}/\text{DOU}_{\text{ins}}$ vs depth}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_4-3.png}
\caption{Flux ratio of \textit{ex situ} / \textit{in situ} determined diffusive oxygen uptake (DOU) versus depth for a mixed data set (Glud et al. 1994, 1998 and 1999; Sauter et al., 2001; Wenzhöfer & Glud, 2002 and this study)\
$y = 0.00033z + 1.09$ $R^2 = 0.20$}
\end{figure}
The number of comparative *ex situ / in situ* flux measurements is very limited. To our knowledge there are no other data sets beyond those used in this study. The obtained relation in Figure 4-3 represents data from the Atlantic as well as the Pacific Oceans and includes equatorial and up-welling regions as well as abyssal plains.

With a coefficient of determination ($R^2$) of 0.20, the obtained regression exhibits a weak correlation between *ex situ / in situ* fluxes and water depth. However, there is a trend towards higher $\text{DOU}_{\text{lab}}/\text{DOU}_{\text{ins}}$ values with increasing water depths which can be generally attributed to pressure artefacts. In addition, temperature-related effects and accelerated bacterial respiration as well as pore water diffusion may cause artefacts effecting the *ex situ* flux measurements.

Since the oxygen profiles were measured in very different environment settings (in respect to water column temperatures or primary production regime) we considered the $\text{DOU}_{\text{lab}}/\text{DOU}_{\text{ins}}$ versus water depth relations for high northern and southern latitudes in detail (Fig. 4-4).

**Figure 4-4:** Flux ratio of *ex situ / in situ* determined diffusive oxygen uptake (DOU) versus depth including only high latitude data (Glud et al., 1998; Sauter et al., 2001 and this study).

Data from the shelf area of Svalbard (Glud et al., 1998) and from the deep northern North Atlantic (Sauter et al., 2001) in combination with own new *in situ* values obtained from the Southern Ocean and the Fram Strait (Sauter and Sachs, unpublished data) were used. As shown in Figure 4-4, the $\text{DOU}_{\text{lab}}/\text{DOU}_{\text{ins}}$ versus water depth ratios obtained for high latitudes are positively correlated with water depth and reveal a much
stronger correlation with a coefficient of determination of 0.64. The depth-dependent correction function derived for the high latitude regression is

\[
DOU_{\text{lab}}/DOU_{\text{corr}} = 0.00039 \cdot z + 0.91
\]  

(1)

\( z \) being the water depth [m] and \( DOU_{\text{corr}} \) being the calculated \( C_{\text{org}} \) flux [mgC m\(^{-2}\) d\(^{-1}\)] as expected to be measured \textit{in situ}. From equation (1), literature \textit{ex situ} flux data can be corrected as follows:

\[
DOU_{\text{corr}} = DOU_{\text{lab}} \cdot (0.00039 \cdot z + 0.91)^{-1}
\]  

(2)

One focus of this paper was to correct literature and own \textit{ex situ} measurements according to the above explained correction function. The corrected fluxes are listed in the Table 4-1 together with sampling techniques and biological provinces of the site of sampling (classification see below).

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<th>Latitude</th>
<th>Longitude</th>
<th>Depth [m]</th>
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<th>Measur-</th>
<th>OPD</th>
<th>cor.</th>
<th>Corg flux</th>
<th>Biological Data</th>
<th>Province</th>
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Note: Unsaturated oxygen diffusion flux is calculated using the formula: F = k * d * A, where F is the oxygen flux, k is the oxygen diffusivity, d is the depth, and A is the surface area.
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Note: Biological data refer to different provinces in the Southern Ocean.
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<td>Longitude</td>
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<td>Longitude</td>
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<td>Gear</td>
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<td>1219</td>
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<td>GKG</td>
<td>ex situ</td>
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<td>2615</td>
<td>GKG</td>
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<td>Expedition No.</td>
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<td>Season</td>
<td>Latitude</td>
<td>Longitude</td>
<td>Depth [m]</td>
<td>Gear</td>
<td>Measure-OPD [cm]</td>
<td>OPD [mgC/m²/d]</td>
<td>uncorr. flux factor</td>
<td>Corr. C&lt;sub&gt;org&lt;/sub&gt; flux [mgC/m²/d]</td>
<td>Biological Province</td>
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<td>4538</td>
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<td>ex situ &gt;100</td>
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<td>70° 49.8' S</td>
<td>13° 57.8' W</td>
<td>2494</td>
<td>KG</td>
<td>ex situ &gt;100</td>
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<td>ex situ 60</td>
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<td>06° 46.3' W</td>
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<td>KG</td>
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<td>-</td>
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<td>31° 05.0' W</td>
<td>351</td>
<td>KG</td>
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<td>30° 32.5' W</td>
<td>259</td>
<td>KG</td>
<td>ex situ 2.0</td>
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<td>Antarctic shelf &amp; slope study</td>
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4.4.2 Organic carbon fluxes reaching the seafloor of the Southern Ocean

The organic carbon fluxes derived for the SO by *in situ* measurements and by correction of *ex situ* measurements are shown in Figure 4-5. Benthic fluxes range from very low values of 0.6 mgC m\(^{-2}\) d\(^{-1}\) (Weddell Sea) to approximately 25 mgC m\(^{-2}\) d\(^{-1}\) below coastal polynias in front of the east Antarctic shelf. Highest fluxes up to 37.1 mgC m\(^{-2}\) d\(^{-1}\) were determined for the Antarctic shelf region (Fig. 4-5). The spatial distribution of oxygen penetration depths (shallow and deep OPD values are a semi-quantitative indicator for continuous high and low organic carbon flux into the sediment, respectively) are shown in Figure 4-6. Furthermore, benthic C\(_{\text{org}}\) fluxes and OPD values show no obvious relation to water depth, oceanic fronts and regions except those at the Polar Front. However, if the oxygen penetration depths are mapped against the context of additional sedimentary parameters, a more systematic pattern is obvious: All open ocean fluxes exceeding 5 mgC m\(^{-2}\) d\(^{-1}\) are in or close to the biogenic silica belt, an area of enhanced sedimentary silicate from diatom export in the SO. For regionalization purposes, several surface sediment mappings by Zielinski & Gersonde (1997), Burckle & Cirilli (1987), Jousé et al. (1962), DeFelice & Wise (1981), Armand et al. (2005), Crosta et al. (2005) and Mohan et al. (2006) were unified into a composite map of high sedimentary inventories of diatom valves (Fig. 4-5).

Figure 4-5: Flux of organic carbon reaching the seafloor. The fluxes were derived from *in situ* measurement of oxygen profiles in surface sediments and correction of *ex situ* determined fluxes according to equation (2). Colors and circle sizes represent different C\(_{\text{org}}\) fluxes. Hatched areas indicate diatom-rich surface sediments according to Zielinski & Gersonde (1997), Jousé et al. (1962), DeFelice & Wise (1981), Burckle & Cirilli (1987), Armand et al. (2005), Crosta et al. (2005) and Mohan et al. (2006).
Benthic organic carbon/lux and oxygen penetration reflect different plankton provinces in the Southern Ocean.

Legend
- Diatom Ooze Belt
- isoline < 2000 m
- *in situ* site

$C_{org}$ flux [mgC m$^{-2}$ d$^{-1}$]
- 1 - 4
- 5 - 8
- 9 - 25
- > 25
Figure 4-5 shows a striking coincidence of high fluxes within the areas of diatom-enriched surface sediments. Highest abundances of diatom valves in surface sediments are known in the circumpolar “Diatom Ooze Belt” (Burckle and Cirilli, 1987), which is one of the most important areas of global biogenic silica accumulation (Tréguer & Van Bennecom, 1991; Nelson et al., 1995; Schlüter et al., 1998, Geibert et al., 2005).

High deep-sea benthic C\textsubscript{org} fluxes as well as shallow OPD values are closely related to the occurrence of diatom ooze (Figs. 4-7 & 4-8). Stations south and north of the diatom ooze belt show very low fluxes ranging between 0.6 and 2.4 mgC m\textsuperscript{-2} d\textsuperscript{-1} and very deep OPD values conspicuously exceeding 100 cm. These results correspond well to data obtained from a sediment particle trap deployed in the central Weddell Sea (Fischer et al., 1988).

Although low in total organic carbon content (0.3-1.4 %C\textsubscript{org}, Schlüter et al., 1998, Fischer et al., 1998 and own data), the sediments of the diatom ooze belt obviously receive high C\textsubscript{org} fluxes. The most recent iron fertilization experiment (Strass et al., subm.), which was sampled in respect to benthic C\textsubscript{org} fluxes after the sink-out of the iron-induced diatom bloom provides the answer for this apparent paradox. Sachs et al. (subm.) found a fresh fluffy diatom layer below the fertilized patch. \textit{In situ} measurements revealed a fresh sedimentation event with a benthic C\textsubscript{org} flux of 9.6 mgC m\textsuperscript{-2} d\textsuperscript{-1} in 3942 m water depth. It was shown by \textit{in situ} flux measurements that naturally occurring diatom blooms at the polar front lead to very high benthic fluxes of up to 13.1 mgC m\textsuperscript{-2} d\textsuperscript{-1} at 4293 m depth. We hypothesize that benthic C\textsubscript{org} fluxes are directly linked with diatom production at the surface: Exceeding the threshold concentration, diatoms aggregate and act as a “carbon carrier” or a short-cut conveyor to the deep-sea, i.e. are responsible for rapid carbon export to the deep. The pulsed sedimentation of this fresh and labile C\textsubscript{org} leads to an episodic enhancement of fluxes whereas OPD values react more sluggish and are a result of perennial changes in flux patterns. Thus, C\textsubscript{org} fluxes represent recent flux events whereas the OPD signature reflects the multi-year influx to the benthic system.

Several studies revealed the importance of diatoms for the transfer of primary produced organic carbon to the seafloor (Scharek et al., 1999; Fischer et al., 2002; Sachs et al., subm.). Other sediment particle trap studies in the SO revealed that the export to the deep is characterized by seasonal and episodically pulsed sedimentation events (Fischer et al., 1988; Wefer & Fischer, 1991; Fischer et al., 2003). Scharek et al. (1999) showed for the oligotrophic north Pacific gyre a pulsed, rapid export of diatoms down to
4000 m depth and suggested that diatoms are more important for the vertical flux of organic carbon than previously assumed. Different sinking velocities due to formation of aggregates or algae mats were observed (Turner, 2002 and references herein). The high transfer of biogenic silica was preserved as a diatom ooze belt in the surface sediment. Investigations of diatom species in surface sediments (e.g. Zielinski & Gersonde, 1997; Abelmann et al., 2006) showed that the opal belt could be subdivided in provinces. *Chaetoceros* spp, which is known for its high carbon efficiency, dominates close to the Antarctic Peninsula and the Scotia Sea whereas in more eastern directions *F. kerguelensis* is dominating, which exports mainly biogenic silica to the sediments (Abelmann et al., 2006). Since the diatom dominated ecosystem changes gradually, we can find areas where both habitats overlap (Fig.4-6).
Diatom provinces

Legend
- Isoline < 2000 m
- In situ site

Oxygen penetration depth [cm]
- < 4
- 4 - 7
- 8 - 14
- 15 - 30
- > 30
Figure 4-6: Oxygen penetration depths (OPD) of surface sediments in the Southern Ocean. Blue colors and circle sizes indicate different OPD values. The orange hatched area shows enhanced Chaetoceros spp. spores (>20%) in surface sediments and corresponds with Region A (The Chaetoceros spp. province, see text) whereas the red hatched area shows elevated Fragilariopsis kerguelensis frustules (>40%) and corresponds with Region B. The hatched areas were established according to Zielinski & Gersonde (1997), Jousé et al. (1962), DeFelice & Wise (1981), Burckle & Cirilli (1987), Kellogg & Kellogg (1987), Crosta et al. (1997), Armand et al. (2005), Crosta et al. (2005) and Mohan et al. (2006). The blue marked area corresponds to Region C (The east Antarctic Shelf and continental slope). Black lines represent transects of selected oxygen microprofiles (A = Fig. 4-10, B = Fig. 4-11, C = Fig. 4-12).

To refine the image, we investigated how our results match the distribution of key species of modern diatomaceous surface sediments. For this purpose we compared the mapped diatom ooze belt with its diatom provinces as suggested by Zielinski & Gersonde (1997) considering the OPD values as a long term signal of benthic C<sub>org</sub> flux. Additional information was taken from surface sediment maps by Jousé et al. (1962), DeFelice & Wise (1981), Burckle & Cirilli (1987), Kellogg & Kellogg (1987), Crosta et al. (1997), Armand et al. (2005), Crosta et al. (2005) and Mohan et al. (2006). Figure 4-5 indicates that high fluxes are directly linked with siliceous, diatom-rich sediments. High fluxes indicate rapid and pulsed deep export which can be observed occasionally as fresh phytodetritus or fluff layer in various regions of the SO. The occurrence of deep organic carbon export (annually, seasonally and/or regionally) is associated with different diatom key species dominating primary production in the surface ocean and generates a typical OPD pattern. Consequently, we distinguish three characteristic SO regions in respect to their C<sub>org</sub> input as a main result of this study (Fig. 4-6).

Region A: The Chaetoceros spp. province
The first region is characterized as a region of shallow sediment oxygen penetration and high abundances of resting spores (20 % around South Georgia and the South Sandwich Islands, up to 100 % at the Antarctic Peninsula). According to Zielinski & Gersonde (1997), Armand et al. (2005) and Abelmann et al. (2006), the surface sediments around the Antarctic Peninsula, the Scotia Sea and the region around South Georgia and the South Sandwich Islands belong to the Chaetoceros spp. province. The resting spores originate from small-celled diatoms belonging to the subgenus Hyalochaetae of the genus Chaetoceros (C. curvisetus, C. debilis, C. socialis, C.
neglectus, C. simplex). Close to the Antarctic Peninsula OPD values are in the range of only 1.5 to 2.5 cm. In more eastern directions, in areas with a resting spore content as low as 20 % (Zielinski & Gersonde, 1997), OPD values increase to over 20 cm sediment depth (examples see Fig. 4-8). This increasing oxygen penetration depth corresponds well with intensive diatom blooms which can be annually observed by remote sensing (e.g. SeaWifs, Modis) in this region, indicating a constant long term signal over several years of enhanced deep carbon export. Abelmann et al. (2006) showed that the diatom genus Chaetoceros has been the key genus for large diatom blooms also during glacial periods, characterising regions of high glacial productivity.

The dominant small and spiny spore forming Chaetoceros species responsible for the enhanced export indicate nutrient rich and iron enriched surface waters within the Region A (Smetacek, 1985; Abelmann et al., 2006). In sediments, the Chaetoceros group and Thalassiosira antarctica – scotia group are normally preserved as resting spores (Zielinski & Gersonde, 1997). Beside this key species other diatoms like the weakly silicified Corethron pennatum [formerly C. criophilum] are locally important in this province. Highest carbon fluxes of 144 mgC m⁻² d⁻¹ derived from sediment particle traps were closely linked to the presence of high Chaetoceros spp. abundances of 60 % to 80 % (Abelmann et al., 2006 and references herein). The highest benthic fluxes of the Southern Ocean (25.7 to 37.1 mgC m⁻² d⁻¹) were consistently observed within the Chaetoceros spp. province (Fig.4-6). Concomitant with the collapse of a phytoplankton bloom, spiny vegetative cells, spores and other phytodetritus aggregate build fast sinking particles (Smetacek, 1999). Repeated fluff observations especially in the Scotia Sea confirm the appearance of fast sinking particles. This pathway of the biological carbon pump is one of the most important mechanisms to efficiently bring down organic carbon to the oceans’ interior (Smetacek, 1999; Smetacek et al., 2004). According to the sedimentary diatom distribution (Fig. 4-7), a smaller region close to Kerguelen Islands is suspected to be of the same type as Region A (Armand et al.; 2005, Blain et al., 2007). However, more field observations of this particular small region are required to verify this observation.
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Figure 4-7: Selected oxygen profiles measured in Region A, the *Chaetoceros* spp. province. Profiles were measured along Transect A (Fig. 4-6) reaching from the Antarctic Peninsula (Station PS1549 (143)) to the South Sandwich Islands (Profile PS2280-1 (776)). Oxygen penetration depths increase from west to east.
Region B: The open ocean *Fragilariaopsis kerguelensis* Province

Sediments of this large area exhibit oxygen penetration depths between 8 cm and more than 100 cm. This region is characterised by a content of more than 40% *Fragilariaopsis kerguelensis* (= *F. kerguelensis*) frustules (Zielinski & Gersonde, 1997). The region is situated in a predominantly iron limited ecosystem within the ACC and is characterized by assemblages of large-celled and heavily silicified diatoms (Smetacek et al., 2004). The primary production regime seems to be closely linked to deep-sea sedimentation patterns, in particular at the meandering band of the Polar Front (Fig. 4-8). This direct linkage is supported by fluff observations in the Atlantic (Mackensen et al., 1993; Fischer et al., 1998; Sachs et al., subm.) and Indian sector (Riaux-Gobin et al., 1997; Pinturier-Geiss et al., 2001).

In contrast to Region A, several sites exist in the *F. kerguelensis* Province, where the oxygen penetration depths suggest a much lower Corg input than the flux values determined from the surface gradients of the oxygen profiles, i.e. some of these profiles exhibit a discontinuous depth progression (compare Fig. 4-8 a, b, f with Fig. 4-7). Apart from potential sampling artefacts (see above), this may be indicative of episodic export events in the *F. kerguelensis* Province. It appears that *F. kerguelensis* is not the main source for episodic sedimentation pulses. For example, Riaux-Gobin et al. (1997) described fluffy layers containing chl-a and phaeopigments with *F. kerguelensis*, *Chaetoceros spp.* and *Corethron pennatum*. A similar species composition, including high pigment concentrations was found in a ~13 cm thick, liquid surface layer at site PS65-705 and in a 0.5 cm fluffy layer at the PF (Sachs et al., subm). Again, the same species composition was obviously responsible for the rapid export at the end of the European Iron Fertilization Experiment (EIFEX, Strass et al., subm). At these stations, however, large oceanic *Chaetoceros* species in combination with the large diatom *Corethron pennatum*, which are poorly preserved in sediments, were identified to be responsible for Corg export.

Beside single local observations such as the sediment accumulation at site PS1782, (Rutgers van der Loeff, 1990b; Rutgers van der Loeff & Berger, 1991) or production hotspots (Sachs et al., subm), the patchiness of the oxygen penetration depth in the *Fragilariaopsis kerguelensis* Province is considered a result of seasonally, annually and regionally changing events. This is also suggested by porewater oxygen profiles which were not in a steady state below fluffy layers (Sachs et al., subm) as well as the discrepancy between high benthic Corg fluxes and great OPD values.
Figure 4-8: Selected oxygen profiles of Region B (Fig. 4-6, Transect B). The transect starts in the north (a) with Station PS1751 and ends with Station 1772 in the south (f). Decreasing oxygen penetration depths close to and south of the Polar Front (PS1759 and PS1765, 1768, respectively) indicate locally enhanced benthic fluxes in the PF area.
Region C: The Antarctic shelf region and the continental slope (without Antarctic Peninsula)

This area includes sediments off the coast up to 2000 m water depth. This province is characterized by a patchy and inhomogeneous sedimentation area (Schlüter, 1991) with varying physical and biological properties. The coastal ecosystem is shaped by local, regional, seasonal and inter-annual ice-conditions including coastal polynyas as well as area-specific topography and hydrography. As shown in Fig. 4-9, this heterogeneity is reflected by the diversity of OPD values (from 1.2 cm up to several meters in some sites) and C$_{org}$ fluxes between 0.5 up to 24.5 mgC m$^{-2}$ d$^{-1}$.

The export of phytodetritus into surface sediments is dominated in Region C by different ice algae such as diatoms of the genus *Fragilariopsis* (especially the ice algae *F. cruta* and *F. cylindrus*), *Chaetoceros* or *Thalassiosira antarctica*. Furthermore, its sea ice habitat is dominated by algae which export large amounts of carbon to the sediment-water interface but are hardly found preserved in the sediment below. The two species that dominate this C$_{org}$ flux are *Phaeocystis* (Dayton, 1990; DiTullio et al., 2000; Smetacek et al., 2004) and *Corethron pennatum* (eg. Estrada & Delgado, 1990; Schloss & Ferreyra, 2002). However, only few direct observations of fluff or fresh phytodetritus layers in surface sediments of the east Antarctic shelf and the upper slope are reported in literature (Riemann, 1992; Barthel, 1997). Riemann (1992) found fluffy material at several Antarctic shelf and slope stations which contained faecal pellets and intact chain forming centric diatoms as well as colonies of *Phaeocystis*. Barthel (1997) described an almost 25 cm thick layer of phytodetrital material which consisted solely of large and fragile frustules of *Corethron pennatum*. These observations suggest *Corethron pennatum* to be rapidly transported to the deep where it scarcely occurs normally due to its fast dissolution (DeFelice & Wise, 1981; Gersonde & Wefer, 1987; Stockwell et al., 1991; Crawford, 1995; Brachfeld et al., 2003). In Antarctic late-Holocene sediments discrete *Corethron pennatum* layers imply high-productivity events with mass sedimentation (Taylor & McMinn, 2001), possibly below polynyas (Pudsey, 1988) or eddies (Jordan et al., 1991). In addition, fluff and aggregate re-distribution caused by bottom currents (Lampitt, 1985) may explain the patchy distribution of phytodetritus layers along the east Antarctic shelf and upper slope (Gutt et al., 1998).

As a result of the variable ice habitats that are reflected by different benthic ecosystems in Region C, oxygen penetration depths as well as benthic fluxes are highly variable. It seems that there is no general flux and OPD pattern as can be found for Regions A and
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B (the *Chaetoceros* spp. and *F. kerguelensis* Provinces, Figs. 4-6 & 4-7). However, so far there is a very limited number of benthic flux data available. To resolve the picture, additional high quality measurements are needed to be performed within this complex region.

Although the differences found in the three provinces are not surprising since they reflect different eco systems, the open ocean regions A and B exhibit interesting parallels: Both are situated within the diatom ooze belt and receive benthic fluxes in the
same range (Fig. 4-10) partly independent from water depth (Fig 4-11).

![Figure 4-10: Corg fluxes of Chaetoceros spp. and F. kerguelensis Provinces.](image)

![Figure 4-11: Corg fluxes of Chaetoceros spp. and F. kerguelensis Provinces. Below 1500 m, fluxes show no clear dependence on water depth.](image)

Benthic fluxes derived from the surface oxygen microgradients can be considered as a short term signal ranging from 0.6 to ~ 10 mgC m\(^{-2}\) d\(^{-1}\) in both provinces. The three flux values from the shelf off the Antarctic Peninsula correspond to sediment particle trap
observations that revealed high fluxes as well (Abelmann et al., 2006 and references herein).

With respect to the oxygen penetration depth, a different pattern is obtained: Whereas OPD values increase from around 2 cm around the Antarctic Peninsula to around 20 cm towards South Georgia and the South Sandwich Islands (Fig. 4-12), they increase up to 60 cm in the periphery of the Chaetoceros spp. Province (Fig. 4-12, red circle). East of South Georgia and the South Sandwich Islands (Region B, F. kerguelensis Province), the picture changes into an inhomogeneous distribution (Fig. 4-12). While the C<sub>org</sub> flux varies from 2.5 to 13.1 mgC m<sup>2</sup> d<sup>-1</sup> (Fig. 4-10), OPD values range between 8 cm and >100 cm (Fig. 4-12 and 4-13) with a main fraction between 20 and 40 cm.

Figure 4-12: OPD values of Chaetoceros spp. and F. kerguelensis Provinces. The red circle shows peripheral OPD values from the Chaetoceros spp. Province (Argentine Basin, Drake Passage and Bellingshausen Sea). See text for explanation.
Figure 4-13: OPD values of Chaetoceros spp. and *F. kerguelensis* Provinces. See text for explanation.

Considering OPD values as a multi-year signal in respect to benthic fluxes, these patterns differ significantly from the distributions of $C_{\text{org}}$ fluxes (Figs. 4-10 & 4-11): Whereas $C_{\text{org}}$ fluxes are similar in both areas, the shallow oxygen penetration depths observed in the *Chaetoceros* spp. Province suggest a more frequent deep export compared to the *F. kerguelensis* Province which displays much more scattered OPD values. This corresponds with *ex situ* observations of Rabouille et al. (1998), and *in situ* observations of Sachs et al. (subm.). Single diatom blooms export fresh and labile organic carbon from the surface to the deep-sea, e.g. at the meandering Polar Front. Immediate bacterial degradation steepens the surface gradients of oxygen profiles of the *F. kerguelensis* Province temporarily before the steady state conditions are established within the subsequent months.

### 4.5 Conclusions

Diatoms play a key role in the ocean carbon cycle (Smetacek, 1999). Complementing the rare sediment particle trap data, our results provide information about carbon fluxes reaching the deep-sea sediments of individual areas of the Southern Ocean. We suggest that diatoms are the major contributors to rapid deep export. The data set presented here allows for mapping the thickness of the oxygenated layer in surface
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sediments as multi-year flux information for different diatom provinces. This proves the concept of Abelmann et al. (2006), which suggests that productive zones are reflected in the sediments. Transferred to glacial/interglacial times, it permits to regionalize sinks of CO₂ of past climate cycles. Furthermore, the determination of paleo C<sub>org</sub> fluxes from this relationship would provide important input for the comprehension of export and burial processes as well as CO₂ modelling. According to Smetacek (1999), there are still fundamental gaps in our knowledge which will have to be bridged in order to completely understand global elementary cycles, their time scales as well as their implications in respect to global change. Connecting modern oceanic phytoplankton provinces with deep-sea carbon fluxes, the present paper aims to contribute to the understanding of controls and feedbacks of biogeochemical cycles in the Southern Ocean.

We conclude from these investigations that diatoms are more important for the vertical flux of organic carbon than previously assumed. It is obvious that diatom-dominated ecosystems such as the Southern Ocean play a major potential role in respect to CO₂ drawdown. This is clearly supported by our flux correction.

Furthermore, we propose to continue enlarging the database of high quality in situ flux measurements (e. g. from the Scotia Sea, Antarctic shelf and slope). In particular, by measuring below specific patches of diatom blooms, one could more exactly determine export capacities, burial efficiencies and remineralization rates of individual diatom species. Doing so, the regional distribution of benthic carbon fluxes can be used as the basis for a more detailed modelling of CO₂ draw down in the Southern Ocean.

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4.6 References


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5 Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean

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Key words: export ratio, benthic organic carbon fluxes, deep-sea sediments, Southern Ocean, microsensors

5.1 Abstract

Datasets of benthic oxygen fluxes, satellite-derived primary production estimates and bathymetry have been used to derive transfer functions for the export of carbon from the surface mixed layer to the sea floor, in the Southern and Atlantic Oceans. Biogeochemical provinces defined a priori using surface chlorophyll or sediment characteristics could not be distinguished by their transfer efficiencies. However, a posteriori definition of provinces based on the transfer efficiency showed a band of high export efficiency along the Southern Ocean opal belt and in the northern North Atlantic. Possible explanations for this are discussed. Basin-wide carbon export values were calculated for the Southern, Atlantic and global oceans using the transfer functions derived for the a posteriori-defined provinces. Areally integrated carbon fluxes were within the range published from sediment trap studies, and lower than published values calculated using inverse modelling of the f-ratio. For the Southern Ocean, areally integrated carbon export to the sea floor in water deeper than 800 m was 0.055 PgC yr\(^{-1}\) (0.6 % of net primary production). Incorporating higher export ratios within the opal belt gave a value of 0.064 PgC yr\(^{-1}\).
5.2 Introduction

Carbon dioxide (CO₂) fixation by phytoplankton via photosynthesis decreases the partial pressure of CO₂ at the ocean surface. This process, combined with the subsequent cycle of grazing and export to the deep, is often referred to as the "biological pump" (Volk and Hoffert, 1985; Sarmiento and Le Quere, 1996), and represents one of the major CO₂ sinks (Cameron et al., 2005). The Southern Ocean (SO) is recognized as one of the world's most important regions of carbon sequestration via the biological pump (Kumar et al., 1995; Sarmiento et al., 2004) as well as for the solubility pump, i.e. the physico-chemical pump of CO₂ (Raven and Falkowski, 1999; Le Quéré et al., 2007). The combination of these two processes in the Southern Ocean is attributed with the uptake of ∼2 Pg of anthropogenic CO₂ per year (Siegenthaler & Sarmiento, 1993; Caldeira & Duffy, 2000) which is ∼32 % of the annual global anthropogenic emissions during the 1990s (Houghton, 2003). The long-term efficacy of the biological pump depends on the depth of carbon export: Delivery of particulate organic carbon to the seafloor represents the longest isolation from the atmosphere (e.g. Boyd & Trull, 2007). Organic carbon deposited at the sea floor is remineralized over days to years depending on composition, microbial and macrobenthic activity and other environmental factors. Refractory components are buried in the sediments for geological time scales (Cai & Reimers, 1995). The effect of photosynthetic carbon fixation on CO₂ partial pressure in the water is negative except when carbon is used to form particulate organic carbon platelets or shells (e.g. Raven & Falkowski, 1999). This means that in order to quantify the efficiency of the biological pump, parameters such as primary production, particulate inorganic and organic matter export and benthic carbon fluxes have to be determined.
The upper limit for export to the deep is determined by surface primary production rates, whereas the actual export into the deep sea is a complex, as yet incompletely understood, function of phytoplankton cell shape, composition, aggregation, grazing and ballasting (Asper et al., 1992; Dunne et al., 2005; Boyd & Trull, 2007; Passow & De La Rocha, 2006; Kemp et al., 2006; Jin et al., 2006; Green & Sambrotto, 2006). Figure 5-1 illustrates some of the mechanisms particularly relevant for the SO. Primary production is largely determined by physical factors (e.g. Longhurst, 1995; Holm-Hansen et al., 2005) which may be typical for a region but vary over time scales of days to millennia.
Figure 5-1: Schematic overview of the pathways of organic matter production, export, sedimentation, and benthic remineralization. This paper investigates possible empirical relationships between sea surface production and benthic fluxes applying a statistical approach.
There exist several approaches to classify production provinces (Platt et al., 2005; Longhurst, 1995). However, routinely discerning provincial boundaries which change over time is difficult. Figure 5-2 shows median summer chl-a and square mean variability (rms) SeaWIFS composites for the SO overlaid with biogeochemical provinces after Longhurst (1995).

Figure 5-2: a) Median chl-a distribution and b) rms variability as an indicator for temporal chl-a variability of the study area over a timescale of 10 years. Provinces are after Longhurst (1995). ANT: Antarctic, APL: Austral Polar, BENG: Benguela Current Coastal, BRAZ: Brazil Current Coastal, CHIL: Chile-Peru Current Coastal, EAFR: East Africa Coastal, FKLD: Southwest Atlantic Continental Shelf, ISSG: Indian Ocean South Subtropical Gyre, SANT: Subantarctic, SATL: South Atlantic Tropical Gyre, SPSG: South Pacific Subtropical Gyre, SSTC: South Subtropical Convergence.
While both concentration and variability are well-contained by the Longhurst province along the Antarctic coast, off-shore, the variability patterns do not lie neatly within the boundaries. The more sophisticated approach of Sokolov & Rintoul (2007) utilises satellite altimetry to track front locations and may solve the problem of determining provincial boundaries in the Southern Ocean. Spatial patterns in flora and fauna have also been observed at the more mysterious sea floor (Beamann & Harris, 2005; Brandt et al., 2007a+b). Among others, Suess (1980) and Martin et al. (1987) proposed transfer functions for the coupling between the two compartments. Some studies suggest the biogeochemical provinces at the surface to have influence on the export regime (Lampitt & Antia, 1997). On the other hand, evidence for a decoupling between ocean surface and sediment was reported e.g. by Buesseler, 1998, Seiter et al. (2004, 2005) and Christensen (2000). Owing to the relative paucity of information about community distributions in the twilight zone between these two domains, a complete surface to benthos mapping of communities or particle export processes is not yet possible, so that all determinations of benthic carbon flux distributions involve implicit assumptions about midwater processes. There is evidence that the ecosystems occupying waters below the euphotic zone are highly adaptable (Richardson et al., 2006; Zaric et al., 2005), which poses the question of the degree to which any regional variability in export production is smoothed out as exported material proceeds to the sea-floor. The problem of regional variability in export efficiency can be considered in four stages: A) how much labile carbon sinks out of the euphotic zone? B) how well is it protected? C) how long is it exposed to remineralising forces? D) how efficient is the remineralising community?

In the case of point A, the most direct method of quantifying organic carbon export production is to use particle traps, which provide estimates of carbon flux at predetermined temporal resolution at a fixed location or drift-depth. These
investigations, mostly carried out within the top 1000 m of the water column, show pulsed and highly variable particle export. Longer term variability of fluxes is difficult to determine due to logistical constraints on the duration of most studies. Well-documented technical limitations with respect to efficiency of different trap types (Gust et al. 1994, Scholten et al., 2001) can, in part, be alleviated using $^{234}$Th correction (e.g. Waples et al., 2006). This method remains invaluable for examining particle sedimentation rates over time-scales of weeks to months. However, the number of particle traps in the ocean is relatively low, particularly in the polar regions (Honjo, 2004 and references therein). Therefore it is difficult to derive basin-wide mean export production rates from particle trap data.

Another method of determining carbon fluxes to the deep ocean involves use of the f-ratio – the ratio of new to regenerated production – and global-scale modelling (Schlitzer, 2002; Schlitzer et al., 2003). However, the validity of the f-ratio for determining export flux has been called into question, since nitrification is now known to take place in the euphotic zone, rather than exclusively below the mixed layer (Dore & Karl, 1996; Raimbault et al., 1999).

A third method is the calculation of benthic carbon fluxes using oxygen measurements at the sediment / water interface. In contrast to sediment traps, this provides values of carbon export through the twilight zone into the benthos. Oxygen uptake rates, i.e. benthic oxygen consumption and pore water gradients, are closely linked to the degradation of labile organic carbon at the sediment surface. Benthic oxygen uptake rates can be derived from oxygen microprofiles and sediment incubations (e. g. Revsbech & Jørgensen, 1986; Reimers et al., 1986; Glud et al., 1994; Berg et al., 1998). Both methods can be applied in situ (at the seafloor) and ex situ (by retrieving samples and measuring aboard ship). Except in the study of Hulth et al. (1997) there exist no sediment incubation measurements for the Southern Ocean. In contrast, many
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flux determinations derived from oxygen microprofiles have been reported in the literature for other regions (e.g. Archer et al., 1989; Sauter et al., 2001; Wenzhöfer & Glud, 2002; Sachs et al. submitted 2007 and references therein). Diffusive oxygen fluxes are converted into organic carbon rain rates on the basis of the Redfield Ratio modified by Anderson & Sarmiento, (1994). Oxygen profiles also allow determination of the depth of sedimentary oxygen penetration depth (oxygen penetration depth, OPD), which is ecologically relevant as O₂ supply can limit benthic faunal growth. Whereas the organic carbon flux determined from oxygen microgradients reflects the recent history of sedimentation and C₅₀ remineralization by microbial activity, the oxygen penetration depth reflects a long-term signal of benthic fluxes and can therefore be used as a measure of long term carbon export to the seafloor. Measurements of total and diffusive oxygen uptake at a range of sites across the globe have shown that benthic C₅₀ flux estimates based on diffusive oxygen uptake rates represent a lower limit on carbon export (Wenzhöfer & Glud, 2002; Seiter et al., 2005; Christensen, 2000).

Sachs et al. (submitted 2006) observed an apparent correlation between in situ determined benthic organic carbon flux measurements and the remotely-sensed surface chl-a concentration at a few stations along the Antarctic Polar Front (APF). The link between primary production (PP) and particle flux reported for mid-water particle traps (e.g. Lampitt & Antia, 1997; Fischer et al., 2000; Francois et al., 2002; Lutz et al., 2002) appeared to be applicable to benthic flux measurements performed in the deep-sea.

In this paper, the relationship between surface primary production and sea-floor carbon remineralisation in the Southern Ocean is examined for the first time with a substantial dataset. Coupling between chl-a concentrations in surface waters and OPD, and between measured organic carbon remineralisation at the sea floor (hereafter assumed to represent the minimum exported carbon, referred to as benthic C₅₀ flux), was examined for provinces defined using surface biomass and sediment characteristics.
The effects of water depth and latitude were also examined. The objectives of this study were:

1) to investigate whether statistically significant relationships could be identified between sea surface productivity and benthic $C_{org}$ fluxes for the SO,

2) to test the hypothesis of whether different biogeochemical provinces, characterized by different key phytoplankton species, can be distinguished from one another by their sea surface : benthos regression characteristics; and

3) to use the sea surface:benthos regression relationships to produce maps of benthic $C_{org}$ flux and OPD.

This analysis differs from previous studies in 3 fundamental respects: a) this study focuses on the SO, which has previously been omitted from large-scale $C_{org}$ flux estimates (e.g. Jahnke, 1996; Antia et al., 2001) due to the very limited data coverage; b) benthic oxygen flux measurements and sediment oxygen penetration depths are used instead of mid-water sediment traps. This avoids the uncertainties of sediment traps and chamber measurements and allows a lower limit for deep $C_{org}$ export to be calculated; c) long-term, median surface chlorophyll and primary production are used. This eliminates the possibility of analysing inter-annual trends but allows the degree to which surface-benthic biogeochemical systems are stable over decadal time scales to be addressed. Time-scales involved are comparable to those used by Schlitzer et al. (2003), but the methodology is quite different.
5.3 Methods

5.3.1 Database and data compilation

5.3.1.1 Point Data at individual sites in the Southern Ocean: $C_{\text{org}}$ fluxes and OPD

Data derived from the measurement of oxygen profiles in surface sediments were compiled from different sources and assessed for suitability for further analysis (Sachs et al., submitted 2007). *In situ* and *ex situ* oxygen microprofiles were measured during Polarstern Expeditions ANT V/4, ANT VI/2-3, ANT VIII/3, 6, ANT X/5-6, ANT XI/3, ANT XXI/4. This covers the following SO regions: Amundsen and Bellingshausen Seas (Pacific Sector), Scotia and Weddell Seas, east Antarctic shelf and continental slope and the Atlantic sector of the Antarctic Circumpolar Current. In total 134 microprofiles were taken from the literature, of which 96 were suitable for derivation of $C_{\text{org}}$ fluxes (Sachs et al. submitted 2007). Additional published *in situ* flux determinations from oxygen microprofiles were used to compare the results obtained for the SO with other domains of the Atlantic Ocean (Archer et al., 1989; Jahnke et al., 1989; Glud et al., 1994; Hales et al., 1994; Hales & Emerson, 1997; Lohse et al., 1998; Schlüter et al., 2000; Sauter et al., 2001; Wenzhöfer et al., 2001; Epping et al., 2002; Wenzhöfer et al., 2002).

* Determination of organic carbon fluxes

Benthic oxygen fluxes were partly determined *in situ* on the basis of oxygen microprofiles obtained by an autonomous deep-sea microprofiler deployed in combination with a free fall lander system. *Ex situ* profiles were measured in undisturbed sediment samples recovered by a multiple corer (MUC, Barnett et al., 1984) in the ship’s cool laboratory at *in situ* temperature (Sachs et al., submitted 2007). *In situ* and *ex situ* oxygen profiles were measured using Clark type glass microelectrodes.
Deep-sea and laboratory electrodes were calibrated prior to each measurement and against the bottom water oxygen concentration determined by Winckler titration (Grassoff et al., 1983). When microprofiles reached the depth of oxygen depletion, this zero reading was used for calibration. Diffusive oxygen fluxes were determined from the uppermost 3-5 mm of in situ and ex situ pore water oxygen profiles using the software PROFILE (Berg et al., 1998) and were converted into organic carbon rain rates on the basis of the modified Redfield Ratio (Anderson & Sarmiento, 1994), under the assumption that in oligotrophic deep-sea sediments the major part of organic carbon is remineralized by oxic respiration. Ex situ determined deep-sea fluxes of the SO were depth corrected using the function $C_{\text{org flux corr}} = C_{\text{org flux ex situ}} \cdot (0.00039 \cdot z + 0.91)$ (Sachs et al., submitted 2007).

**Determination of oxygen penetration depth**

The in situ oxygen microprofiles were measured with a vertical resolution of 0.1-0.5 mm. For ex situ measurements, laboratory microsensors were mounted into a micromanipulator and profiles were measured with a vertical resolution of 0.1-2 mm. The maximum profile depth was 32 cm. At cores where the anoxic zone was not reached during the measurement, OPD was estimated by fitting a double exponential function (Sachs et al., submitted 2007; Andersson et al., 2004) to the oxygen profile, using the Matlab 'cftool' program.

### 5.3.1.2 Chlorophyll and primary production data (SeaWifs/MODIS)

Sea surface chl-a concentration data were obtained from the NASA internet portal (http://oceancolor.gsfc.nasa.org). Chl-a concentrations at the sediment stations were extracted from weekly, level 2 SeaWiFS data, with a spatial resolution of 9 km, for the
period November 1997 to December 2006. SeaDAS v.5 was used for data extraction, while Matlab v.7.3 was used for subsequent analyses.

Two suites of net primary production data, based on the Vertically Generalized Production Model (VGPM) and on the VGPM model with a correction for photo-acclimation (Eppley) were also obtained from NASA (http://oceancolor.gsfc.nasa.gov). These primary production estimates are derived from SeaWiFS / MODIS chl-a and photosynthetically available irradiance data along with MODIS / AVHRR sea surface temperature data. The native spatial resolution for primary production was 9 km, and the suitability of this was examined using a general circulation model (section 2.1.3). The native temporal resolution is one month and the temporal range September 1997 to October 2006. These data were preferred to the Coastal Zone Colour Scanner (CZCS)-derived dataset of Antoine et al. (1996) which has been used by many other studies because the emphasis here is on the long-term median values of both chlorophyll and primary production. As the CZCS was more a proof-of-concept mission for coastal remote sensing, it was not designed or positioned for daily/two-daily repeat coverage which both SeaWiFS and MODIS acquire. For median values, therefore, the more modern sensors are more suitable. VGPM PP data were selected for further analysis, while the Eppley PP data were retained, being similar in approach to the Antoine et al., (1996) data set, for comparison with the VGPM approach. Different sensor characteristics of MODIS and SeaWiFS necessitate the use of different corrections and chlorophyll algorithms: the resulting chlorophyll values are significantly different only in highly turbid waters (oceancolor.gsfc.nasa.gov/VALIDATION). Comparison of the weekly and monthly SeaWiFS and MODIS chlorophyll products at all stations used in this study showed no systematic bias in the range of values at any location (data not shown). Muller-Karger et al. (2005) found that CZCS- and SeaWiFS-derived global net primary production estimates agreed to within ± 20%.
Median, mean and maximum chl-a and primary production values were calculated over the full range of remote-sensing data for each location where benthic measurements were performed, for comparison with sediment variables. However, results are significantly biased towards summer values for high latitudes: Since the focus of this paper is the relationship between long-term carbon sequestration and primary production in varying ecological regimes and at varying latitudes, it was decided not to fix potentially arbitrary boundaries for ‘summer’. This approach has the additional advantage of maximizing coverage in cloudy / icy regions. A similar temporal bias is also present in other datasets used to estimate $C_{org}$ flux, with the exception of long-term sediment trap deployments.

5.3.2 Consideration of lateral advection

Our comparison of surface production and benthic carbon input parameters (OPD, $C_{org}$ flux) is based on the assumption of a predominately vertical export. This approach is most accurate if the grid size of the satellite chl-a observation is chosen to encompass the likely distance of lateral advection. Mean monthly modelled velocities together with a range of realistic sinking velocities (10, 200, 1000 m d^{-1}) taken from literature (e.g. Suzuki et al., 2001; Turner, 2002) were used to reconstruct, from the station location at the sea-floor upwards, the lateral distance which could have been travelled by particles deposited at the site during each month of the year.

Horizontal advection distances were calculated for each station using velocities from the BRIOS-1 ice-ocean model (Beckmann et al., 1999; Schodlok et al., 2002) with 24 model depths and a horizontal resolution of 1/6 x 1/3 deg within -50° to -80° S, and using World Hydrographic Atlas data to the north. Despite the relatively high vertical resolution of the model at the sea-floor compared to the inner ocean, the BRIOS-1
model was not designed to simulate near-bottom turbidity currents, so that the possibility of large near-bottom transport distances was not considered. To the best of our knowledge, no large-scale ice-ocean models currently running have the capability to predict bottom currents, and efforts to overcome this limitation are hindered by a lack of data for validating such predictions and by poor bathymetric charts – necessary for accurately predicting near-bottom flow – over large areas of the Southern Ocean.

5.3.3 Connecting surface chl-a with benthic C\textsubscript{org} fluxes and OPD values

To test whether the relationships between surface and benthos vary regionally, two approaches were taken to \textit{a priori} classification of ecological provinces: The first method uses only surface chlorophyll data from the last ten years’ remote sensing record. The second method uses only benthic sediment information from the literature. Results of these grouping procedures were also compared with the provinces determined by Longhurst (1995) and by Seiter et al. (2004).

5.3.3.1 \textit{A priori} groups based on surface chlorophyll data (CD groups)

The chl-a distribution groups were determined using root mean square variability (rms) on the summer chl-a concentration and the log-transformed chl-a concentration at all stations. Gaussian curves were fit to histograms of these two variables. Best fits were obtained by assuming two Gaussian distributions for rms and three for chl-a. ‘Low’, ‘medium’ and ‘high’ value thresholds were chosen as the intersection points between Gaussian distributions. The 134 stations were then assigned to one of the six groups according to their chl-a and rms–chl-a values. The group defined as ‘low chl-a, high rms’ was found to be empty. The group defined as ‘high chl-a, low rms’ contained only two stations which, since this is insufficient for statistical testing, were re-assigned to the
group 'med chl-a, low rms'. The remaining four chlorophyll data groups are henceforth referred to as 'CD groups':

- CD1: low chl-a / low rms,
- CD 2: median chl-a / low rms,
- CD X: high chl-a / low rms, (2 stations reassigned to CD2)
- CD Y: low chl-a / high rms, (empty)
- CD 3: medium chl-a / high rms,
- CD 4: high chl-a / high rms.

5.3.3.2 A priori groups based on surface sediment data (SED groups)

Groupings based on sediment data from the literature were assigned to each station using sediment surface distributions of *Fragilariopsis kerguelensis*, *Chaetoceros* spp. and depth (Jousé et al., 1962; DeFelice & Wise, 1981; Burckle & Cirilli, 1987; Zielinski & Gersonde, 1997; Armand et al., 2005; Crosta et al., 1997; Mohan et al., 2006). Owing to a lack of information in the Amundsen and Bellingshausen Seas, the stations in this area were placed in a separate group. Similarly, stations in the Atlantic, north of 30°S, were also placed into a separate group. The resulting six sediment record groups are henceforth referred to as 'SED groups'.

One-way analysis of variance (ANOVA) was used to determine whether each of the grouping systems produced distinctive subsets of stations based on oxygen penetration depth (OPD), organic carbon flux, chl-a, PP and rms-chl-a.

5.3.3.3 Coupling between the sea surface and benthos

Direct coupling of sea surface to benthic data was tested using linear regression analyses between PP and *C*org flux and between chl-a and OPD, i.e.:
5 Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean

\[ C_{\text{org}} \text{ flux} = a_1 \cdot \text{PP} \quad \text{Eq. 1} \]
\[ \ln \text{OPD} = a_2 \cdot \ln \text{median chl } a + a_3 \quad \text{Eq. 2} \]

Subsequently, several equations relating \( C_{\text{org}} \) flux, PP and depth from the literature were considered:

Antia et al. (2001): \( \ln C_{\text{org}} \text{ flux} = a_1 \cdot \ln \text{PP} + a_2 \cdot \ln z + a_3 \quad \text{Eq. 3} \)

Schlüter et al. (2000): \( \ln (C_{\text{org}} \text{ flux}) = a_1 \cdot \ln (\text{PP}) + a_2 \cdot \ln (z) \quad \text{Eq. 4} \)

Suess (1980): \( C_{\text{org}} \text{ flux} = \frac{\text{PP}}{(a_1 \cdot z + a_2)} \quad \text{Eq. 5} \)

Multiple-ANOVA tests were performed to establish whether the CD or SED groups were distinctive in the 2-dimensional (chl-\( a \) and OPD / PP and \( C_{\text{org}} \) flux) and 3-dimensional (including depth) parameter space.

The most statistically significant of the resulting fits was applied to the ten-year Southern Ocean (40°S to 80°S, circumpolar) and Atlantic (70°W to 20°E, 80°S to 80°N) median PP data to produce a map of benthic \( C_{\text{org}} \) flux. \( C_{\text{org}} \) flux was then integrated over basin and depth intervals. Area per pixel of the primary production product was calculated by taking each value as a pixel-midpoint, locating a square midway to the neighbouring pixels and calculating area as:

\[ A = \left(\frac{\pi}{180}\right) \cdot R^2 \cdot | \sin \lambda_1 - \sin \lambda_2 | \cdot | \phi_1 - \phi_2 | \quad \text{Equation 9} \]

Where the Earth’s radius \( R \) was assumed to be 6371 km, \( \lambda_1 \) and \( \lambda_2 \) are the northern and southern latitude boundaries and \( \phi_1 \) and \( \phi_2 \) the west and east longitude boundaries.
5.4 Results and discussion

5.4.1 Lateral advection

As reported in Table 5-1, mean net lateral advection calculated using monthly current fields produced by the BRIOS circulation model was found to be less than 5 km for even the slowest sinking particles. One station at 74° 15' S, 26° 17' W (PS1596-2) was an extreme outlier with extreme advection distances up to ~32 km. Based on these results and the resolution of available NASA level 3 data, the native satellite data resolution of 9 km was retained. The linkage between surface chl-a values and benthic C$_{org}$ fluxes should not be severely affected by lateral advection except where bottom currents, which could not be modelled, are strong. In a similar study, Muller-Karger et al., 2005 also retained 9 km resolution with the reasoning that only a small proportion of POC undergoes lateral transport. However, it should be noted that anecdotal evidence (U. Bathmann, AWI, pers. comm.) as well as point studies (Geibert et al., 2005) indicate that the influence of bottom currents may be significant in many areas, including the Southern Ocean opal belt. In this case, correlations between surface production and benthic oxygen uptake rates will be determined not only by the transfer function with depth but also by the spatial coherence of the surface biomass. In order for advection along the sea floor to produce a systematic bias in statistical analyses, the deposition area for advective currents would have to be large (traversing gradients of at least an order of magnitude in surface chlorophyll values) and spatially coherent, producing an over-estimate of the export efficiency for the region in question. Such an effect can only be ruled out by intensive _in situ_ sampling or by focussed modelling efforts.
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Tab. 5-1: Estimated diatom sinking rates (frustules, aggregates, pellets) and the corresponding mean lateral advection distances computed using results of the BRIO-S-1 ice-ocean model (Beckmann et al., 1999; Schodlok et al., 2002).

<table>
<thead>
<tr>
<th>sinking rate [m d⁻¹]</th>
<th>mean lateral advection [km]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.68 ± 1.11</td>
</tr>
<tr>
<td>200</td>
<td>0.23 ± 0.06</td>
</tr>
<tr>
<td>1000</td>
<td>0.05 ± 0.01</td>
</tr>
</tbody>
</table>

5.4.2 Use of long-term median chlorophyll concentration and primary production estimates

Previous studies investigating the coupling between sediment trap and surface primary production data have taken the latter from contemporaneous satellite overpasses or used the compilation of Antoine et al. (1996) based on the CZCS dataset for the period 1978 - 1986. Investigation of the relation between surface production and benthic C_{org} fluxes requires data obtained for comparable time scales at both the ocean surface and the sea floor. For the benthic dataset examined here, which was collected between 1986 and 2004, long-term median values should be much more robust since gaps in the data are smoothed, and the decadal time-scale over which OPO develops is approximated.

The sediments of the deep SO are commonly deeply oxygenated. On this account the measured oxygen microprofiles do not reach suboxic or anoxic depths. The OPO values used here were mostly extrapolated beyond the actual measurement depth (Andersson et al., 2004; Sachs et al., submitted 2007). Note that the resulting OPO values, which sometimes exceed several metres in the SO, represent a 'virtual OPO', which could be expected if the recent sedimentation conditions had prevailed over long geological timescales. In reality, processes such as diagenesis, resedimentation etc. almost certainly eliminate oxygen from deeper sediments. These OPO values should therefore be considered as mathematical constructs which capture the OPO profile curvature, not as measured OPO depths. The deepest oxygen measurements were made at 39 cm (Sachs et al., submitted 2007).

To answer the question of whether short- or long-term surface chlorophyll and production data are more suitable for comparison with the benthic flux data analysed
here, the mechanisms of POC transport to the seafloor have to be taken into account: If benthic measurements were carried out in the presence of freshly deposited organic matter which is increasingly believed to contribute significantly to total benthic POC fluxes, particularly at high latitudes (Nodder et al., 2005; Kemp et al. 2006), the resulting C$_{org}$ flux may not be representative for the site as the labile organic carbon of this phytodetritus may be remineralised over time scales of days to weeks (e.g. Carney 1989; Turley & Lochte 1990; Conte et al. 1995). A measurement made a month after a sedimentation event would therefore yield a different profile for the upper centimetres of sediment, and hence a much lower value of benthic C$_{org}$ flux (see Figure 5-1).

In contrast, the oxygen penetration depth represents the long-term benthic influx of organic carbon and can therefore be used to gauge the representativeness of an instantaneous C$_{org}$ flux estimate. Assuming that remineralization and burial covary with changing carbon rain rates, and that the export systems responsible for the development of the sediment oxygen profile remain stable over many years, pairs of measurements of OPD and C$_{org}$ flux should fall along a line which describes the depletion of O$_2$ in the deeper sediments with increasing, regular rain rate and associated O$_2$ demand. Any measurement points affected by recent carbon deposition should fall above this line, since more carbon is present that would be expected for the long-term steady state. Figure 5-3 shows the strong coupling found between C$_{org}$ flux and OPD for the dataset employed here. Regression curves are described by:

For all data:  $C_{org}$ flux = 63.8 $\cdot$ OPD$^{-0.6476}$, $r = -0.4557$, $n = 194$  
Equation 6a.

For the SO:  $C_{org}$ flux = 8.23 $\cdot$ OPD$^{-0.4694}$, $r = -0.667$, $n = 126$  
Equation 6b.

For the Atlantic N of 30°S:

$C_{org}$ flux = 14.9 $\cdot$ OPD$^{-0.7723}$, $r = -0.8312$, $n = 32$  
Equation 6c.
5 Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean

Figure 5-3: Correlation between \( C_{\text{org}} \) flux and OPD at 126 sites for which both parameters were available in this study. AP 1 and AP 3 represents data subgroups introduced in Section 3.4. The regression curve for all data is: 
\[
\ln(C_{\text{org}} \text{ flux}) = (-0.4882 \pm 0.0460) \times \ln(\text{OPD}) + [2.1076 \pm 0.1385], \\ n=126, r = -0.667.
\]
For stations north of 30° S: \[
\ln(C_{\text{org}} \text{ flux}) = (-0.6775 \pm 0.0649) \times \ln(\text{OPD}) + [2.6218 \pm 0.0988], \\ n=32, r = -0.8312.
\]
Dashed lines represent the 95% confidence interval for the fit to all data.

Based on this, it was assumed in the following that the \( C_{\text{org}} \) flux measurements were generally not dominated by recent rapid export events. The question of whether the difference in fit parameters between the Southern Ocean and the more northerly stations results from under-sampling in the north (n = 32 c.f. 126) will remain unanswered until more \( O_2 \) profiles have been amassed: ANOVA testing found no significant difference between the two groups of data used here (\( \alpha = 0.05 \)).

The use of long-term median net primary production (PP) data is of particular advantage in the SO, which is the focus of this paper, since frequent cloud and ice-cover lead to poor temporal and spatial coverage over much of the SO. The establishment of significant relationships between long-term surface productivity patterns and benthic oxygen profiles allows the use of older, pre-satellite era benthic measurements. The strength of such relationships represents the stability over time of the surface mixed layer productivity (Gregg et al., 2005) and of the pelagic and benthic remineralising communities (assuming measurement errors to be constant over time).
A further consideration is the choice of the primary production model. Since the publication of Antoine et al. (1996), ten years of daily SeaWiFS and MODIS satellite chlorophyll estimates have been gathered, as well as ongoing daily sea surface temperature measurements. The NASA Ocean Color group (http://oceancolor.gsfc.nasa.gov) has made available global PP time series which use these datasets together with a range of primary production models, including one similar to the Eppley primary production algorithm used by Antoine et al. (1996), Lampitt & Antia (1997); Schütter et al. (2000), Lutz et al. (2002) and the widely used Vertically Generalised Production Model (VGPM, Behrenfeld & Falkowski, 1997). In contrast to the VGPM model the Eppley algorithm uses a temperature-dependent photosynthetic efficiency which, coincidentally, approximates photo-acclimation (http://web.science.oregonstate.edu/ocean.productivity/index.php). Figure 5-4 shows the relationship between Eppley and VGPM median primary production values for the stations included in this study.

![Figure 5-4: Comparison of Eppley and VGPM primary production estimates at the stations for which benthic flux data were used in this study: a) blue-outlined diamonds denote agreement to within ±20% between Eppley and VGPM; red circles indicate stations where VGPM estimate exceeds the Eppley estimate by >20%; green squares denote stations at which Eppley estimates exceeds VGPM estimates by >20%. b) Location of stations, using same color as a).](image)
No PP data were available from either model for 30 stations in the marginal ice zone of the Southern Ocean and at ~40°N, 10°W. No chlorophyll concentration data were available at all for 5 stations in the MIZ owing to persistent cloud and ice cover.

The comparison of the models revealed that the VGPM model estimates exceeded those of the Eppley model by ~60% in the mid-latitudes, and fell short of the Eppley estimates by a little over 20% in the tropics (-20° to +20°N). However, in the Southern Ocean and at a few scattered sites in the mid- and north polar latitudes, the two models were in agreement to within 20% (Fig. 5-4a, b). The VGPM PP values are related to the Eppley estimates as follows:

For the tropics (green stations in Fig. 5-4):

\[
\text{VGPM} = 0.8027 \times \text{EPPLEY} - 101.4, \quad r = 0.9978, \quad n = 23 \quad \text{Equation 7.}
\]

For the mid-latitudes (red stations in Fig. 5-4):

\[
\text{VGPM} = 1.6375 \times \text{EPPLEY} - 25.3, \quad r = 0.9954, \quad n = 97 \quad \text{Equation 8.}
\]

Given the uncertainty in the importance of photo-acclimation across the range of latitudes investigated here, and the strong correlation between the two PP models, the VGPM model is used as the 'standard' throughout this study, but can be converted back to the Eppley estimates using Equations 7 and 8. A comparison of 3-dimensional curve-fitting results using both Eppley and VGPM PP values is given in table 5-5.

### 5.4.3 A priori station groups

Locations of the a priori groups are illustrated in figure 5-5. Note that, in figures 5-5 and 5-6, both sets of a priori groups are colour coded (see legend for figure 5-5), and CD groups are always denoted by circles, SED groups by squares.
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5.4.3.1 Chl-a distribution groups (CD groups)

Characteristics of the CD groups are summarised in Table 5-2. CD1 stations (low chl-a / low rms) were mostly off-shore. In the SO, this group was found in typical high-nutrient, low-chlorophyll regions including south of the APF, the central Weddell Sea and off the Antarctic shelf and slope (Amundsen and Bellingshausen Seas, north of Gunnerus Ridge with the surrounding Riiser Larsen and Cosmonaut Seas). Among stations in the whole Atlantic Ocean dataset, CD1 was found off North and South America as well as in the central South Atlantic. The main domain of CD2 (median chl-a / low rms) was west of the Antarctic Peninsula and the frontal systems of the SAF and APF. Other locations included several stations close to the Marginal Ice Zone (MIZ) in the Amundsen and Bellingshausen Seas and deep waters of east Antarctica. In the whole Atlantic dataset, CD2 was associated with upwelling areas along the west coast of Africa, south and north Europe and in the Greenland MIZ. In polar seas, CD3
Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean

(medium chl-a / high rms) was found predominantly in the MIZ. At lower latitudes in the Atlantic Ocean, CD3 was occasionally found on the continental shelf. CD4 (high chl-a / high rms) stations were always found close to CD3, and mostly inshore of CD3, suggesting that the chlorophyll values here fall into the overlap between adjoining Gaussian curves fitted to the chl-a and rms chl-a histograms, or that sharp gradients occur in the geographical distribution of chl-a characteristics (see Tab. 5-2). A decoupling of chlorophyll concentration and PP was observed: chl-a increased, by definition, with increasing CD group number, whereas PP was lower for CD 3 than for CD 2.

Tab. 5-2: Characteristics of the four chl-a distribution groups (CD). CD1 = low chl-a / low rms, CD2 = median chl-a / low rms, CD3 = median chl-a / high rms, CD4 = high chl-a / high rms

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>Median Mean</th>
<th>Stddev</th>
<th>rms</th>
<th>Skew</th>
<th>Similar to:</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data</td>
<td>26778</td>
<td>0.01</td>
<td>64</td>
<td>0.54</td>
<td>0.26</td>
<td>1.2</td>
<td>1.27</td>
<td>17</td>
<td>0.90</td>
</tr>
<tr>
<td>CD1</td>
<td>8536</td>
<td>0.01</td>
<td>4.5</td>
<td>0.19</td>
<td>0.15</td>
<td>0.18</td>
<td>0.26</td>
<td>8.6</td>
<td>0.73</td>
</tr>
<tr>
<td>CD2</td>
<td>12831</td>
<td>0.046</td>
<td>12</td>
<td>0.44</td>
<td>0.29</td>
<td>0.49</td>
<td>0.66</td>
<td>5.9</td>
<td>0.92</td>
</tr>
<tr>
<td>CD3</td>
<td>1569</td>
<td>0.047</td>
<td>31</td>
<td>0.93</td>
<td>0.42</td>
<td>2.1</td>
<td>2.3</td>
<td>7.7</td>
<td>1.1</td>
</tr>
<tr>
<td>CD4</td>
<td>3842</td>
<td>0.085</td>
<td>64</td>
<td>1.5</td>
<td>0.89</td>
<td>2.3</td>
<td>2.7</td>
<td>11</td>
<td>0.39</td>
</tr>
</tbody>
</table>

| Median chlorophyll-a concentration (ug/l-1) | All data | 26778 | 0.01 | 64  | 0.54 | 0.26 | 1.2 | 1.27 | 17 | 0.90 | n.a. |
| CD1   | 8536 | 0.01 | 4.5 | 0.19 | 0.15 | 0.18 | 0.26 | 8.6 | 0.73 | / |
| CD2   | 12831 | 0.046 | 12  | 0.44 | 0.29 | 0.49 | 0.66 | 5.9 | 0.92 | / |
| CD3   | 1569 | 0.047 | 31  | 0.93 | 0.42 | 2.1 | 2.3 | 7.7 | 1.1 | / |
| CD4   | 3842 | 0.085 | 64  | 1.5  | 0.89 | 2.3 | 2.7 | 11 | 0.39 | / |

| Median primary productivity (gCm·2 yr⁻¹) | All data | 26778 | 0.01 | 64  | 0.54 | 0.26 | 1.2 | 1.27 | 17 | 0.90 | n.a. |
| CD1   | 8536 | 0.01 | 4.5 | 0.19 | 0.15 | 0.18 | 0.26 | 8.6 | 0.73 | / |
| CD2   | 12831 | 0.046 | 12  | 0.44 | 0.29 | 0.49 | 0.66 | 5.9 | 0.92 | / |
| CD3   | 1569 | 0.047 | 31  | 0.93 | 0.42 | 2.1 | 2.3 | 7.7 | 1.1 | / |
| CD4   | 3842 | 0.085 | 64  | 1.5  | 0.89 | 2.3 | 2.7 | 11 | 0.39 | / |

| Root mean squared variability in log(chl-a concentration) | All data | 26778 | 0.01 | 64  | 0.54 | 0.26 | 1.2 | 1.27 | 17 | 0.90 | n.a. |
| CD1   | 8536 | 0.01 | 4.5 | 0.19 | 0.15 | 0.18 | 0.26 | 8.6 | 0.73 | / |
| CD2   | 12831 | 0.046 | 12  | 0.44 | 0.29 | 0.49 | 0.66 | 5.9 | 0.92 | / |
| CD3   | 1569 | 0.047 | 31  | 0.93 | 0.42 | 2.1 | 2.3 | 7.7 | 1.1 | / |
| CD4   | 3842 | 0.085 | 64  | 1.5  | 0.89 | 2.3 | 2.7 | 11 | 0.39 | / |

| Oxygen penetration depth (cm) | All data | 26778 | 0.01 | 64  | 0.54 | 0.26 | 1.2 | 1.27 | 17 | 0.90 | n.a. |
| CD1   | 8536 | 0.01 | 4.5 | 0.19 | 0.15 | 0.18 | 0.26 | 8.6 | 0.73 | / |
| CD2   | 12831 | 0.046 | 12  | 0.44 | 0.29 | 0.49 | 0.66 | 5.9 | 0.92 | / |
| CD3   | 1569 | 0.047 | 31  | 0.93 | 0.42 | 2.1 | 2.3 | 7.7 | 1.1 | / |
| CD4   | 3842 | 0.085 | 64  | 1.5  | 0.89 | 2.3 | 2.7 | 11 | 0.39 | / |

| Organic carbon fluxes (gCm·2 yr⁻¹) | All data | 26778 | 0.01 | 64  | 0.54 | 0.26 | 1.2 | 1.27 | 17 | 0.90 | n.a. |
| CD1   | 8536 | 0.01 | 4.5 | 0.19 | 0.15 | 0.18 | 0.26 | 8.6 | 0.73 | / |
| CD2   | 12831 | 0.046 | 12  | 0.44 | 0.29 | 0.49 | 0.66 | 5.9 | 0.92 | / |
| CD3   | 1569 | 0.047 | 31  | 0.93 | 0.42 | 2.1 | 2.3 | 7.7 | 1.1 | / |
| CD4   | 3842 | 0.085 | 64  | 1.5  | 0.89 | 2.3 | 2.7 | 11 | 0.39 | / |

| Depth (m) | All data | 26778 | 0.01 | 64  | 0.54 | 0.26 | 1.2 | 1.27 | 17 | 0.90 | n.a. |
| CD1   | 8536 | 0.01 | 4.5 | 0.19 | 0.15 | 0.18 | 0.26 | 8.6 | 0.73 | / |
| CD2   | 12831 | 0.046 | 12  | 0.44 | 0.29 | 0.49 | 0.66 | 5.9 | 0.92 | / |
| CD3   | 1569 | 0.047 | 31  | 0.93 | 0.42 | 2.1 | 2.3 | 7.7 | 1.1 | / |
| CD4   | 3842 | 0.085 | 64  | 1.5  | 0.89 | 2.3 | 2.7 | 11 | 0.39 | / |

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5.4.3.2 Sediment provinces (SED groups)

Characteristics of the sediment groups are given in Tab. 5-3. SED1, SED2, SED3 and SED4 contain stations which were located in regions of reported enhanced diatom sedimentation. According to Crosta et al. (1997), Zielinski & Gersonde (1997), Armand et al. (2005) and Abelmam et al. (2006), the surface sediments around the Antarctic Peninsula, the Scotia Sea and the region around South Georgia and the South Sandwich Islands are abundant in Chaetoceros spp. resting spores (accounting for 20 % of identified diatom frustules around South Georgia and the South Sandwich Islands, up to 100 % at the Antarctic Peninsula). The SED1 group mirrors the distribution of this Chaetoceros province. Diatoms of the genus Chaetoceros are normally weakly silicified and their frustules poorly preserved in sediments (e.g. Zielinski & Gersonde, 1997). The domain of SED2 is characterised by a content of >40 % Fragilariopsis kerguelensis (F. kerg.) frustules. The distribution of this more heavily silicified species corresponds with the distribution of the silica belt in the open ocean of the region of the SO considered here (Jousé et al., 1962; DeFelice & Wise, 1981; Zielinski & Gersonde, 1997; Crosta et al., 1997; Mohan et al., 2006). SED3 lies within the east Antarctic shelf region and the continental slope with water depths of up to 2000 m. This province is characterized by patchy and inhomogeneous sedimentation (Schlüter, 1991) with varying physical and biological properties. The coastal ecosystem is shaped by local, regional, seasonal and inter-annual ice-conditions including coastal polynyas as well as area-specific topography and hydrography. All stations in the SO Atlantic Sector which could not be assigned to one of the other three groups were assigned to SED4. These locations are generally characterized by lower sedimentation of siliceous material.
Tab. 5-3: Characteristics of the five sediment (SED) group systems. SED1 = *Fragilariopsis kerguelensis* province; SED2 = *Chaetoceros* spp. province; SED3 = East Antarctic shelf and continental slope \((z < 2000 \text{ m})\); SED4 = Amundsen and Bellingshausen Seas, SED5 = ungrouped SO, SED6 = N of 40°S (Atlantic Ocean)

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>Min</th>
<th>Max</th>
<th>Median Chlorophyll-a concentration (μg l⁻¹)</th>
<th>Median Phytoplankton Primary Productivity ((\text{gCm}^{-2} \text{yr}^{-1}))</th>
<th>Root mean squared variability in log (summer chl-a concentration)</th>
<th>Oxygen penetration depth (cm)</th>
<th>Organic carbon fluxes ((\text{gCm}^{-2} \text{yr}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SED 1</td>
<td>4255</td>
<td>0.03</td>
<td>1.8</td>
<td>0.23</td>
<td>0.20</td>
<td>0.15</td>
<td>0.28</td>
<td>3.6</td>
</tr>
<tr>
<td>SED 2</td>
<td>2457</td>
<td>0.051</td>
<td>31</td>
<td>0.44</td>
<td>0.29</td>
<td>0.87</td>
<td>0.98</td>
<td>21</td>
</tr>
<tr>
<td>SED 3</td>
<td>774</td>
<td>0.062</td>
<td>44</td>
<td>1.3</td>
<td>0.53</td>
<td>2.5</td>
<td>2.8</td>
<td>8.6</td>
</tr>
<tr>
<td>SED 4</td>
<td>1591</td>
<td>0.047</td>
<td>64</td>
<td>0.96</td>
<td>0.21</td>
<td>4.0</td>
<td>4.1</td>
<td>12</td>
</tr>
<tr>
<td>SED 5</td>
<td>1772</td>
<td>0.032</td>
<td>25</td>
<td>0.75</td>
<td>0.28</td>
<td>1.7</td>
<td>1.9</td>
<td>7.3</td>
</tr>
<tr>
<td>SED 6</td>
<td>17136</td>
<td>0.01</td>
<td>28</td>
<td>0.56</td>
<td>0.28</td>
<td>0.98</td>
<td>1.1</td>
<td>10</td>
</tr>
</tbody>
</table>

The SED5 group consists of sites in the Amundsen and Bellingshausen Seas which, according to Burkle and Cirilli (1987), are situated outside the silica belt. Owing to insufficient species-specific sediment data, these locations could not be assigned to any of the other provinces. Stations north of 40°S were also assigned to a separate group,
SED6, owing to paucity of information across the Atlantic. Figure 5-5 illustrates the CD and SED group locations.

In respect of the surface parameters, the SED groups are largely similar, with the exception of SED1 which has distinctive chl-a, PP and rms chl-a values. Distributions of the benthic parameters OPD and benthic $C_{org}$ flux, and of water depth, were likewise similar among all groups, with the exception of SED2, for which OPD was always shallower than 60 cm.

5.4.4 Benthic carbon export ratio (BER)

Regressions of net primary production against carbon remineralization rate were calculated, yielding the export ratio at the sea floor. Since the term 'export ratio' describes the proportion of surface primary production exported out of the surface mixed layer, we apply the term 'benthic export ratio': the difference between ER and BER at a given site represents the fraction of carbon which is remineralised in the meso-pelagic zone, so that BER represents a lower limit on carbon export ratio. BER was calculated for the entire data set and separately for the CD and SED groups.

Systematically overestimated PP would result in a lower BER: For example, if Eppley primary production is closer to the truth than VGPM PP, then the export ratios calculated here are too high in the mid-latitudes (Fig. 5-4, red points). Since Eppley and VGPM agree well in Southern Ocean, BER values presented here for the SO can be taken as a best estimate for this method and dataset. Further research into the accuracy of the various PP models is still urgently required.

As an indication of long-term benthic $C_{org}$ flux (Hartnett et al., 1998), median chlorophyll a was regressed against oxygen penetration depth. Figure 5-6 illustrates these regressions. A priori groupings were not generally significantly different in either $C_{org}$ flux/PP or OPD/chl-a space (MANOVA, $\alpha = 0.05$). Table 5-4 lists significant correlations.
The relationships between chl-a and OPD for CD groups (Fig. 5-6a) emphasize the use of chl-a characteristics in the definition of the groups: each group occupies a narrow sector of the x-axis, and it is found that OPD varies considerably regardless of the group, i.e., regardless of the typical duration and strength of phytoplankton blooms. The SED groups each include stations with a wide range of chl-a (see also Table 5-3), and are correspondingly more scattered in the chl:OPD space (Fig. 5-6b). Of note in the chl-a :OPD regression curves is that, while all statistically significant regressions showed the same trend, the slopes and y-intercepts differed by a factor of three and ~10, respectively.
Tab. 5-4: Significant correlations between surface chlorophyll (productivity) and benthic oxygen penetration depth (carbon flux).

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>a₁</th>
<th>a₂</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD2</td>
<td>60</td>
<td>-1.8593</td>
<td>±0.6219</td>
<td>0.2119 ±0.8098</td>
</tr>
<tr>
<td>SED4</td>
<td>11</td>
<td>-1.1917</td>
<td>±0.5993</td>
<td>1.8693 ±0.8377</td>
</tr>
<tr>
<td>SED6</td>
<td>30</td>
<td>-0.7865</td>
<td>±0.1327</td>
<td>0.3366 ±0.1896</td>
</tr>
<tr>
<td>All data</td>
<td>163</td>
<td>-0.5488 (±0.1586)</td>
<td>2.2033 (±0.2150)</td>
<td>0.0789</td>
</tr>
<tr>
<td>AP1</td>
<td>22</td>
<td>-1.1893</td>
<td>±0.1043</td>
<td>4.1145 ±0.1092</td>
</tr>
<tr>
<td>AP2</td>
<td>139</td>
<td>-1.0371 (±0.1586)</td>
<td>1.2476 (±0.2221)</td>
<td>0.5603</td>
</tr>
</tbody>
</table>

Ln(OPD) = a₁ ln(chl) + a₂

<table>
<thead>
<tr>
<th>Group</th>
<th>N</th>
<th>a₁</th>
<th>a₂</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD1</td>
<td>61</td>
<td>0.1436</td>
<td>±0.0139</td>
<td>/</td>
</tr>
<tr>
<td>CD2</td>
<td>87</td>
<td>0.1862</td>
<td>±0.0154</td>
<td>/</td>
</tr>
<tr>
<td>CD4</td>
<td>24</td>
<td>0.3185</td>
<td>±0.0107</td>
<td>/</td>
</tr>
<tr>
<td>SED6</td>
<td>102</td>
<td>0.2373 (±0.0119)</td>
<td>/</td>
<td>0.4536</td>
</tr>
<tr>
<td>All data</td>
<td>185</td>
<td>0.2009 (±0.0104)</td>
<td>/</td>
<td>0.1998</td>
</tr>
<tr>
<td>AP3</td>
<td>48</td>
<td>0.2576</td>
<td>±0.0189</td>
<td>/</td>
</tr>
<tr>
<td>AP4</td>
<td>137</td>
<td>0.1844 (±0.0123)</td>
<td>/</td>
<td>0.2192</td>
</tr>
</tbody>
</table>

Since the regression coefficient for ‘All Data’ is rather low (although significant), it remains likely that an alternative grouping system may provide clearer distinction between stations with different surface: benthic couplings (see section 3.4).

In contrast, the scatter between PP and benthic $C_{org}$ flux was much better constrained, and very similar slopes were found for all statistically significant regression curves (Fig. 5-6c, d). Variability indicated by the errors in fit parameters and by the correlation between predicted and measured values (Table 5-4) represents the effects of non-conservative processes, e.g. lateral advection by bottom currents, as well as variability in the efficiency of remineralisation.

5.4.5 A posteriori groups

Although none of the a priori groupings were significantly different in the 2-dimensional $C_{org}$ flux/PP or OPD/chl-a spaces, distinctive groupings in the scatter between each of these parameter pairs could be observed by eye (Fig. 5-7). Based on this observation, two new, a posteriori groupings were formed by choosing exceptionally high OPD and $C_{org}$ flux values across the range of median chlorophyll-a and PP. These were denoted...
AP 1, 2 (chl-a/OPD space) and AP 3, 4 (PP/C$_{org}$ flux) respectively, and are illustrated in figure 5-7.

**Figure 5-7:** As fig. 5-6 but coloured according to a posteriori groupings: a) Groups AP1 and AP2 derived from the chl-a:OPD scatter, with ‘+’ for AP 1, open diamonds for AP 2 and the stations north of 30° S shown as filled diamonds; b) Groups AP3 and AP4 derived from PP:C$_{org}$ flux, with blue triangles representing AP3 and pink triangles AP4, solid black lines representing fit curves and dashed lines indicating 10%, 3%, 1%, 0.5% and 0.2% benthic carbon export ratio (ER) curves; c) same as b) but using linear axes for comparison with e.g. Wenzhoefer & Glud, 2002.

Figure 5-8 shows the locations of the new groupings. Particularly high values of OPD / median chl-a (Group AP1) were located on the continental shelf and slope of Antarctica as well as in the Weddell Sea. However, in each of these locations, AP1 and AP2 were mixed together, suggesting either: a) patchy distribution of ‘deeply oxygenated’ sediments or b) OPD at the nearby AP2 stations is actually affected by sporadic C$_{org}$ flux, reducing the oxygenated sediment layer, so that OPD does not mirror the long-term situation here.
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Figure 5-8: Locations of *a posteriori* groups based on a) chl-a : OPD (red ‘+’ denotes AP 1, green diamonds denote AP 2) and b) PP : $C_{org}$ flux (blue = AP 3, ~2% export ratio, magenta = AP 4, ~0.7% export ratio)

Considering the high values of OPD in both AP1 and AP2 along the shelf (see Sachs et al., submitted, 2007), the latter explanation is unlikely. Patchy distributions, on the other hand, could be explained by bottom currents (Gutt et al., 1998). In the Weddell Sea, Ito et al. (2005) calculated net upward velocities at the AP1 locations, which indicates a possible physical explanation for low deposition in this area. Weddell Sea sediment traps show extremely low but highly variable annual fluxes (Fischer et al., 1988). Benthic investigations from Schlüter et al. (1998) and Geibert et al. (2005) indicate very low benthic Si fluxes in this area, while Usbeck et al. (2002) suggested the prevalence of shallow remineralization in the central Weddell Sea. Each of these proposed processes would result in low $C_{org}$ flux, corresponding to deep OPD, despite the regular occurrence of phytoplankton blooms in spring and summer.

A *posteriori* groupings for $C_{org}$ flux vs. PP fell into a clear band along the opal belt, extending westwards along the Antarctic Peninsula and into the Amundsen and Bellingshausen Seas (fig. 5-8b). Again, the distribution is patchy, similar to the Si map produced by Schlüter et al. (1998) or Seiter et al. (2004). Scattered high BER stations (AP3) were also found in the northern North Atlantic, including the Greenland MIZ, and
close to the upwelling area off Namibia and along the NW European Continental Margin. However, the bulk of the known upwelling areas, e.g. off NW Africa, fell into group AP4 (lower BER).

5.4.6 Relationships between OPD, $C_{org}$ flux, depth and latitude

Many previous studies have investigated the impact of depth on $C_{org}$ export efficiency (e.g. Suess, 1980; Pace et al., 1987; Jahnke, 1996; Antia et al., 2001). For comparison between the SO and other regions studied, and before extending the relationship between $C_{org}$ flux and PP to include depth in a multiple regression, the variability of OPD and benthic $C_{org}$ flux with depth was investigated. Figures 5-9 a) and b) illustrate these relationships.

![Figure 5-9: Variability of a) OPD, b) benthic $C_{org}$ flux with depth, for stations in the SO (open circles) and in the Atlantic (north of 40°S, filled circles) and c) variability of $C_{org}$ flux with latitude.](image)
The relationship between depth and OPD was weak but statistically significant, with a tendency for weaker effects of depth on OPD at stations north of 30° S. Considerable scatter in this relationship in the SO suggests either diverse or highly variable export regimes (large-scale variability), or patchiness in the macrobenthic communities which both depend upon and influence the benthic O2 supply (Jahnke, 2001; Wenzhöfer & Glud, 2002) (small-scale variability), or both. Such patchiness has been observed in shelf and deep-sea environments (Gutt et al., 1998; Brandt et al., 2007a+b). Gutt et al. (1998) also demonstrated a weak pelagic-benthic coupling between primary production and the distribution of macrobenthic communities in the region of the Antarctic shelf and upper slope.

In contrast, the scatter in the short-term benthic Corg flux parameter with depth was similar for the SO and stations north of 30° S. The range of values of the slope of this relationship in the literature, particularly from trap studies, encompasses the values found here. Comparable curves have been found in pelagic trap studies (Francois et al., 2002; Lutz et al., 2002) as well as at the sediment / water interface (Wenzhöfer & Glud, 2002).

In agreement with Behrenfeld and Falkowski (1997) and Christensen (2000) and in contrast to the results of Jahnke (1996) and Lampitt & Antia (1997), strong latitudinal gradients were observed in Corg flux (Fig. 5-9c). Three latitudinal bands of high Corg flux are observed at 70° S, 20° S and 40° N, with an indication – but too few data – of high values in the northern North Atlantic. These locations correspond to upwelling and high latitudes, where production is high (see figure 5-2).
The relationship between ER and depth (Fig. 5-10, a) indicates that the strong slope observed in trap studies (e.g. Suess 1980; Pace et al., 1987; Lampit & Antia, 1997; Armstrong et al., 2002; Francois et al., 2002) has vanished for stations at all latitudes when ER is calculated using benthic fluxes, with the exception of the high ER opal belt stations (AP3, see fig. 5-8).

Figure 5-10c illustrates the variability in BER with latitude, showing a clear tendency toward higher BER at polar latitudes. This contradicts previous studies including Francois et al., 2002, Jahnke, 1996, Lampitt & Antia, 1997 and Christensen, 2000, and
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is in agreement with Buesseller, 1998. These conflicting results most likely reflect the sparsity of data available at high latitudes: The dataset compiled by Sachs et al., submitted 2007 is the first study with substantial coverage of the SO. However, it is also possible that the efficiency of the meso-pelagic community varies with latitude, perhaps affected by temperature, so that upper water column sediment trap studies to date have correctly observed lower ER at high latitudes, which subsequently evolves into higher BER on account of more efficient scavenging of the available carbon at lower compared to higher latitudes.

Having found significant, variable, effects of depth on benthic $C_{org}$ flux, a 3-D regression was used to relate these parameters to surface PP. Following Antia et al. (2001), $C_{org}$ flux was regressed against median primary production and water depth for all 185 stations using Eq. 3. Additional regressions were calculated for the a posteriori subgroups AP 3 and AP 4, and also using alternative equations from the literature (Eq. 4 and 5). Table 5-5 presents the regression coefficients and statistics for each of these regressions. Figure 5-11 shows the 3-dimensional fit corresponding to Eq. 3 applied to groups AP 3 and 4. Proceeding on the assumption that benthic remineralization represents the lower limit on carbon flux to the sea floor, the AP 4 algorithm was selected to calculate conservative estimates of carbon rain rate in the Atlantic, described in the next section.
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Figure 5-11: Multiple regression of \( C_{\text{org}} \) flux against median VGPM primary production and water column depth for a) AP 4 and b) AP 3. In each case, the coloured mesh represents the functions defined in Table 5-5 using the equation form of Antia et al. (2001).

| Tab. 5-5: Regression coefficients obtained by applying equation forms from the literature to the SO and Atlantic \( C_{\text{org}} \) flux and median VGPM or Eppley primary production dataset. |
|---|---|---|---|---|---|---|---|---|
| Group | \( A_1 \) | \( a_2 \) | \( a_3 \) | \( r^2 \) | \( N \) | \( a_1 \) | \( a_2 \) | \( a_3 \) | \( r^2 \) | \( N \) |
| Antia et al., 2001: \( \ln C_{\text{org}} \) flux = \( a_1 \cdot \ln PP + a_2 \cdot \ln z + a_3 \), \( [a_1 = 1.77, a_2 = -0.68, a_3 = -2.3, r^2 = 0.53, N = 24] \) |
| All data | 0.4232 | -0.4759 | 2.2657 | 0.5459 | 185 | 0.3925 | -0.5301 | 2.9321 | 0.5171 | 185 |
| AP 3 | 0.6495 | -0.4704 | 1.6219 | 0.7927 | 48 | 0.7677 | -0.4375 | 0.8796 | 0.7515 | 48 |
| AP 4 | 0.8331 | -0.2330 | -2.3251 | 0.7154 | 137 | 0.7822 | -0.3501 | -0.9662 | 0.6609 | 137 |
| Schlüter et al., 2000: \( \ln (C_{\text{org}} \text{flux}) = a_1 \cdot \ln (PP) + a_2 \cdot \ln (z) \), \( [a_1 = 1.873, a_2 = -1.172, PP > 0, z > 500 \text{ m}, r = 0.92] \) |
| All data | 0.5756 | -0.2995 | / | 0.5217 | 185 | 0.6036 | -0.3078 | / | 0.4743 | 185 |
| AP 3 | 0.8554 | -0.3800 | / | 0.7489 | 48 | 0.7885 | -0.3524 | / | 0.7801 | 48 |
| AP 4 | 0.6613 | -0.3964 | / | 0.6978 | 137 | 0.7056 | -0.4156 | / | 0.6575 | 137 |
| Suess, 1980: \( C_{\text{org}} \text{flux} = PP / (a_1 \cdot z + a_2) \), \( [a_1 = 0.0238, a_2 = 0.212, z \geq 50 \text{ m}, r^2 = 0.79, N = 33] \) |
| All data | 0.0107 | 88.6107 | / | 0.4635 | 185 | 0.0146 | 57.3771 | / | 0.2509 | 185 |
| AP 3 | 0.0069 | 27.2503 | / | 0.6730 | 48 | 0.0059 | 18.5504 | / | 0.5273 | 48 |
| AP 4 | 0.0074 | 123.4166 | / | 0.7236 | 137 | 0.0147 | 79.6460 | / | 0.3965 | 137 |
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Statistically significant regression coefficients were found for each of the equations when applied to all stations as well as to the \textit{a posteriori} groups AP 3 and AP 4. Cluster analysis and MANOVA testing ($\alpha = 0.05$) was used to establish whether the \textit{a priori} groups were distinctive in the 3-dimensional C$_{org}$ flux / z / PP space. Only CD 4 (chlorophyll distribution groups; high chl / high rms) and SED 8 (sediment groups; stations north of 30°S) were significantly different from other groups. In the absence of an \textit{a priori} grouping system by which multiple groups could be distinguished, the \textit{a posteriori} groups, which were significantly different from one another according to MANOVA testing, were retained for further analysis.

The equation form used by Antia et al., 2001 was chosen on account of to the similarity of datasets and consideration of the trends in C$_{org}$ flux, z and PP: The equation of Suess (1980) includes a term [C$_{org}$ flux · z] (re-arranging the equation to calculate PP from z and C$_{org}$ flux). This was deemed less appropriate than an expression based on exponents of z and PP, as in Antia et al. (2001) and Schlüter et al. (2000), since this allows the inverse trend between C$_{org}$flux and depth to be expressed in a single term. The difference between these two latter models is the inclusion of a constant logarithmic term by Antia et al. (2001) which, by allowing greater freedom in the fit, has the advantage of highlighting inappropriate data fitting. The constant term represents the loss or gain of carbon in the water column which is not a function of water depth or net primary production at the surface. Values of this constant term greater than 1 indicate that the fitted curve is readjusted upwards after exponential ‘decay’ in the carbon flux: This resembles a source term, which could be caused by introduction of carbon into the water column by lateral advection (an unlikely scenario considering the geographical scatter in the AP3 and 4 groupings), or it can be interpreted as an under-estimation of NPP by the satellite data. The latter explanation is consistent with reports of underestimation of chlorophyll-a in the SO, possibly by errors in the atmospheric
correction at high latitudes (n.b. while it is often mooted that underestimation of chlorophyll-a in the SO is caused by the prevalence of deep chlorophyll maxima, this reasoning is rejected on the grounds that a) other oligotrophic regions at lower latitudes typified by DCMs were included in development of the satellite algorithms and b) this does not account for systematic underestimation of chlorophyll in the Arctic, where DCMs are less usual). The de facto exclusion of springtime data in the MIZ which arises from using the monthly PP product, for which more robust masking for variable cloud and ice cover is employed than the daily or weekly chlorophyll products, may also be important: Consultation of the weekly chlorophyll data showed that the median values measured during the summertime represent consistently lower concentrations than were attained during the spring bloom at AP3 stations (data not shown). This implies that the satellite median PP data are not so much erroneous as not representative. Peak values are of course also smoothed out by monthly compositing, but this affects the data at all locations, and will produce a regional bias only where the duration of blooms in one region is always significantly shorter than at other locations. Values of the constant term in Equation 3 less than 1 resemble a linear sink term. This could be interpreted as the proportion of organic carbon which is remineralised most rapidly, i.e. regardless of the length of time over which the material is exposed to oxygen. In the AP 4 data fit, the constant term was close to that obtained by Antia et al. (2001) with $\exp\{-2.3\} = 0.1$, i.e. a sink term. In contrast, the constant term for AP 3 was $\exp\{1.6\} = 5$ – a source term, while for the fit to all data a value of 9.6 was obtained. It is likely that this massive source term for all data resulted from unsuitable fitting of a single expression to a dataset which clearly falls into more than one group. However, the precise meaning of the apparent source term for AP 3 remains unclear, especially given the similarity of $a_1$ and $a_2$ for AP 3 and AP 4. This could indicate a true source term, such as sea-floor winnowing, or simply reflect lack of data.
Another factor which must be considered here because of the use of ‘snapshot’ \( C_{\text{org}} \) flux measurements is the possibility that the AP3 group represents those stations at which \( C_{\text{org}} \) flux measurements were affected by recent sedimentation events. Re-examining Figure 5-3, where the AP3 stations are shown as filled blue circles, indicates that there is a slight tendency toward higher \( C_{\text{org}} \) flux : OPD ratios within the AP3 group. However, the range of ratios remains broad for both AP3 and AP4, and ANOVA analysis indicated that the two groups were not distinctive within the \( C_{\text{org}} \) flux : OPD space (alpha = 0.05).

The implications of the data fits for AP3 and AP4 are intriguing and can only be resolved by long-term *in situ* measurement programs. Mathematical conundrums aside, the fact that the AP3 grouping, selected purely by means of the export ratio fell mostly in SO waters, supports the notion that mass export of fresh, giant (Kemp et al., 2006, Smetacek et al., 2002) or heavily silicified (Smetacek, 2004) diatoms, result in unusually high export efficiency. Returning to the arguments A to D presented in the introduction; AP3 represents stations at which either a) more labile carbon is exported and/or b) the labile carbon is better protected than at other locations and/or c) the exported carbon is exposed to remineralisation for less time and/or d) remineralisation is less efficient here. These possibilities are discussed below:

a) **Disproportionately high concentrations of carbon are exported:**

Higher export production can be discarded immediately by consulting Figure 5-2: AP3 does include regions of relatively high surface biomass close to the Antarctic Peninsula, but also areas of very low biomass further to the west – these concentrations are not the highest in the SO and are an order of magnitude lower than is found on shelf regions in the northern hemisphere: high BER in AP3 is not caused simply by higher input of particulate organic carbon at the water surface.
b) **Exported carbon is well protected against remineralisation:**

Dissolution of the protective silicate diatom frustule has been found to be slower when phytoplankton cells sink out before dying (Moriceau et al., 2007), and inorganic coatings may also slow cell degradation (Burdige, 2007). It is unlikely that inorganic matrices are produced exclusively in AP 3 and not, for example, at more southerly stations with similar environmental characteristics. Sedimentation of fresh phytoplankton has, on the other hand, been reported in the locality of the opal belt (Sachs et al., submitted 2006; Riaux-Gobin et al., 1997). Such mass precipitation events may be caused by matting of spined species such as Chaetoceros and Corethron or by loss of buoyancy, for example under nutrient stress. The former requires sufficiently high chlorophyll concentrations that cells are highly likely to lock together; this is not consistent with the satellite chlorophyll record for the eastern end of the opal belt, and even if satellite estimates are too low, Holm-Hansen et al. (2005) reported that chlorophyll in DCMs of the SO has not yet been found to exceed 0.7 mgm$^{-3}$. Slow but steady sinking out could be explained by deep mixed layer depths which, together with low iron availability, could maintain growth at very slow rates (see also Figure 5-2b), resulting in phytoplankton communities dominated by heavier, more strongly silicified cells (e.g. *F. kergeulensis*, used in this study to denote province SED 2, see section 3.3.2) and in a steady grazing pressure, leading to the dominance of larger cells (Smith & Lancelot, 2004; Smetacek et al., 2002, 2004). Loss of buoyancy control could affect a higher than usual proportion of cells as they are subjected to low light levels in the deep mixed layer. Since the AP 3 group comprises regions of low, steady chlorophyll concentrations as well as high, variable concentrations (Figure 5-2a and b) it can not be ruled out that both slow and rapid sinking of large or heavy diatoms before cell death causes the higher BER values.
c) Exported carbon is exposed to remineralisation over disproportionately short time scales:
This explanation can be discarded since the range of depths over which cells sink out in AP 3 is not distinct from that in AP 4, and there is neither evidence nor reason to suspect that sinking velocities are exceptionally high in the opal belt.

d) Remineralisation is inefficient
Low temperatures slow down bacterial activity (e.g. Matsumoto et al., 2007). However, the range of water temperatures found in the AP 3 region is similar to that found across the SO, so that this effect can be ruled out as being exclusive to the AP 3 region. High turbulence, caused by strong wind mixing at the surface or by strong currents in the mesopelagic, may make grazing by chemotaxis inefficient (Kiorboe & Jackson, 2001; Visser & Jackson, 2004). However, neither the wind nor the current regime along AP 3 is unique – strong easterly winds dominate most of the SO and the currents they produce are found in several concentric rings (e.g. Orsi, 1995; Sokolov & Rintoul, 2007), not just along AP 3.
It is possible that high BER in AP 3 results from combinations of processes categorised as b) and d) above. However, suggestions in the literature that winnowing of benthic deposits by bottom currents (Geibert et al., 2005, Seiter et al., 2005) may also explain the grouping found here.
5.4.7 Calculation of $C_{org}$ flux for the Southern (-80° to 120° E, < 30°S) and Atlantic Oceans

Figure 5-12 shows the distribution of benthic $C_{org}$ flux across the Atlantic Ocean calculated using the AP 4/Eq.3 algorithm. These results are comparable to those of Wenzhöfer & Glud (2002) in the temperate Atlantic Ocean.

![Figure 5-12: Spatial distribution of benthic $C_{org}$ flux](image)

This calculation was repeated using the Eq. 3 / AP 3 algorithm along the AP 3 domain (Figure 5-13). The mask for AP 3 can be discerned in Figure 5-13 as a discontinuity in concentrations in a ring proceeding along and extending from the Antarctic Peninsula.
This mask was drawn to avoid the subtropical front but to include all the AP3 stations. However, the sub-tropical and sub-Antarctic fronts merge together, particularly toward the east, making the mask difficult to define. In the event that further research confirms the high BER along the opal belt, 'operational' definition of the AP 3 mask would require smooth gradients at the boundaries between AP 3 and 4. This is beyond the scope of the current study. Since the region described here is restricted to the coverage of stations grouped within AP3, whereas the opal belt extends much further both to the east and the west (e.g. Seiter et al., 2004), it is assumed that this still represents a conservative estimate of the importance of the opal belt.

Figure 5-13: Spatial distribution of $C_{\text{org}}$ flux calculated using Eq. 3/AP 3 for the opal belt, and Eq. 3/AP 4 everywhere else (see table 5-5).
Integrating by area, it was found that the flux of carbon to the sea floor in the whole SO (> 45°S) is 0.055 PgCyr⁻¹ for water depths greater than 800 m when Eq. 3/AP 4 was used; slightly less than that for the North Atlantic or South Atlantic. Table 5-6 lists the integrated benthic C₉org flux estimates found in this study by region, and provides several values from other studies for comparison.

Application of the AP3 / Eq. 3 algorithm to the SO opal belt region, yielded an increase in SO benthic C₉orgflux of 0.0087 PgCyr⁻¹. This corresponds to 15% of the integrated carbon flux in the SO calculated using only AP 4/ Eq. 3, and to ~8 % of the Atlantic C₉org flux estimate (see Table 5-6).

Tab. 5-6: Areally integrated C₉org flux values in this study and from the literature. a) Schlitzer (2002), Schlitzer et al. (2003), b) Muller-Karger et al. (2005), c) Seiter et al. (2005), d) Schlüter et al. (2000), e) Christensen (2000), f) Wenzhöfer & Glud (2002)

*Since the Eq.3/AP4 algorithm was developed using only SO and Atlantic data, these values are included for comparison only and should be viewed with caution.

<table>
<thead>
<tr>
<th>Region</th>
<th>Area (mil. km²)</th>
<th>Median PP (PgCyr⁻¹)</th>
<th>Corg flux (PgCyr⁻¹)</th>
<th>%PP</th>
<th>Flux / Area (gCm⁻²yr⁻¹)</th>
<th>Corg flux (gCyr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Ocean (south of 45°S)</td>
<td>53.5</td>
<td>9.25</td>
<td>0.055</td>
<td>0.60</td>
<td>1.03</td>
<td>3.0⁹</td>
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<td>S. Ocean (south of 30°S)</td>
<td>99.4</td>
<td>27.7</td>
<td>0.15</td>
<td>0.55</td>
<td>1.52</td>
<td></td>
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<tr>
<td>S. Ocean (south of 45°S, AP 3&amp;4)</td>
<td>53.5</td>
<td>9.25</td>
<td>0.064</td>
<td>0.69</td>
<td>1.20</td>
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<td>South Atlantic</td>
<td>28.9</td>
<td>12.1</td>
<td>0.061</td>
<td>0.51</td>
<td>2.12</td>
<td>0.062</td>
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<tr>
<td>North Atlantic</td>
<td>32.7</td>
<td>12.6</td>
<td>0.065</td>
<td>0.52</td>
<td>2.00</td>
<td>0.095⁹</td>
</tr>
<tr>
<td>N. Atlantic Arctic</td>
<td>2.33</td>
<td>1.06</td>
<td>0.006</td>
<td>0.60</td>
<td>2.70</td>
<td>0.204⁹, 0.134¹</td>
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<td>Global ocean*</td>
<td>314.8</td>
<td>101.4</td>
<td>0.545</td>
<td>0.54</td>
<td>1.73</td>
<td>0.478</td>
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</tbody>
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Figure 5-14a illustrates the contribution of different water depths to the total sea-floor carbon flux expressed as a percentage of global $C_{\text{org}}$ flux calculated using Eq. 3 / AP 4. Depth intervals of 500 and 800 m were chosen to represent the permanent thermocline in shelf and open ocean waters, respectively, following Ostlund et al. (1987) and Muller-Karger et al. (2005). Subsequent 1000 m depth intervals were segregated to illustrate the importance of water depths. As suggested by Muller-Karger et al. (2005), the continental shelves (< 500 m water depth) contribute disproportionately to $C_{\text{org}}$ flux, as can be seen in figure 5-14b (area-normalised $C_{\text{org}}$ flux). In the deep ocean, regions of 4000 to 5000 m depth contributed most to carbon flux below 1000 m, while the area-normalised $C_{\text{org}}$ flux decreased gently with depth, as also found by Jahnke (1996) and Schlüter et al. (2000).

$\text{C}_{\text{org}}$ flux for the North Atlantic Arctic, North Atlantic, South Atlantic, Southern Ocean (all longitudes) and ‘rest of the world’, at different depth intervals, calculated using Eq. 3 / AP 4, as a percentage of global $C_{\text{org}}$ flux to all depths; b) $C_{\text{org}}$ flux in $\text{gCm}^{-2}\text{yr}^{-1}$ calculated by normalising the area-integrated values by the total area of each region.

Integrated benthic $C_{\text{org}}$ flux values calculated in this study were within the range published for various regions (table 5-6), with the notable exception of the value calculated by Schlitzer (2002) for the SO (south of 30°S). However, this discrepancy could have arisen because Schlitzer (2002) did not explicitly calculate carbon deposition.
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at the sea-floor, but rather remineralisation within the lower water masses, or because of the significant nitrification within the euphotic zone, rendering the f-ratio invalid.

While global application of the Eq.3/AP 4 algorithm enabled comparison with other studies using a range of methodologies, it is difficult to assess how well it performs in basins other than the SO and Atlantic: Seiter et al. 2005 concluded that Pacific sub and anoxic remineralization processes are more important outside of the Southern and Atlantic Oceans on account of the time since these waters were last ventilated. This would imply that our estimates considerably underestimated the benthic C$_{org}$ flux. In contrast, Cai & Reimers (1995) found similar remineralisation rates in the Pacific and Atlantic. In general, the global dataset, particularly of oxygen microprofiles, is still sparse.

5.4.8 Open questions

**Relationships between benthic C$_{org}$ flux and OPD**

One of the greatest weaknesses of this study is the scatter in the relationship between benthic C$_{org}$ flux and OPD (figure 5-3). In the absence of more temporal monitoring of C$_{org}$ flux variability at any given location, the use of the relationship between these two parameters remains the best option for determining whether C$_{org}$ flux measurements are contaminated by recent sedimentation events. Clearly, a tighter relationship, or better understanding of interactions between the upper millimetres and deeper layers of sediment, is desirable.

_Could more sophisticated definition of ecological provinces better capture the variability in BER?_

The study of Sokolov & Rintoul (2007) promises a routine method for establishing ecological province boundaries in the Southern Ocean. If this, or a similar, approach can be expanded to other regions, then determining the strength of coupling between...
surface carbon fixation and benthic rain rates will be limited only by the size of the
benthic dataset.

Does the mesopelagic community eliminate the surface ecological province footprint at
depth?
As pointed out by Cai & Reimers (1995), remineralisation of carbon at the sediment
interface depends not only on the degradability of particulate organic matter but also on
the benthic environment, i.e. parameter such as on oxygen concentration,
sedimentation rate and bioturbation rates. Since these conditions influence one another
over both short and geological time scales, the system is clearly highly evolved and
complex: this may mean it is susceptible to disturbance by sudden changes in input or
that it is highly adaptive, so that regional variability is mostly damped out within days of
$C_{org}$ reaching the sea floor.
Several elements of the mesopelagic community have been shown to adapt to $C_{org}$
export variability (e.g. Žarić et al., 2005; Richardson et al., 2006; Countway et al., 2007),
suggesting that the ecosystem across the breadth of the water column is able to
compensate for the mode and speed of particle export and make maximal use of
available $C_{org}$. Export models, while becoming increasingly sophisticated, still lack a
detailed parametrisation of mesopelagic variability (e.g. Gehlen et al., 2006; Stemmann
et al, 2004).
This dataset used here suffers very poor coverage in the mid-latitude gyres, reported to
have the lowest export ratio. Despite this, the values found here are lower than those
reported from sediment traps in the vicinity of the gyres. This implies that sufficient
remineralisation occurs between the lowest trap positions and the sea floor that, even in
the more productive zones of the current dataset, benthic remineralisation rates are
lower than in the mesopelagic of the oligotrophic gyres.
What is the inter-annual variability in benthic $C_{org}$ flux?
The results presented here represent the long-term (decadal) situation. While Gregg et al., 2005 found no significant trend in chl-a concentrations in the SO over the last ten years, Antia et al. (2001) reported a shift in biological pump efficiency caused by reduced opal content. On a global scale, the interannual variability in $C_{org}$ flux reported by Muller-Karger et al. (2005) far exceeded the inter-decadal trend derived by Gregg et al. (2005). Such trends can not be analysed using the current oxygen microelectrode dataset since fewer than 10 measurements concurrent with the SeaWIFS or CZCS flight periods have been recorded so far.

How efficient is the biological pump in the SO?
Similar to Schlitzer (2002) this study was not intended to be a stand-alone approach to quantifying the rate of biological pump efficiency since no indication of rain ratio can be gleaned from satellite data at present. The rain ratio has been found to be low in the SO (Seiter et al., 2004): their data show an inverse correlation between opal and calcite over much of the global ocean. In the SO and Arctic, CaCO$_3$ concentrations are conspicuously low, whereas opal appears high in the SO, low in the Arctic. This implies that the AP 3 stations in the SO are likely to have a reinforcing effect on the biological pump, while the same may not be true for the Arctic. The results presented here represent a lower limit on the carbon flux to the sea floor; the algorithms derived may be used in models which distinguish the soft- and hard-tissue pumps to quantify the effects of primary production on alkalinity as well as determining carbon export.
5.5 Conclusions

A large dataset of benthic oxygen microprofiles and satellite primary production data have been used to explore regional variability in the export of organic carbon to the seafloor in the Southern and Atlantic oceans. 

A priori determination of ecological provinces using satellite-derived chlorophyll concentrations or sediment characteristics did not capture regional differences in the benthic export ratio, whereas a posteriori groupings, defined using the BER, highlighted a band of high export along the Southern Ocean opal belt (BER ~ 2 % compared to 0.7 % in the rest of the Atlantic).

Benthic organic carbon flux was found to be elevated within three latitudinal bands – at 70°S, 20°S and 40°N, whereas high BER was clearly a feature of high latitudes. Spatially-integrated carbon export was calculated for the North and South Atlantic, northern North Atlantic, Southern Ocean and ‘rest of the world’, yielding comparable values to most values published based on quite different techniques, with the exception of the calculations of Schlitzer (2002) for the Southern Ocean south of 30°S which exceeded our estimates by a factor of ~5.

The implications of our findings affect estimates of present and past contributions to CO₂ draw-down in the Southern Ocean and possibly in other areas of the world ocean. There is evidence that during glacial periods export in the SO was significantly enhanced (Kumar et al., 1995; Anderson et al., 2002; Fennel et al., 2003; Abelmann et al., 2006). Our results for the modern SO could be used to reconstruct detailed palaeoproductivity scenarios such as that proposed by Abelmann et al., 2006.
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Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean


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5 Spatial variability of the transfer efficiency of primary produced carbon to the seafloor of the Atlantic Ocean
6 Synthesis and Outlook

This chapter summarises the main results of the previous chapters and describes additional co-operations with other scientific groups. Developed research programs are also introduced and an outline for further planned projects given.

In the framework of this cumulative thesis, evidence for an enhanced carbon export to the deep Southern Ocean was found. The collapse of an artificially induced plankton bloom as well as the breakdown of a large natural bloom at the Antarctic Polar Front was observed by satellite observations and the response of the subsequent carbon export to the deep-sea floor could be measured in situ at the water/sediment interface for the first time. It also could be shown for the first time that organic carbon reached the deep-sea floor after an iron fertilization experiment. During the same field campaign, reference measurements were carried out in an oligotrophic area characterised by much lower phytoplankton production at the surface. Proceeding from these results, existing benthic data from the Southern Ocean were evaluated and benthic fluxes were revised for numerous locations using a correction function established from the relation of in situ and ex situ flux determinations. This allowed comparison regional benthic fluxes with the diatom composition of surface sediments. Organic matter fluxes to the seafloor could be linked with diatom provinces and, in a further step with long-term satellite observations of surface ocean chlorophyll-concentrations. This allowed the determination of biogeochemical provinces at the seafloor in terms of benthic fluxes. One of the most prominent results was the high export efficiency of organic carbon which in the Southern Ocean silica belt, which is considerably enhanced in comparison to the mid and low latitude Atlantic. These benthic results could be used as ground truth data for further modelling studies. Up to now, little is known about the seasonality of deep-sea benthic fluxes. Only a few in situ measurements exist in the region of the Antarctic Circumpolar Current. It is important to gather more in situ data and long term measurements in the near future.

Apart from the key results shown above, vital co-operations with other research groups developed which led or will lead to several additional research papers and conference contributions (see appendix). One of the highlights to be mentioned was the targeted measurement of oxygen microprofiles at porpoise carcases in water depths of 2500 and
5400 m at the Arctic deep-sea long-term observation site “AWI Hausgarten”: These measurements, performed during the German-French cruise "Arctic Ocean 2005" with R/V "L'Atalante" by means of a small deep-sea microprofiler unit operated by a ROV (remotely operated vehicle), revealed that benthic communities are able to change the benthic milieu within days or a few weeks subsequent to the input of large food falls (see appendix). Due to time constraints, these findings will only be evaluated in the aftermath of this PhD thesis, under consideration of additional data obtained by collaborators in 2007.
7 Appendix

Other publications and conference contributions further associated with this thesis:

Peer-reviewed publications


Not peer-reviewed Publications


Invited talks


Talks


Posters


Publications of this series:

No. 1  Wefer, G., E. Suess and cruise participants  

No. 2  Hoffmann, G.  
Holozänsstratigraphie und Küstenlinienverlagerung an der andalusischen Mittelmeerküste. 173 pages, Bremen, 1988. (out of print)

No. 3  Wefer, G. and cruise participants  

No. 4  Wefer, G., G.F. Luize, T.J. Müller, O. Pfannkuche, W. Schenke, G. Siedler, W. Zenk  

No. 5  Fischer, G.  

No. 6  Berger, W.H. and G. Wefer  
Partikelfluß und Kohlenstoffkreislauf im Ozean.  

No. 7  Wefer, G. and cruise participants  

No. 8  Kölling, M.  

No. 9  Heinze, P.-M.  
Das Auftriebgeschehen vor Peru im Spätquartär. 204 pages, Bremen, 1990. (out of print)


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No. 12  Dahmke, A., H.D. Schulz, A. Kölling, F. Kracht, A. Lücke  

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No. 15  Kölling, A.  

No. 16  SFB 261 (ed.)  
Der Südatlantik im Spätquartär: Rekonstruktion von Stoffhaushalt und Stromsystemen.  

No. 17  Pätzold, J. and cruise participants  

No. 18  Wefer, G. and cruise participants  
No. 19 **Schulz, H.D. and cruise participants**

No. 20 **Berner, H.**

No. 21 **Schneider, R.**

No. 22 **Hebbeln, D.**

No. 23 **Lücke, A.**

No. 24 **Wefer, G. and cruise participants**

No. 25 **Schulz, H.D. and cruise participants**

No. 26 **Gingele, F.**

No. 27 **Bickert, T.**

No. 28 **Schmidt, H.**

No. 29 **Meinecke, G.**


No. 31 **Damm, E.**

No. 32 **Antia, E.E.**

No. 33 **Duinker, J. and G. Wefer (ed.)**

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No. 38 **Willems, H. (ed.)**
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Bachmann, M.  

Kemle-von Mücke, S.  

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