## Reviewer 1

We would like to thank the reviewer for taking the time to carefully read and comment on our manuscript. Below is a point-by-point response to the questions and comments raised.

The paper reports on lipid composition in five sediment traps placed in different sites of the Southern Ocean, characterized by different productivity: two of them (M6 and P2) were in HNLC waters, while three other sites (A3, M5 and P3) were located in naturally iron-fertilized areas characterized by higher productivity. Lipid composition markedly differed among these sites, with higher proportion of labile lipids in the naturally iron-fertilized waters. For one of the sediment traps (A3 located in the Kerguelen Plateau), quantitative data on the composition of settled material were available from a previous study. These data have been used to depict the seasonal trend in lipid composition as related to the biological components (diatom cells, resting spores and faecal pellets). Samples collected during the summer period were dominated by diatom resting spores, which transferred to depth a considerable amount of lipids, dominated by the labile The study is interesting since provides the link between qualitative composition of sediment traps and the composition in lipids, which are also used as biomarkers to infer the origin of sinking material.

R1 - Q/C - 1: I have the following comment: The comparison between trap content and lipids was done for the sediment trap A3, which was deployed at relatively shallow depth as compared to the other traps. It is mentioned that the labile lipids can be degraded/ remineralized with depth. Can the 'fingerprint' of lipids derived from diatom spores be preserved in the deeper layers? The other sediment traps placed in iron-enriched areas (P3 and M5) were much deeper; is it possible to state that the composition of lipids in these deep stations still reflects the contribution of diatom spores? Or of diatoms in general? The role of diatom spores in mediating a considerable carbon flux for the benthic organism has been demonstrated for the shallower areas: can it be extended to the deep stations in the productive areas as well? I would suggest the points listed above be addressed in the discussion.

R1 - R - 1: We would like to thank the reviewer for this comment. To clarify, we have available detailed diatom counts and lipid analyses for all of the sediment trap samples, including the deeper stations P3 and M5. In the current manuscript, we thus aim to compare the trap content with lipid composition for all the samples.

We know from our previous work that diatom-resting spores account for 60% of annual carbon export from at 300m from an iron-fertilized bloom on the Kerguelen plateau (Rembaubille et al. 2015). We have observed similar patterns in deep samples (>1500m) from the productive regime at South Georgia (P3), whereby 42% of annual carbon export could be attributed to resting spores (Rembauville et al. 2016). At the productive Crozet site (M5), *Eucampia antarctica* resting spores dominate flux in the bathypelagic and are strongly correlated with total POC flux (Salter et al. 2012). This is in stark contrast to the HNLC sites from these areas, which have very few resting spores with a negligible contribution to organic carbon flux. These findings, from different island systems, provide strong evidence that diatom flux, in particular resting spores of Chaetoceros and Eucampia, are the dominant vector of organic carbon flux to the bathypelagic (>1500m) ocean following iron fertilized blooms. In the present

manuscript we are also able to demonstrate that these resting spore-dominated systems not only transfer significant amounts or organic carbon to the deep ocean, but also mediate a bathypelagic flux of labile lipids in the form of mono- and polyunsaturated fatty acids. For example, consulting Table 2 and Figure 2 in the manuscript, it is clear that the relative abundance and concentration of MUFAs and PUFAs is considerably higher in the productive sites, when compared to the HNLC sites (cf M5 and M6; P3 and P2). All of these samples are >1500m in depth. We thus take this as strong evidence that the signature of enhanced unsaturated fatty acids associated with resting spores is transferred to the bathypelagic ocean.

We acknowledge that this was perhaps not stated as explicitly as it might have been. We have rewritten the first paragraph of section 4.4 (Implications for pelagic-benthic coupling) in order to express these considerations more thoroughly (Lines 363-378).

# Reviewer 2

We would like to thank the reviewer for taking the time to carefully read and comment on our manuscript. Below is a point-by-point response to the questions and comments raised.

R2 - Q/C - 1: This manuscript by Rembuaville et al describes lipid fluxes and compositions for five deep-water sediment traps deployed in the Southern Ocean to evaluate relationships between Fe fertilization and organic matter (OM) flux to the seafloor and the effects of seasonality in upper ocean ecology and particle morphologies on the ON flux. The major conclusions are that labile lipid fluxes are higher at the three iron-fertilized sites that at the two lower productivity HNLC sites, that lipid fluxes are greatly attenuated with depth, and that specifics of lipid flux and composition depend on ecological factors in the upper ocean. The conclusion that diatom resting spores and zooplankton grazing on the main phytoplankton that produces fecal pellets of various morphologies are major determinants on OM and lipid flux to the seafloor at these sites, and specifics of the fluxes and types of particles varies between the site. Unfortunately there are some serious flaws with the present form of the manuscript that would require attention of the authors before proceeding further.

R2 - R - 1: We thank the reviewer for the precise synopsis of our manuscript. In the detailed comments below we aim to address the issues concerning the reviewer.

R2 - Q/C - 2: First and foremost, the lipid compositional data are actually given short shrift. Are they supposed to be in Supplemental table 1 (noted at line 137 and again at line 297), which apparently was either not included (intended or otherwise?) or simply not available to this reviewer. This would actually include the seasonal data for the plot shown in Fig 4.

R2 - R - 2: We would like to assure the reviewer that we would not reference a supplementary file containing the lipid compositional data and then intentionally exclude it from the manuscript. It seems for some reason the reviewer did not receive the supplementary tables, most probably due to an error during the submission process. The lipid data is highly complex: it is a matrix containing 2832 elements that clearly precludes a detailed discussion of all the patterns observed. We have attempted to present and discuss the lipid data we consider most pertinent to our objectives of examining the link between ecological flux vectors and organic matter composition. We agree with the reviewer that this data should be available to validate the patterns we describe, which is why we intended to present it as supplementary information. We also recognize the some of the detail in the patterns of specific compounds we don't fully describe in the manuscript might be of interest to a certain sector of the readership. As originally intended, tables of lipid fluxes and concentrations are presented as Supplementary Tables 1-5 in the revised version of the manuscript.

R2 - Q/C - 3: Without a more complete data set (indeed at line 276 "quantitative datasets on both compound and organisms fluxes are required" tells all).

R2 - R - 3: This comment is somewhat confusing. At line 276 we make a general statement that quantitative flux datasets are required for both chemical elements (in this case lipids) and biological elements (diatoms, fecal pellets etc) in order to provide a quantitative framework and examine mechanistic processes related to pelagic-benthic coupling. By "referencing a complete dataset" we assume the reviewer is revisiting their previous point concerning the lipid compositional data. As stated above, the intention was to provide this complete dataset and it is available as part of our revised submission.

R2 - Q/C - 4: The lipid compositional data that are included in the text are too sparse for the generalized conclusions that are drawn.

R2 - R - 4: We have added more quantitative references to the text, in addition to providing full supplementary tables of lipid compositional data that may be used as a reference supporting our general conclusions.

R2 - Q/C - 5: Throughout the text, and in Table 2, there is some confusion about fluxes vs concentration. E.g., at line 284, the "spring lipid flux is low (0.3 mg/m2)

", but this is a rate not a flux without some time frame. Is it supposed to be per day, or over the deployment period, or annualized?

R2 - R - 5 We acknowledge that there might be some confusing terminology throughout the manuscript, which we have tried to address in the revised version (see below). It is perhaps worth clarifying that a rate, by definition, describes some change in a property as a function of time. We would therefore politely disagree with the reviewer that 0.3 mg/m2 would be considered a rate, since it lacks a time component. A flux, on the other-hand, is a special kind of rate that describes the passage of some property through a defined area, integrated over a certain time interval. In sediment trap studies, it is sometimes the case that the time interval over which fluxes are integrated corresponds to the sediment trap deployment period (which is of course a unit of time), in which case it is entirely correct to write xx mg/m2 over the deployment period as a flux, if the time period is specified. The collection periods for the sediment traps are of course known and were presented in Table 1 of the original version of the manuscript.

The reviewer is specifically referencing our use of the term flux at line 284. However, in the submitted version of the manuscript the units at line 284 are 0.3 mg m<sup>-2</sup> d<sup>-1</sup> (i.e. including the time component), not 0.3 mg m<sup>-2</sup> (excluding the time component) stated by the reviewer, who appears to have misquoted our original text.

R2 - Q/C - 6: At line Likewise, in Table 2, the "normalized total lipid fluxes, mg lipid/g OC" are concentrations not fluxes (it is correct that lipid flux/OC flux will give a concentration of mg lipid/g OC). (Note that in figs 2a, c, g, and e fluxes have correct units.)

R2 - Q/C - 6: The reviewer has a valid point here concerning terminology. It is of course the case that normalizing lipid fluxes to organic carbon fluxes removes both the units of area and time, resulting in two mass quantities expressed as a ratio that

can also therefore be considered as a concentration. In the original version of the manuscript we had chosen the terminology "normalized lipid flux", but in order to avoid unnecessary confusion we follow the reviewers suggestion and have changed this to concentration throughout the manuscript.

R2 - Q/C - 7: Other comments: P 6 - were the traps treated

with some sort of poison or preservative to preserve the integrity of the OM over the entire deployment period (if this is given in one of the references it was not clear)?

R2 - R - 7: Yes, the detailed processing of samples is in the references in Table 1. This has now been referenced in this section.

R2 - Q/C - 8 Line 173 - this is the first instance of the flux "units" being incorrect. See also line 185– a concentration

# R2 - R - 8.

**(a)**line 173 - As explained above these are fluxes integrated over the deployment period. In the original text this was phrased as "The total lipid flux…" However, this is clearly causing some confusion and so the text has been modified as follows:

Total lipid fluxes integrated over the sediment trap deployment period (Table 1.)

**@line 185** – As stated above we have changed our terminology from normalized lipid flux to concentration.

**R2-** Q/C - 9: What are the annualized primary productivity levels at the five sites? And annualized chl-a concentrations (is that what's in fig 1?).

This information is important to give some sense of the quality of the OM produced at each site, as this impacts the comparative fluxes near the seafloor.

R2 - R - 9: The chlorophyll maps presented in Figure 1 show the annual climatologies of MODIS-chl data at each site. This information has been added to the figure legend. The purpose of presenting these maps was primarily to show the different biomass regimes at the iron-fertilised and "HNLC" sites where the sediment traps were deployed. We do not have a good estimate of primary productivity levels at each site, as these would depend on using satellite data and a model to convert chlorophyll to productivity. Such algorithms are not well validated in the Southern Ocean. Furthermore, in order to achieve this one would need to estimate the surface catchment area over which the sediment traps are integrating based on particle trajectories. In order to compute particle trajectories one would need a good estimation of particle sinking speed and vertically resolved current vectors. None of these variables are well constrained at our deployment sites.

We are also not clear that annualized primary productivity levels would offer much insight concerning the quality of OM produced at each site. OM quality is related to the geochemical composition of OM. The reviewer appears to be suggesting that there might be some relationship between the magnitude of organic matter production and it's lipid composition. We are not aware of any studies supporting this notion.

**R2-** Q/C - 10: Line 187- what are monounsaturated FAMES MUFAs, and polyunsaturated FAMES PUFA, but saturated FAMES are FAMES (why not Sat-FAMES or SFMES) for consistence. After all, everything measured is a FAME.

**R2-**  $\mathbf{R}$  – 10: I am not sure we used the terminology described above. At line 187 we say:

"....displayed high contributions from MUFAs (57.7 mg lipid g OC-1), PUFAs (13.8 mg lipid g OC-1) and FAMEs (44.6 mg lipid g OC-1)"

MUFAs are monounsaturated fatty acids (1 double bond) PUFAs are polyunsaturated fatty acids (>1 double bond) FAMES are saturated fatty acids.

The reviewer is correct that it is unnecessary to include the ME suffix for FAMES, although this nomenclature is sometimes encountered in the litereature. However, we have followed the reviewer's suggestion and changed to FAMES to saturated fatty acids throughout the manuscript.

**R2-** Q/C - 11: Line 201 - isn't "unsaturated alkenols" redundant since alkenols are unsaturated by definition?

**R2-**  $\mathbf{R}$  – 11: Yes, this is true. I think in a previous version we had used the terms saturated and unsaturated alcohols, the latter of course also being an alkenol. Somehow we changed the terminology to alkenol but unsaturated was not removed. Thank your for picking up on this mistake. We have corrected it throughout.

R2- Q/C – 12: Line 209 - maybe spell out the name of EPA the first time it is used.

**R2- R** – **12:** Done.

**R2-** Q/C - 13: Line 252 - why does the cholesterol reflect the dominance of diatoms are the base of the food web? The references cited later (e.g., Rampen et al., 2010; line 328) shows that C27-5 is a relatively minor component of many diatoms. What about 24-methylene C2 cholesterol (C28-5,24(28)? It's hard to evaluate these statements without the data, which as noted above are missing for some reason. See also paragraph at line 326.

**R2- R** – **13:** This was a typing mistake,  $C_{27}\Delta^5$ , should have been written as  $C_{27}\Delta^{5,22}$ , which appears to be more prevalent in Bacillariophycaea (Volkman, 2003). However, upon further reflection we have decided to remove the paragraph that links patterns in sterols to phytoplankton composition. There is too much ambiguity as many sterols are not completely diagnostic as they occur in different groups of phytoplankton.

**R2-** Q/C - 14: Line 266 – The conclusion that lipids are selectively degraded/remineralized during sinking relative to OC because lipid/OC ratios decrease between the shallower and the deepest traps also depends in part on the lipid/OC ratios of the starting material. Since there are apparently differences in production, or chl-a, or ecology between the Fe-fertilized sites and the HNLC sites,

what are lipid/OC ratios in the material that is initially exported out of the surface waters?

**R2-** $\mathbf{R}$  – 14: We agree with the reviewer that the composition of organic matter produced had not been explicitly mentioned. The reason being that we do not have time-series, or point measurements, of lipid/OC ratios in organic matter produced in the mixed layer that could be sensibly compared with our sediment trap measurements. As mentioned above we are not familiar with reports that changes in productivity or biomass are linked to lipid/OC ratios directly, although they may of course be linked indirectly due to patterns related to the taxonomic composition of plankton under different productivity regimes. However, we would not be able to draw any strong inferences on diatom/plankton community structure from productivity estimates and would be therefore unable to link these to variability in lipid/OC concentrations from different bloom areas. As stated in the text, the lipid flux decreases by 5 orders of magnitude between the shallowest and deep trap, which is accompanied by a loss of labile lipid classes such as MUFAs and PUFAs. These features are entirely consistent with degradation over depth. However, we now mention in the manuscript that part of the difference observed at different depths may be related in part to that lipid/OC of "starting material"

**Line 331-333**: It is possible that some of the differences observed over depth may be related to the initial lipid composition of organic material produced in the photic zone by different phytoplankton taxa

**R2-** Q/C - 15 Fig. 2. Are the units on the abscissa supposed to be fluxes. Under "refractory", what is the "other" category? Table 2 – are POC and BSi annual "fluxes" with flux units? There is no discussion of BSi in the manuscript.

**R2-** $\mathbf{R}$ **-15:** Yes these are fluxes integrated over the sediment trap deployment period (c.f. R2-R-5). We have added some extra information to the Figure caption to clarify this point.

**Line 962-963**: Total lipid fluxes (grey bars, left axis) integrated over the sediment trap deployment periods (Table 1).....

The "other" category is all of the other lipid compounds that were measured but do not fall into any of the listed categories. A full list of these compounds is available in the supplementary files and these files have now been referenced in the figure caption. We have also made the same correction for the table captions where the category "other" appears.

Yes the fluxes in Table 1 are integrated over the sediment trap deployment period. The table caption has been modified to clarify this point.

**Line 293-294:** Information on sediment trap deployments and fluxes of particulate organic carbon (POC) integrated over the deployment period.

Biogenic silica data has been removed.

# 1 The role of diatom resting spores for pelagic-benthic coupling in the

2 Southern Ocean.

Mathieu Rembauville<sup>1</sup>, Stéphane Blain<sup>1</sup>, Clara Manno<sup>3</sup>, Geraint Tarling<sup>3</sup>, Anu
Patel<sup>4</sup>, George Wolff<sup>4</sup>, Ian Salter<sup>1,2\*</sup>

<sup>1</sup>Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire d'Océanographie Microbienne (LOMIC),

7 <sup>2</sup>Faroe Marine Research Institute, Box 3051, FO-110, Torshavn, Faroe Islands

<sup>3</sup>British Antarctic Survey, Natural Environmental Research Council, High Cross, Madingley Road, Cambridge,
 CB3 0ET, United Kingdom.

<sup>4</sup>School of Environmental Sciences, 4 Brownlow Street, University of Liverpool, Liverpool, L69 3GP, United
 Kingdom

<sup>\*</sup>Corresponding author: ian.salter@obs-banyuls.fr

# 13 Abstract

Natural iron fertilization downstream of Southern Ocean island plateaus support large 14 phytoplankton blooms and promote carbon export from the mixed layer. In addition to 15 sequestering atmospheric CO<sub>2</sub>, the biological carbon pump also supplies organic matter (OM) 16 to deep-ocean ecosystems. Although the total flux of OM arriving at the seafloor sets the 17 energy input to the system, the chemical nature of OM is also of significance. However, a 18 quantitative framework linking ecological flux vectors to OM composition is currently 19 20 lacking. In the present study we report the lipid composition of export fluxes collected by five-moored sediment traps deployed in contrasting productivity regimes of Southern Ocean 21 island systems (Kerguelen, Crozet and South Georgia) and compile them with quantitative 22 23 data on diatom and faecal pellet fluxes. At the three naturally iron fertilized sites, the relative contribution of labile lipids (mono- and polyunsaturated fatty acids, unsaturated fatty 24

<sup>6</sup> Observatoire Océanologique, F-66650, Banyuls/mer, France

25	alcohols) is 2-4 times higher than at low productivity sites. There is a strong attenuation of
26	labile components as a function of depth, irrespective of productivity. The three island
27	systems also display regional characteristics in lipid export. An enrichment of zooplankton
28	dietary sterols, such as $C_{27}\Delta^5$ , at South Georgia is consistent with high zooplankton and krill
29	biomass in the region and the importance of faecal pellets to POC flux. There is a strong
30	association of diatom resting spore fluxes that dominate productive flux regimes with energy
31	rich unsaturated fatty acids. At the Kerguelen Plateau we provide a statistical framework to
32	link seasonal variation in ecological flux vectors and lipid composition over a complete
33	annual cycle. Our analyses demonstrate that ecological processes in the upper ocean, e.g.
34	resting spore formation and grazing, not only impact the magnitude and stoichiometry of the
35	Southern Ocean biological pump, but also regulate the composition of exported OM and the
36	nature of pelagic-benthic coupling.
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# **1. Introduction**

The biological pump transfers organic carbon (OC) from photosynthetic production to 46 the deep ocean (Volk and Hoffert, 1985) with important implications for the sequestration of 47 atmospheric CO<sub>2</sub> (Sarmiento et al., 1988; Kwon et al., 2009). Only a minor fraction of the 48 carbon fixed in the sunlit ocean reaches the deep ocean and sediments (Martin et al., 1987; 49 Honjo et al., 2008), but this carbon and energy supply is essential for the functioning of deep-50 sea benthic ecosystems (Billett et al., 1983, 2001; Ruhl and Smith, 2004; Ruhl et al., 2008). 51 Commonly referred to as pelagic-benthic coupling (Graf, 1989), the composition, lability and 52 timing of organic matter (OM) flux arriving at the seafloor can exert a large influence on 53 benthic communities (Billett et al., 2001; Galeron et al., 2001; Mincks et al., 2005; Smith et 54 55 al., 2006; Wolff et al, 2011).

Understanding the factors influencing the functioning of the biological pump remains 56 a central question in biogeochemical oceanography (Boyd and Newton, 1995; Rivkin et al., 57 1996; Boyd and Trull, 2007; Guidi et al., 2016). Many different approaches have been 58 adopted to study the biological pump, including carbon budgets (Emerson et al. 1997, 59 Emerson 2014), mixed layer nutrient inventories (Eppley and Peterson, 1979; Sarmiento et al. 60 2004), radionuclide disequilibria (Buesseler et al., 1992; Savoye et al., 2006), optical methods 61 (Gardner et al., 1990; Guidi et al. 2016), neutrally buoyant- (Buesseler et al. 2000; Salter et al. 62 2007) and moored-sediment traps (Berger, 1971; Honjo, 1976). Although all of these methods 63 have their own caveats, sediment traps offer the distinct advantage of collecting and 64 preserving sinking particles for subsequent biological and chemical analysis. Moored 65 sediment traps allow the direct quantification of sinking protists including dinoflagellates (e.g. 66 67 Harland and Pudsey, 1999), diatoms (e.g. Salter et al. 2012), coccolithophores (e.g. Ziveri et al. 2007), radiolarians (e.g. Takahashi et al., 1991), silicoflagellates (Rigual-Hernández et al., 68 2010), foraminifera (Salter et al. 2014) and zooplankton faecal pellets (Wilson et al., 2008, 69 70 2013). Indirect approaches use biomarkers such as lipids and amino acids to identify the

source (algal, zooplanktonic, bacterial) and diagenetic status (lability, degree of preservation)
of the exported OM (Wakeham, 1982; Wakeham et al., 1980, 1984, 1997; Kiriakoulakis et
al., 2001; Wakeham et al., 2009; Lee et al., 2009; Salter et al., 2010). Although it is generally
well-acknowledged that ecological vectors of flux are linked to the geochemical composition,
studies providing a coupled description of biological components and OM composition of
export fluxes remain relatively scarce (e. g. Budge and Parrish, 1998).

Southern Ocean island plateaus such as Kerguelen (Blain et al., 2007), Crozet (Pollard 77 et al., 2009) and South Georgia (Tarling et al., 2012) provide a natural source of iron to the 78 iron-poor waters of the Antarctic Circumpolar Current (de Baar et al., 1990; Martin et al., 79 1990). Currents and the topography of the sea floor lead to enrichment of iron in waters 80 adjacent to the islands which supports large diatom-dominated phytoplankton blooms 81 (Armand et al., 2008; Korb et al., 2008; Quéguiner, 2013) that contrast with the high nutrient, 82 low chlorophyll (HNLC, Minas et al., 1986) regime that generally prevails in Antarctic 83 waters. Previous studies of Southern Ocean island plateaus have identified the significance of 84 resting spore formation by neritic diatom species (Eucampia antarctica var. antarctica, 85 Chaetoceros Hyalochaete, Thalassiosira antarctica) in response to nutrient limitation in mid-86 summer (Salter et al., 2012; Rembauville et al., 2015, 2016a). The export of resting spores 87 generally occurs during short and intense events but they can account for a significant fraction 88 (40-60 %) of annual carbon flux out of the mixed layer at these naturally fertilized sites. This 89 process contributes to the  $\sim 2$  fold increase in annual carbon export when compared to the 90 HNLC sites (Salter et al., 2012; Rembauville et al., 2015, 2016a). 91

Despite the general importance of resting spore ecology for POC export from naturally iron-fertilized systems in the Southern Ocean, there are some notable differences in the nature of export fluxes from Crozet, Kerguelen and South Georgia. At Crozet, in the Polar Front Zone (PFZ), the abundance of foraminifers and pteropods leads to a high inorganic to organic

carbon export ratio (1 mol:mol, Salter et al., 2014). At Kerguelen, south of the Polar Front in 96 the Antarctic Zone (AAZ) the inorganic to organic carbon ratio is much lower (0.07) and 97 CaCO<sub>3</sub> flux is mainly attributed to coccoliths (Rembauville et al., 2016). At South Georgia 98 (AAZ), the faecal pellet contribution to carbon export is higher (~60 % in summer-autumn 99 Manno et al., 2015) when compared to Kerguelen (34 % of annual POC flux; Rembauville et 100 al., 2015). The strong gradients in productivity and ecosystem structure that characterize these 101 island systems offer a valuable framework to address the link between biological and 102 103 geochemical composition of particle export.

The impact of different carbon export vectors on the lability of the exported OM is 104 necessary to understand the impact of upper ocean ecology for pelagic-benthic coupling (Ruhl 105 106 and Smith, 2004; Ruhl et al., 2008). High biomass of meio-, micro- and macrofuna in abyssal sediments of the Southern Ocean (Brandt et al., 2007) suggests a transfer of OM originating 107 from photosynthetic autotrophs down to the seafloor. This diversity and biomass is not 108 109 geographically homogeneous, but rather constrained by upper ocean productivity levels (Wolff et al., 2011; Lins et al., 2015). In this context, the comparison of lipid biomarkers in 110 export fluxes originating from different sites in the Southern Ocean may help to understand 111 how ecological processes at the origin of export flux also shape the magnitude and lability of 112 OM supply to deep-sea benthic communities. 113

This study compiles lipid biomarker data from five annual sediment trap deployments in the vicinity of Southern Ocean Island plateaus in order to (i) compare the composition of lipid biomarkers in export fluxes collected in sites of various productivity levels and across different depths, (ii) identify how ecological export vectors, in particular resting spores, shape the lability of POC fluxes over a complete annual cycle and (iii) derive the potential implications of ecological flux vectors for pelagic-benthic coupling.

# 121 **2 Material and Methods**

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# 2.1 Trap deployments and sample processing

We compile 5 long-term sediment trap deployments located in the vicinity of island plateaus 123 in the Southern Ocean (Fig. 1, Table 1). Two sediment traps were located upstream of the 124 islands in HNLC waters (M6 and P2 at Crozet and South Georgia, respectively) and three 125 were located in naturally iron-fertilized and productive waters characterized by enhanced 126 phytoplankton biomass (A3, M5 and P3 at Kerguelen, Crozet and South Georgia, 127 respectively). The detailed hydrological settings of deployments, preservative conditions of 128 samples and bulk chemical analyses of biogeochemical fluxes have been published previously 129 (Table 1). After the retrieval of each sediment trap, swimmers (organisms actively entering 130 the trap funnel) were manually removed from the samples and therefore do not contribute to 131 132 the lipid fluxes we report.

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# 2.2 Lipid analysis

Lipid analyses were performed on 1/8 wet aliquots resulting from the splitting of original samples. Because of the low amount of material collected in some cups, 1/8 wet aliquots were combined prior to the lipid analyses (supplementary information). Some samples were lost upon recovery of sediment traps and two were contaminated with fish debris and therefore not included in lipid analyses. Full details of all sediment trap samples and those included in lipid analyses is summarized in Supplementary Tables 1-5.

Lipids analyses of Crozet sediment trap samples were performed as described by 140 Kiriakoulakis et al. (2001) and Wolff et al. (2011). For the Kerguelan and South Georgia 141 samples a similar protocol was used. Briefly, separate 1/8 aliquots were spiked with an 142 sonicated 143 internal standard  $(5\alpha(H)$ -cholestane), (filters: 3 x 15 min;

dichloromethane:methanol 9:1), transmethylated (methanolic acetyl chloride) and silvlated 144 (bistrimethylsilvltrifluoroacetamide; 1 % trimethylsilane chloride; 30–50 µL; 40°C; 0.5–1 h). 145 GC-MS analyses were carried out using a GC Trace 1300 fitted with a split-splitless injector, 146 using helium as a carrier gas (2 mL min<sup>-1</sup>) and column DB-5MS (60m x 0.25mm (i.d.), film 147 thickness 0.1µm, non-polar solution of 5% phenyl and 95% methyl silicone). The GC oven 148 was programmed after 1min from 60°C to 170°C at 6°C min<sup>-1</sup>, then from 170°C to 315°C at 149 2.5 °C min<sup>-1</sup> and held at 315 °C for 15 min. The eluent from the GC was transferred directly 150 to the electron impact source of a Thermoquest ISQMS single quadrupole mass spectrometer. 151 Typical operating conditions were: ionisation potential 70 eV; source temperature 215°C; trap 152 current 300 µA. Mass data were collected at a resolution of 600, cycling every second from 153 50-600 Thompsons and were processed using Xcalibur software. Compounds were identified 154 either by comparison of their mass spectra and relative retention indices with those available 155 156 in the literature and/or by comparison with authentic standards. Quantitative data were calculated by comparison of peak areas of the internal standard with those of the compounds 157 of interest, using the total ion current (TIC) chromatogram. The relative response factors of 158 the analytes were determined individually for 36 representative fatty acids, sterols and 159 alkenones using authentic standards. Response factors for analytes where standards were 160 unavailable were assumed to be identical to those of available compounds of the same class. 161

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## 2.3 Statistical analyses

The lipid composition of sediment trap samples from the five sites was investigated using principal component analysis (PCA) and the similarity of samples was studied using clustering (Ward aggregation criteria) based on lipid classes. This methodology has been used previously to study the organic geochemistry of sinking particles in the ocean (Xue et al., 2011). Prior to both PCA and clustering, raw lipid fluxes were transformed by calculating the square root of their relative abundance within each sample. This transformation followed by the calculation of the Euclidian distance is also known as the Hellinger distance, which
provides a good compromise between linearity and resolution in ordination analyses
(Legendre and Legendre, 1998; Legendre and Gallagher, 2001).

172 **3 Results** 

# **3.1 Lipid class distribution and seasonality**

Total lipid fluxes integrated over the sediment trap deployment period (Table 1.) were five 174 orders of magnitude higher in the shallow deployment at A3 (229 mg m<sup>-2</sup> at 289 m) compared 175 to the deep sediment trap at M6 (0.08 mg m<sup>-2</sup> at 3160 m, Fig. 2, Table 2). The contribution of 176 labile lipid compounds (defined as unsaturated fatty acids and alkenols, Wolff et al., 2011, 177 Table 2) to total lipid fluxes was 2-4 times higher in the naturally fertilized sites (20 - 39 % at 178 A3, P3 and M5) relative to the HNLC deployments (<10 % at P2 and M6) (Table 2.). 179 Unsaturated fatty acids were dominated (>80 %) by monounsaturated fatty acids (MUFA) at 180 all sites. Semi-labile lipids (saturated fatty acids analysed as their methyl esters; FAMEs, 181 branched fatty acids and alkanols (saturated alcohols); Table 2) accounted for a small fraction 182 (8-12 %) of total lipids at South Georgia, but a higher fraction (40-46 %) at Crozet. Semi-183 labile lipids were dominated by saturated fatty acid contributions at all sites (64-80 %). 184 Sterols were the dominant lipids at South Georgia (65-82 %) and were less abundant (26-35 185 %) at the other sites. 186

The concentration total lipids, expressed as total lipid flux normalized to organic carbon flux, decreased by four orders of magnitude between the shallowest (A3, 193.1 mg lipid g  $OC^{-1}$ ) and the deepest (M6, 0.9 mg lipid g  $OC^{-1}$ ) deployment (Table 2). In the shallow deployment at Kerguelen (A3) high concentrations of MUFAs (57.4 mg lipid g  $OC^{-1}$ ), PUFAs (13.7 mg lipid g  $OC^{-1}$ ) and saturated fatty acids (44.4 mg lipid g  $OC^{-1}$ ) were observed. All other deployments (P3, P2, M5 and M6) had much lower concentrations of labile and semilabile compounds and were dominated by more refractory sterols  $(0.3 - 6.9 \text{ mg lipid g OC}^{-1})$ .

Samples from Crozet (M5 and M6) were positively projected on the first axis of the PCA together with saturated fatty acids, ,  $C_{28}$ - $C_{29}$  sterols and long chain unsaturated fatty acids ( $C_{22}$ ,  $C_{24}$ ) (Fig. 3a). Samples from South Georgia (P3 and P2) were negatively projected on the first axis, close to  $C_{27}$  sterols. Samples from Kerguelen (A3) were positively projected on the second axis and mainly associated with  $C_{16}$ - $C_{20}$  unsaturated fatty acids.

Using the lipid composition, four main clusters of sediment trap samples could be 199 identified based on the largest distance break after the first node of the dendrogram (Fig. 3b). 200 Cluster A contained most of the spring and summer samples from the naturally-fertilized sites 201 of Kerguelen and Crozet (A3 and M5) characterized by the highest relative abundance of 202 203 labile lipids (PUFA and MUFA). Cluster B was composed of summer and winter samples from A3 displaying a high abundance of alkenols. Cluster C contained spring and summer 204 samples from the naturally fertilized site of South Georgia (P3), several samples from 205 Kerguelen and Crozet and was characterized by a mixture of labile, semi-labile and refractory 206 lipids (MUFA, saturated fatty acids and sterols). Finally, cluster D was composed mostly of 207 samples from the HNLC site of South Georgia (P2) and displayed a large dominance of 208 sterols. 209

210 **3.2 Seasonality at A3** 

In spring, vegetative diatoms were the most important constituents of relatively low POC fluxes, followed by cylindrical faecal pellets (Fig. 4a). Lipid fluxes were dominated by 9Zhexadecenoic acid ( $C_{16:1}$  (cis-9); palmitoleic acid), hexadecanoic acid ( $C_{16}$ ), eicosapentaenoic acid; EPA ( $C_{20:5}$  (cis-5,8,11,14,17)), 9Z-octadecenoic acid ( $C_{18:1}$  (cis-9)), and cholesterol ( $C_{27}\Delta^5$ ) that altogether contributed >75% of total lipids (Fig. 4b). Diatom resting spores dominated the enhanced POC fluxes during summer with a notable contribution of cylindrical and ovoid faecal pellets (Fig. 4c). MUFA and PUFA classes were the most significant components of lipid export. The principal compounds in these classes were  $C_{16:1}$  (cis-9) (47% of total lipids),  $C_{18:1}$  (cis-9) (10%) and  $C_{20:5}$  (cis-8) (5.3%). Sterols accounted for 21% of total lipids and were primarily comprised of  $C_{27}\Delta^5$  (cholesterol) and  $C_{29}\Delta^0$  (Fig. 4d).

In autumn, tabular faecal pellets are the major vectors for POC flux (Fig. 4e), accompanied by 222 a shift to more significant contributions of refractory sterols to the lipid composition, notably 223  $C_{27}\Delta^5$ . The  $C_{16}$  fatty acid and  $C_{18:1}$  (cis-9), 11Z, 14Z, 17Z-eicosatrienoic acid ( $C_{20:3}$  (cis-11) 224 and *n*-hexadecanol ( $C_{16}$  OH) were also important components of the lipid composition in 225 Autumn (Fig. 4f). During winter POC flux is mediated almost entirely by large faecal pellets 226 (tabular and ellipsoid shapes) (Fig. 4g) and the unsaturated alcohols eicosenol (C<sub>20:1</sub> OH) and 227 228 octadecenol (C<sub>18:1</sub> OH) were the major constituent of lipids, with smaller contributions from  $C_{16}$  fatty acids,  $C_{27}\Delta^5$  and  $C_{18:1}$  (cis-9)), (Fig. 4h). 229

230

# 231 **4 Discussion**

# 4.1 Geographical differences in lipid export composition across the Southern Ocean island systems

Annual lipid export at the naturally fertilized sites of Crozet and South Georgia was characterized by relatively high fluxes of labile and semi-labile compounds compared to the HNLC sites. Similarly, at the iron-fertilized productive site on the Kerguelen Plateau, labile and semi-labile lipid classes dominate the annual flux profile. The labile lipid class was dominated by MUFAs, and to a lesser extent, PUFAs. In particular, two lipid compounds  $(C_{16:1}$  (cis-9) and EPA) commonly associated with diatoms (Kates and Volcani, 1966; Lee et al., 1971) were important components of the labile lipid class. These observations confirm
that the large diatom-dominated phytoplankton blooms observed downstream of island
plateaus (Armand et al., 2008; Korb et al., 2010; Quéguiner, 2013), which are supported by
enhanced iron supply (Blain et al., 2008; Pollard et al., 2009 Nielsdóttir et al., 2012; Bowie et
al., 2015), result in significant export of diatom-derived labile OM out of the mixed layer.

The PCA and clustering analyses reveal a notable degree of regional structure and 245 highlight the prevalence of specific lipid classes in the different island systems. The first axis 246 of the PCA (23.7 % of variance) represents the location of the sediment trap deployments and 247 the second axis corresponds to the deployment depth. The P3 and P2 sites at South Georgia 248 both display  $\sim 2$  times higher relative abundance of sterols compared to the Kerguelen (A3) 249 and Crozet (M5 and M6) sites. Sterols are important components of the plasma membrane 250 found in almost all eukaryotic organisms (Dufourc, 2008). Zooplankton use dietary sterols of 251 phytoplankton origin, preferentially assimilating  $C_{27}\Delta^5$ , or converting phytosterols to  $C_{27}\Delta^5$ 252 (Volkman, 1986, 2003) that are ultimately egested in faecal pellets (Bradshaw and Eglinton, 253 1993; Prahl et al., 1984). An enrichment in  $C_{27}\Delta^5$  (and other  $C_{27}$  sterols such as  $C_{27}\Delta^{5,22}$  and 254  $C_{27}\Delta^{22}$ ) in sinking OM is thus considered indicative of a high contribution of faecal material 255 (Ternois et al., 1998) to export flux. The relative abundance of  $C_{27}\Delta^5$ ,  $C_{27}\Delta^{22}$ ,  $C_{27}\Delta^{5,22}$ 256 compounds is highest in the export fluxes around South Georgia, consistent with the higher 257 contribution of faecal pellets to carbon export at South Georgia (Manno et al., 2015) 258 compared to Kerguelen (Rembauville et al., 2015). The biomass of zooplankton groups such 259 as copepods and pteropods reach some of their highest Southern Ocean abundances in the 260 northern Scotia Sea, which is also inhabited by Antarctic krill (Ward et al. 2012, Mackey et 261 al. 2012). 262

#### 4.2 Depth-related trends in lipid composition 264

The decrease in the total lipid flux of five orders of magnitude between the shallowest 265 (289 m) and the deepest (>3000 m) deployment is consistent with the trend generally 266 observed in the global ocean (Wakeham and Lee, 1993; Wakeham et al., 1997, 2009). 267 Moreover, the strong decrease in OC-normalized lipid flux, particularly in the case of MUFA 268 and PUFA compounds, suggests that these labile lipid classes are selectively 269 degraded/remineralized during the sinking of the OM. It is possible that some of the 270 differences observed over depth may be related to the initial lipid composition of organic 271 material produced in the photic zone by different phytoplankton taxa. In the shallowest trap 272 (A3, 289 m), the high OC-normalized MUFA flux and the abundance of diatom-derived 273 essential PUFAs (C<sub>16:3</sub>, C<sub>18:6</sub>, C<sub>20:4</sub>, C<sub>20:5</sub> and C<sub>22:6</sub>) reflects the export of fresh and highly 274 labile diatom-derived OM (Dunstan et al., 1993). By contrast, the presence of branched iso-275 and anteiso- C<sub>15</sub> and C<sub>17</sub> compounds in the deeper trap samples may be attributed to the 276 activity of bacterial reworking of the particulate OM during settling (Kaneda, 1991; Wakeham 277 et al., 1997). 278

279

# 4.3 A quantitative framework linking seasonal variations in ecological flux vectors to particulate lipid composition 280

In order to advance our understanding of the role of ecosystem structure in driving the 281 composition of particle export, quantitative datasets characterizing both the chemical and 282 biological nature of fluxes are required. The dataset from the Kerguelen Plateau was selected 283 as a basis for constructing a quantitative framework linking dominant ecological flux vectors 284 the particulate lipid composition of exported particles. Kerguelen was selected as a case study 285 as we have previously reported detailed quantitative partitioning of POC fluxes between 286 diatom and faecal pellet fluxes that reveal major seasonal shifts in the importance of different 287

ecological flux vectors (Rembauville et al. 2015). The trap at Kerguelen was deployed 100 m beneath the mixed layer, and is therefore also characterized by the highest concentrations and fluxes of lipids (Table 2), thus providing the best possible resolution to examine seasonal changes in lipid composition in relation to ecological flux vectors.

292 **4.3.1 Spring** 

During spring on the Kerguelen Plateau the lipid flux is low (0.3 mg m<sup>-2</sup> d<sup>-1</sup>), as is the 293 corresponding POC flux (~0.15 mmol  $m^{-2} d^{-1}$ ), which is mainly driven by vegetative diatoms 294 belonging to the genera Fragilariopsis, Pseudo-nitzschia and Thalassionema, as well as small 295 faecal pellets (Rembauville et al., 2015). Diatoms are known predominantly to accumulate 296 unsaturated fatty acids such as C<sub>16:1</sub> (cis-9), EPA and C<sub>18:1</sub> (cis-9) (Kates and Volcani, 1966; 297 Opute, 1974; Chen, 2012; Levitan et al., 2014). Diatoms also produce saturated fatty acids, 298 mainly the C<sub>16</sub> homologue (Lee et al., 1971; Matsumoto et al., 2009; Liang et al., 2014). Thus, 299 although the spring lipid flux is quite low, the major compounds ( $C_{16:1}$  (cis-9),  $C_{16}$ , EPA and 300  $C_{18,1}$  (cis-9)) represent an export assemblage dominated by vegetative diatoms. 301

### 302 **4.3.2 Summer**

During summer POC fluxes are enhanced by an order of magnitude and are 303 characterized by intense export of diatom resting spores (Chaetoceros Hyalochaete spp. and 304 to a lesser extent Thalassiosira antarctica) that contribute 60% of the annual POC flux 305 (Rembauville et al. 2015). This resting spore flux event is associated with the highest export 306 of total lipids (2.4 mg m<sup>-2</sup> d<sup>-1</sup>, supplementary Table 1). The summer lipid profile is dominated 307 by  $C_{16:1}$  (cis-9) and  $C_{18:1}$  (cis-9), with a marked contribution of EPA. Higher total lipid 308 contents have been documented in resting spores of Chaetoceros Hyalochaete and 309 Thalassiosira antarctica when compared to vegetative cells (Doucette and Fryxell, 1983; 310 Kuwata et al., 1993). More specifically, our results are consistent with the 8-12 fold increase 311

in the content of  $C_{16:1}$  (cis-9) and  $C_{18:1}$  (cis-9) in *Chaetoceros pseudocurvisetus* resting spores when compared to the vegetative stages (Kuwata et al., 1993). An increase in the cell content of EPA during the formation of resting spores has also been reported for *Chaetoceros salsugineus* (Zhukova and Aizdaicher, 2001).

Resting spore formation is an ecological strategy utilized by certain diatom species to 316 persist in environments where unfavorable conditions (e.g. light or nutrient limitation) occur 317 (Smetacek, 1985; French and Hargraves, 1985; McQuoid and Hobson, 1996). Lipids produce 318 more energy per unit mass than polysaccharides and can be stored in concentrated forms by 319 diatoms (Obata et al., 2013). The accumulation of energy-rich unsaturated fatty acids in the 320 resting spore, associated with a reduced metabolism (Oku and Kamatani, 1999) and sinking to 321 deeper waters (Smetacek, 1985) act in concert to increase the survival rate of the cells. In 322 order for this ecological strategy to work the cells must be reintroduced to the surface mixed 323 layer during a period favorable for growth. Nevertheless, sediment trap studies from Southern 324 Ocean island systems clearly document that a significant portion of the resting spores formed 325 in the surface are exported out of the mixed layer and reach bathypelagic depths (Salter et al. 326 2012, Rembauville et al. 2015, 2016). Consequently, the ecological survival strategy of 327 resting spore formation in diatoms can mediate large fluxes of labile lipid compounds to the 328 seafloor. 329

Cholesterol  $(C_{27}\Delta^5)$  was a significant component (>10 %) of particulate lipid composition throughout the year. However, it reached its highest highest contribution (18 %) in autumn when the contribution of faecal pellets to POC flux increased. Unlike many eukaryotes, crustaceans are incapable of *de novo* biosynthesis of sterols and show a simple sterol composition dominated by  $C_{27}\Delta^5$  (Goad, 1981; Baker and Kerr, 1993; Kanazawa, 2001). Its presence throughout the year may thus be explained by the continuous export of spherical, ovoid and cylindrical faecal pellets (Figure 4) which are typically attributed to copepods, amphipods and euphausiids (Wilson et al., 2008, 2013). Notably we observed the presence of a  $C_{29}\Delta^0$  sterol during summer.  $C_{29}$  sterols are abundant in diatoms (Volkman, 2003), and can account for 60 % and 80 % of total lipids of *Navicula* sp., and *Eucampia antarctica var antarctica*, respectively (Rampen et al., 2010), both of which showed a clear seasonality with a marked summer maximum (Rembauville et al., 2015).

342 **4.3.3 Winter** 

In winter, the lowest lipid fluxes were recorded and in contrast with other samples 343 were dominated by mono-unsaturated alkenols ( $C_{18:1}$  OH and  $C_{20:1}$  OH). These compounds are 344 generally absent in phytoplankton lipids but are an abundant component in zooplankton wax 345 ester (Lee et al., 1971), and are often utilized as a marker for zooplankton-derived OM 346 (Wakeham et al., 1997). More specifically, salp faecal pellets (tabular shape) have been 347 shown to contain important amounts of  $C_{18:1}$  OH and  $C_{20:1}$  OH (Matsueda et al., 1986). This is 348 in good agreement with the dominance of tabular faecal pellets in the winter POC flux at 349 Kerguelen. Tabular faecal material is present in the export flux during autumn but alkenols 350 represent a minor constituent of the lipid flux. We expect this difference is primarily related to 351 the larger contribution of diatoms to export flux (as both single cells or present in faecal 352 pellets), but it may also reflect changes in zooplankton lipid composition across the season 353 (Lee et al., 2006). Wax esters are used as energy reserve (Lee et al., 1970) but also contribute 354 to adjust buoyancy in cold and deep waters in winter (Pond and Tarling, 2011). The 355 abundance of wax ester-derived compounds we report in winter is also consistent with 356 observations from neritic areas of the Kerguelen Islands (Mayzaud et al., 2011). Another 357 indicator of a seasonal shift from diatom (spring) to faecal pellet-dominated export system 358 359 (autumn and winter) is the absence of long chain PUFAs in autumn and winter. It has been previously reported that this energy-rich compound is preferentially assimilated by 360 zooplankton and is therefore typically absent in faecal pellets (Stübing et al., 2003). 361

# 4.4 Implications for pelagic-benthic coupling

363	Diatom-resting spores account for 60% of annual particulate organic carbon (POC) export at 300m
364	from the iron-fertilized bloom on the Kerguelen plateau (Rembaubille et al. 2015). Similar patterns
365	are observed in deeper trap samples (>2000m) from the productive regime at South Georgia (P3),
366	whereby 42% of annual POC export can be attributed to resting spores (Rembauville et al. 2016a). At
367	the productive Crozet site (M5), Eucampia antarctica winter growth stages dominate flux at 3000m
368	and are strongly correlated with total POC flux (Salter et al. 2012). These findings are in contrast to
369	sediment trap diatom assemblages from the low productivity/HNLC sites upstream of Kerguelen,
370	Crozet and South Georgia that contain much lower quantities of resting spores (<5%) with a negligible
371	contribution to POC (Salter et al. 2012, Rembauville et al. 2016a, 2017). The consistent feature from
372	Southern Ocean island systems is that the flux of diatom resting spores, in particular those of
373	Chaetoceros spp. and E. antarctica, are important vectors of POC transport to the bathypelagic
374	(>1500m). In the bathypelagic ocean (>1500m), concentrations of MUFAs and PUFAs are 2-25 times
375	higher in particulate flux originating from the productive regimes of these iron-fertilized systems
376	(Table 1; Wolff et al. 2011). These data demonstrate that resting spore flux also mediates enhanced
377	fluxes of freshly labile organic matter, in the form of unsaturated fatty acids, to the bathypelagic
378	ocean.

379

The oxidation of unsaturated fatty acids (MUFA and PUFA) classes produces more energy 380 than their saturated fatty acid counterparts (Levitan et al., 2014). An energy-rich food supply 381 associated with the resting spore flux appears to have an important impact on benthic systems. 382 For example, the decoupling of abundance between megafaunal invertebrates and OM input at 383 Crozet appears in part to be related to enhanced labile lipid and pigment fluxes supporting 384 higher fecundity of the dominant megafaunal invertebrate, Peniagone crozeti (Wolff et al. 385 2011). At South Georgia, nematode biomass is 10 times higher in deep-sea sediments 386 (>3000m) underlying iron-fertilized productivity regimes (Lins et al. 2015) whilst OM input 387

varies by considerably less (Rembauville et al. 2016). Nematode fatty acids are significantly 388 enriched  $C_{16:1}$  (cis-9) and EPA, two major lipid compounds we have shown to be statistically 389 associated with summer export events dominated by diatom resting spores. A resistance to 390 grazing (Kuwata and Tsuda, 2005) and enhanced sinking velocities of resting spores 391 compared to vegetative cells (McQuoid and Hobson, 1996) result in their effective transfer to 392 the seafloor (Rembauville et al. 2016), consistent with the fact they are a common feature of 393 sediments underlying productive regimes (Crosta et al. 1997; Armand et al. 2008; Tsukazaki 394 et al. 2013). The ecology of resting spore formation therefore acts as an efficient conduit to 395 transfer energy rich storage lipids to the sediment and they may thus play a particularly 396 397 important role in pelagic-benthic coupling.

Deep-sea ecosystems are strongly dependent on OM food supply originating from 398 photosynthesis in the surface ocean (Billett et al., 1983, 2001; Ruhl and Smith, 2004; Ruhl et 399 al., 2008). In the Southern Ocean, it has been demonstrated how the composition of the upper 400 ocean plankton community, and their associated ecological strategies, can influence climate 401 dynamics associated with the biological carbon pump (Smetacek at al. 2004; Salter et al., 402 2012; Assmy et al., 2013; Salter et al. 2014 Rembauville et al., 2015) The present study 403 reveals how changes in major ecological flux vectors, and in particular the process of diatom 404 resting spore formation, can also influence pelagic-benthic coupling by moderating the supply 405 of energy rich storage lipids to deep-sea communities. 406

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# 749 Tables

# **Table 1:** Information on sediment trap deployments and fluxes of particulate organic carbon

# 751 (POC) integrated over the deployment period..

Location and reference	Sediment trap model	Collection period	Total fluxes (mmol m <sup>-2</sup> ) POC
Kerguelen (Rembauville et al., 2015b)			
A3 50°38.30' S – 72°02.60' E 289 m	Technicap PPS3/3 0.125 m <sup>2</sup>	21/10/2011 – 07/09/2012 No sample lost Total: 322 days	98
South Georgia (Rembauville et al., 2016a)			
P3 52°43.40' S - 40°08.83' W 2000 m	Mclane	15/01/2012 – 01/12/2012 1 sample lost Total: 291 days	41
P2 55°11.99' S - 41°07.42' W 1500 m	0.5 m <sup>2</sup>	15/01/2012 – 01/12/2012 3 samples lost Total: 231 days	26
Crozet (Salter et al., 2012)			
M5 46°00.00' S – 56°05.00' E 3195 m	Mclane	28/12/2005 – 29/12/2005 No sample lost Total 360 days	40
M6 49°00.03' S – 51°30.59' E 3160 m	0.5 m <sup>2</sup>	05/01/2005 – 03/01/2006 No sample lost Total 359 days	14

**Table 2:** Total annual lipid flux, relative contribution of lipid classes and lipid concentrations

for the five sediment trap deployments. Labile – MUFA (monounsaturated fatty acids), PUFA

756 (polyunstaurated fatty acids) and unsaturated alcohols; Semi-labile – saturated fatty acids,

branched fatty acids and saturated alcohols; Refractory – Sterols, Other (Wolff et al., 2011).

- 758 Sediment trap deployment periods are presented in Table 1. Individual compound fluxes,
- concentrations and relative contributions are included in Supplementary Tables 1-5. A full list
- <sup>760</sup> of the compounds categorized as others can also be found in the supplementary tables.

Site	A3	P3	P2	M5	M6
<b>Integrated lipid flux</b> (mg m <sup>-2</sup> )	228.8	3.83	2.67	1.20	0.08
<b>Relative contribution</b> (%)					
MUFA	29.7	18.0	8.1	18.1	5.2
PUFA	7.1	1.3	0.2	3.1	0.3
Unsaturated alcohols (alkenols)	2.3	1.1	0.6	2.2	0.5
Saturated fatty acids	23.0	9.7	5.9	26.0	30.5
Branched fatty acids	1.4	0.2	0.3	1.3	0.8
Saturated alcohols (alkanols)	8.5	2.3	1.7	13.2	14.5
Sterols	26.0	64.8	81.9	34.6	35.0
Other	2.0	2.5	1.3	1.5	13.3
<b>Total lipid concentration</b> (mg lipid g OC <sup>-1</sup> )	193.1	7.8	8.4	3.1	0.9
<b>Lipid concentration</b> (µg lipid g OC <sup>-1</sup> )					
MUFA	57403.2	1397.6	687.6	565.8	49.1
PUFA	13736.4	102.3	18.4	97.7	2.7
Unsaturated alcohols (alkenols)	4403.6	82.5	47.7	68.2	5.1
Saturated fatty acids	44359.3	755.2	497.5	810.7	289.0
Branched fatty acids	2792.1	18.7	24.5	39.6	7.4
Saturated alcohols (alkanols)	16325.6	176.2	145.2	411.7	137.0
Sterols	50261.1	5021.9	6911.4	1077.7	331.6
Other	3777.8	196.3	108.3	47.0	126.0

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### 763 Figures captions.

**Figure 1:** Location of the five annual sediment trap deployments in the Southern Ocean.

Color refers to annual surface satellite-derived chlorophyll *a* climatology (MODIS 2002-2016

full mission product accessed at <u>http://oceancolor.gsfc.nasa.gov/cms/</u>). Dashed and

continuous lines represent respectively the Subantarctic Front (SAF) and Polar Front (PF)

from Sallée et al., 2008. SAZ: Subantarctic Zone, PFZ: Polar Frontal Zone, AAZ: Antarctic

769 Zone.

**Figure 2:** Total lipid fluxes (grey bars, left axis) integrated over the sediment trap deployment

periods (Table 1) and the relative contribution of lipid classes (coloured bars, right axis) to

this total flux from five moored sediment trap deployments in the Southern Ocean. Individual

<sup>773</sup> compound fluxes, concentrations and relative contributions are included in Supplementary

Tables 1-5. A full list of the compounds categorized as others can also be found in the

775 supplementary tables.

**Figure 3:** Association of lipid compounds with sediment trap samples. a) Principal

component analysis of the relative abundance of lipids (n = 121). Black and white symbols

represent respectively the naturally-fertilized and the low productivity sites. b) Clustering of

the sediment trap samples based on the relative abundance of lipid classes (Euclidian distance,

780 Ward aggregation criteria). Clusters A, B, C and D were defined based on the highest distance

break after the first node. In a) and b), color refers to the lability of lipids according to (Wolffet al., 2011).

**Figure 4:** Seasonal evolution of carbon export vectors and associated lipid composition over

the central Kerguelen Plateau (A3, 289 m). Left panels: carbon export vectors from

785 Rembauville et al., 2015. Right panels: sorted relative abundance (coloured bars) and

cumulated relative abundance (dots) of major lipids. a) and b) cups 1-3, c) and d) cup 9, e)

787 and f) cup 11, g) and h) cup 12.



791 Figure 1



**Figure 2** 



814 Figure 3

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819			
820			





823 Figure 4