The role of diatom resting spores for pelagic-benthic coupling in the Southern Ocean.

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Abstract

Natural iron fertilization downstream of Southern Ocean island plateaus support large phytoplankton blooms and promote carbon export from the mixed layer. In addition to sequestering atmospheric CO_2, the biological carbon pump also supplies organic matter (OM) to deep-ocean ecosystems. Although the total flux of OM arriving at the seafloor sets the energy input to the system, the chemical nature of OM is also of significance. However, a quantitative framework linking ecological flux vectors to OM composition is currently 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 island systems (Kerguelen, Crozet and South Georgia) and compile them with quantitative 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

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

1. Introduction

The biological pump transfers organic carbon (OC) from photosynthetic production to the deep ocean (Volk and Hoffert, 1985) with important implications for the sequestration of atmospheric CO_2 (Sarmiento et al., 1988; Kwon et al., 2009). Only a minor fraction of the carbon fixed in the sunlit ocean reaches the deep ocean and sediments (Martin et al., 1987; Honjo et al., 2008), but this carbon and energy supply is essential for the functioning of deep-sea benthic ecosystems (Billett et al., 1983, 2001; Ruhl and Smith, 2004; Ruhl et al., 2008) . Commonly referred to as pelagic-benthic coupling (Graf, 1989), the composition, lability and timing of organic matter (OM) flux arriving at the seafloor can exert a large influence on benthic communities (Billett et al., 2001; Galeron et al., 2001; Mincks et al., 2005; Smith et al., 2006; Wolff et al, 2011).

Understanding the factors influencing the functioning of the biological pump remains a central question in biogeochemical oceanography (Boyd and Newton, 1995; Rivkin et al., 1996; Boyd and Trull, 2007; Guidi et al., 2016). Many different approaches have been adopted to study the biological pump, including carbon budgets (Emerson et al. 1997, Emerson 2014), mixed layer nutrient inventories (Eppley and Peterson, 1979; Sarmiento et al. 2004), radionuclide disequilibria (Buesseler et al., 1992; Savoye et al., 2006), optical methods (Gardner et al., 1990; Guidi et al. 2016), neutrally buoyant- (Buesseler et al. 2000; Salter et al. 2007) and moored-sediment traps (Berger, 1971; Honjo, 1976). Although all of these methods have their own caveats, sediment traps offer the distinct advantage of collecting and preserving sinking particles for subsequent biological and chemical analysis. Moored sediment traps allow the direct quantification of sinking protists including dinoflagellates (e.g. 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., 2010), foraminifera (Salter et al. 2014) and zooplankton faecal pellets (Wilson et al., 2008, 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 et al., 2009) and South Georgia (Tarling et al., 2012) provide a natural source of iron to the iron-poor waters of the Antarctic Circumpolar Current (de Baar et al., 1990; Martin et al., 1990). Currents and the topography of the sea floor lead to enrichment of iron in waters adjacent to the islands which supports large diatom-dominated phytoplankton blooms (Armand et al., 2008; Korb et al., 2008; Quéguiner, 2013) that contrast with the high nutrient, low chlorophyll (HNLC, Minas et al., 1986) regime that generally prevails in Antarctic waters. Previous studies of Southern Ocean island plateaus have identified the significance of resting spore formation by neritic diatom species (*Eucampia antarctica* var. *antarctica*, *Chaetoceros Hyalochaete*, *Thalassiosira antarctica*) in response to nutrient limitation in mid-summer (Salter et al., 2012; Rembauville et al., 2015, 2016a). The export of resting spores generally occurs during short and intense events but they can account for a significant fraction (40-60 %) of annual carbon flux out of the mixed layer at these naturally fertilized sites. This process contributes to the ~2 fold increase in annual carbon export when compared to the HNLC sites (Salter et al., 2012; Rembauville et al., 2015, 2016a).

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 the Antarctic Zone (AAZ) the inorganic to organic carbon ratio is much lower (0.07) and $CaCO_3$ flux is mainly attributed to coccoliths (Rembauville et al., 2016). At South Georgia (AAZ), the faecal pellet contribution to carbon export is higher (~60 % in summer-autumn Manno et al., 2015) when compared to Kerguelen (34 % of annual POC flux; Rembauville et al., 2015). The strong gradients in productivity and ecosystem structure that characterize these island systems offer a valuable framework to address the link between biological and geochemical composition of particle export.

The impact of different carbon export vectors on the lability of the exported OM is necessary to understand the impact of upper ocean ecology for pelagic-benthic coupling (Ruhl 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 from photosynthetic autotrophs down to the seafloor. This diversity and biomass is not 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 export fluxes originating from different sites in the Southern Ocean may help to understand how ecological processes at the origin of export flux also shape the magnitude and lability of OM supply to deep-sea benthic communities.

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.

2 Material and Methods

2.1 Trap deployments and sample processing

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

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 Kiriakoulakis et al. (2001) and Wolff et al. (2011). For the Kerguelan and South Georgia samples a similar protocol was used. Briefly, separate 1/8 aliquots were spiked with an internal standard (5α(H)-cholestane), sonicated (filters; 3 x 15 min;

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

162 ## 2.3 Statistical analyses

163 The lipid composition of sediment trap samples from the five sites was investigated using
164 principal component analysis (PCA) and the similarity of samples was studied using
165 clustering (Ward aggregation criteria) based on lipid classes. This methodology has been used
166 previously to study the organic geochemistry of sinking particles in the ocean (Xue et al.,
167 2011). Prior to both PCA and clustering, raw lipid fluxes were transformed by calculating the
168 square root of their relative abundance within each sample. This transformation followed by

169 the calculation of the Euclidian distance is also known as the Hellinger distance, which
170 provides a good compromise between linearity and resolution in ordination analyses
171 (Legendre and Legendre, 1998; Legendre and Gallagher, 2001).

172 3 Results

173 3.1 Lipid class distribution and seasonality

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

187 The concentration total lipids, expressed as total lipid flux normalized to organic
188 carbon flux, decreased by four orders of magnitude between the shallowest (A3, 193.1 mg
189 lipid g OC^{-1}) and the deepest (M6, 0.9 mg lipid g OC^{-1}) deployment (Table 2). In the shallow
190 deployment at Kerguelen (A3) high concentrations of MUFAs (57.4 mg lipid g OC^{-1}), PUFAs
191 (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 semi-labile compounds and were dominated by more refractory sterols (0.3 – 6.9 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 identified based on the largest distance break after the first node of the dendrogram (Fig. 3b). Cluster A contained most of the spring and summer samples from the naturally-fertilized sites of Kerguelen and Crozet (A3 and M5) characterized by the highest relative abundance of 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 samples from the naturally fertilized site of South Georgia (P3), several samples from Kerguelen and Crozet and was characterized by a mixture of labile, semi-labile and refractory lipids (MUFA, saturated fatty acids and sterols). Finally, cluster D was composed mostly of samples from the HNLC site of South Georgia (P2) and displayed a large dominance of sterols.

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 9Z-hexadecenoic 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 a shift to more significant contributions of refractory sterols to the lipid composition, notably $C_{27}\Delta^5$. The C_{16} fatty acid and $C_{18:1}$ (cis-9), 11Z, 14Z, 17Z-eicosatrienoic acid ($C_{20:3}$ (cis-11) and *n*-hexadecanol (C_{16} OH) were also important components of the lipid composition in Autumn (Fig. 4f). During winter POC flux is mediated almost entirely by large faecal pellets (tabular and ellipsoid shapes) (Fig. 4g) and the unsaturated alcohols eicosenol ($C_{20:1}$ OH) and octadecenol ($C_{18:1}$ 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).

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

4.2 Depth-related trends in lipid composition

The decrease in the total lipid flux of five orders of magnitude between the shallowest (289 m) and the deepest (>3000 m) deployment is consistent with the trend generally observed in the global ocean (Wakeham and Lee, 1993; Wakeham et al., 1997, 2009). Moreover, the strong decrease in OC-normalized lipid flux, particularly in the case of MUFA and PUFA compounds, suggests that these labile lipid classes are selectively degraded/remineralized during the sinking of the OM. 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. In the shallowest trap (A3, 289 m), the high OC-normalized MUFA flux and the abundance of diatom-derived essential PUFAs ($C_{16:3}$, $C_{18:6}$, $C_{20:4}$, $C_{20:5}$ and $C_{22:6}$) reflects the export of fresh and highly labile diatom-derived OM (Dunstan et al., 1993). By contrast, the presence of branched *iso*- and *anteiso*- C_{15} and C_{17} compounds in the deeper trap samples may be attributed to the activity of bacterial reworking of the particulate OM during settling (Kaneda, 1991; Wakeham et al., 1997).

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

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

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.

4.3.1 Spring

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

4.3.2 Summer

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

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

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

330 Cholesterol ($C_{27}\Delta^5$) was a significant component (>10 %) of particulate lipid
331 composition throughout the year. However, it reached its highest highest contribution (18 %)
332 in autumn when the contribution of faecal pellets to POC flux increased. Unlike many
333 eukaryotes, crustaceans are incapable of *de novo* biosynthesis of sterols and show a simple
334 sterol composition dominated by $C_{27}\Delta^5$ (Goad, 1981; Baker and Kerr, 1993; Kanazawa,
335 2001). Its presence throughout the year may thus be explained by the continuous export of
336 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).

4.3.3 Winter

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

4.4 Implications for pelagic-benthic coupling

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

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

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

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

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Tables

Table 1: Information on sediment trap deployments and fluxes of particulate organic carbon (POC) integrated over the deployment period.

Location and reference	Sediment trap model	Collection period	Total fluxes (mmol m^{-2}) POC
Kerguelen (Rembauville et al., 2015b)			
A3 50°38.30' S – 72°02.60' E 289 m	Technicap PPS3/3 0.125 m^2	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 PARFLUX 0.5 m^2	15/01/2012 – 01/12/2012 1 sample lost Total: 291 days	41
P2 55°11.99' S - 41°07.42' W 1500 m		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 PARFLUX 0.5 m^2	28/12/2005 – 29/12/2005 No sample lost Total 360 days	40
M6 49°00.03' S – 51°30.59' E 3160 m		05/01/2005 – 03/01/2006 No sample lost Total 359 days	14

754 **Table 2:** Total annual lipid flux, relative contribution of lipid classes and lipid concentrations
755 for the five sediment trap deployments. Labile – MUFA (monounsaturated fatty acids), PUFA
756 (polyunstaurated fatty acids) and unsaturated alcohols; Semi-labile – saturated fatty acids,
757 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,
759 concentrations and relative contributions are included in Supplementary Tables 1-5. A full list
760 of the compounds categorized as others can also be found in the supplementary tables.

Site	**A3**	**P3**	**P2**	**M5**	**M6**
Integrated lipid flux ($mg\ m^{-2}$)	228.8	3.83	2.67	1.20	0.08
Relative contribution (%)					
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
Total lipid concentration (mg lipid g OC^{-1})	193.1	7.8	8.4	3.1	0.9
Lipid concentration (µg lipid g OC^{-1})					
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

761

762

763 **Figures captions.**

764 **Figure 1:** Location of the five annual sediment trap deployments in the Southern Ocean.
765 Color refers to annual surface satellite-derived chlorophyll *a* climatology (MODIS 2002-2016
766 full mission product accessed at http://oceancolor.gsfc.nasa.gov/cms/). Dashed and
767 continuous lines represent respectively the Subantarctic Front (SAF) and Polar Front (PF)
768 from Sallée et al., 2008. SAZ: Subantarctic Zone, PFZ: Polar Frontal Zone, AAZ: Antarctic
769 Zone.

770 **Figure 2:** Total lipid fluxes (grey bars, left axis) integrated over the sediment trap deployment
771 periods (Table 1) and the relative contribution of lipid classes (coloured bars, right axis) to
772 this total flux from five moored sediment trap deployments in the Southern Ocean. Individual
773 compound fluxes, concentrations and relative contributions are included in Supplementary
774 Tables 1-5. A full list of the compounds categorized as others can also be found in the
775 supplementary tables.

776 **Figure 3:** Association of lipid compounds with sediment trap samples. a) Principal
777 component analysis of the relative abundance of lipids (n = 121). Black and white symbols
778 represent respectively the naturally-fertilized and the low productivity sites. b) Clustering of
779 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
781 break after the first node. In a) and b), color refers to the lability of lipids according to (Wolff
782 et al., 2011).

783 **Figure 4:** Seasonal evolution of carbon export vectors and associated lipid composition over
784 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) and f) cup 11, g) and h) cup 12.

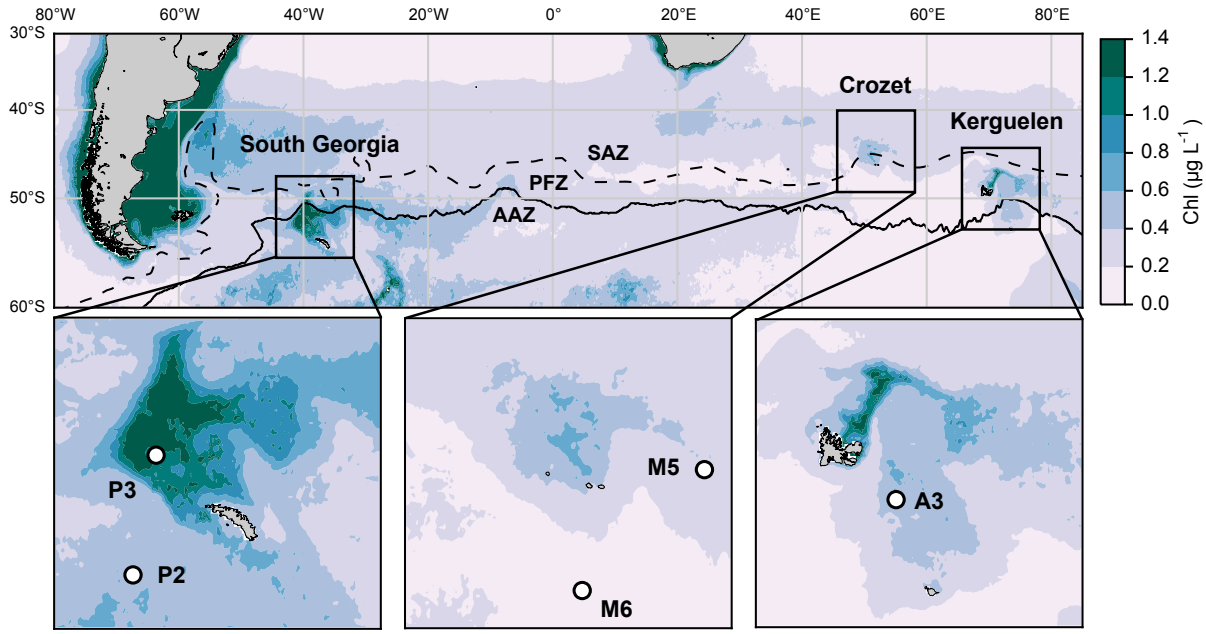

Figure 1

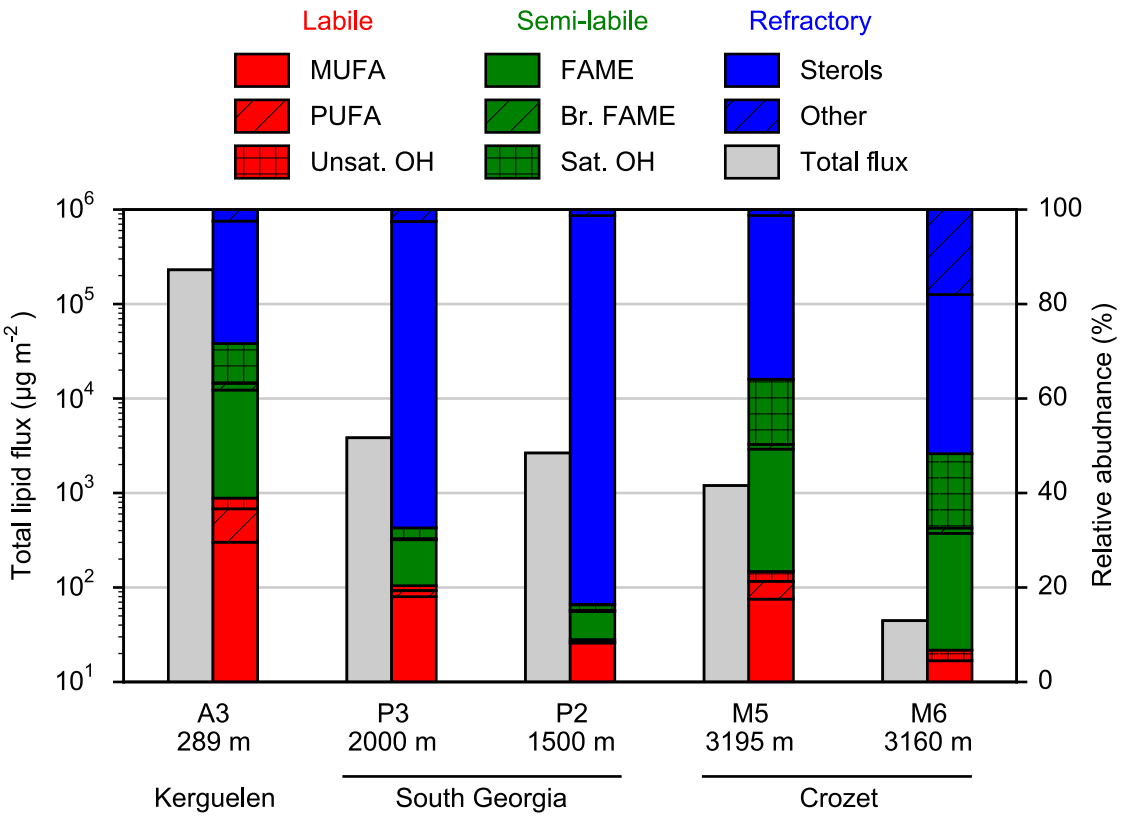
Labile
Semi-labile
Refractory
MUFA
PUFA
Unsat. OH
FAME
Br. FAME
Sat. OH
Sterols
Other
Total flux
Total lipid flux (µg m-2)
Relative abudnance (%)
A3
289 m
P3
2000 m
P2
1500 m
M5
3195 m
M6
3160 m
Kerguelen
South Georgia
Crozet

Figure 2

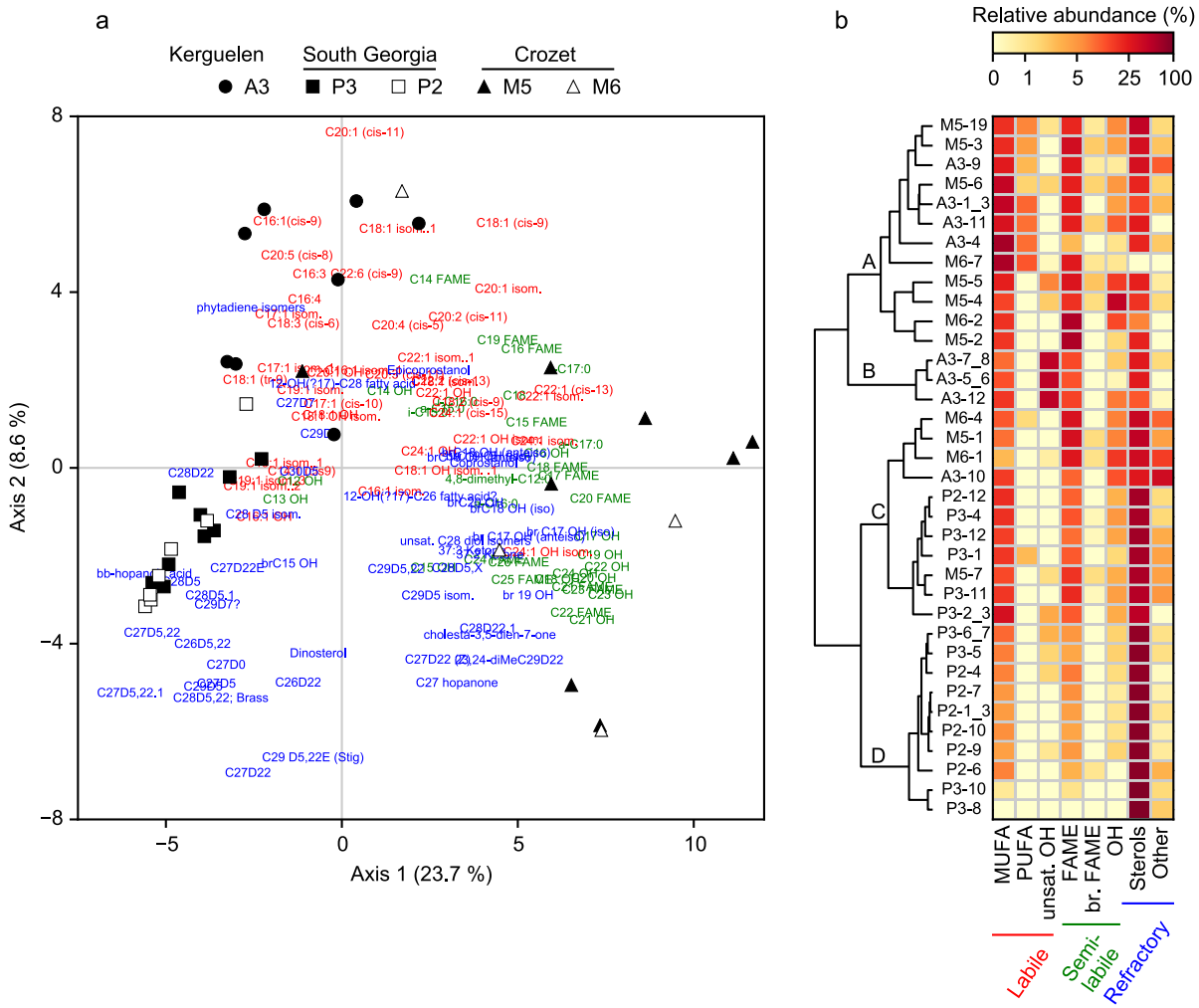
a
Kerguelen
South Georgia
Crozet
A3
P3
P2
M5
M6
Axis 2 (8.6 %)
Axis 1 (23.7 %)
b
Relative abundance (%)
0 1 5 25 100
M5-19
M5-3
A3-9
M5-6
A3-1_3
A3-11
A3-4
M6-7
M5-5
M5-4
M6-2
M5-2
A3-7_8
A3-5_6
A3-12
M6-4
M5-1
M6-1
A3-10
P2-12
P3-4
P3-12
P3-1
M5-7
P3-11
P3-2_3
P3-6_7
P3-5
P2-4
P2-7
P2-1_3
P2-10
P2-9
P2-6
P3-10
P3-8
A
B
C
D
MUFA
PUFA
unsat. OH
FAME
br. FAME
OH
Sterols
Other
Labile
Semi-labile
Refractory

Figure 3

818

819

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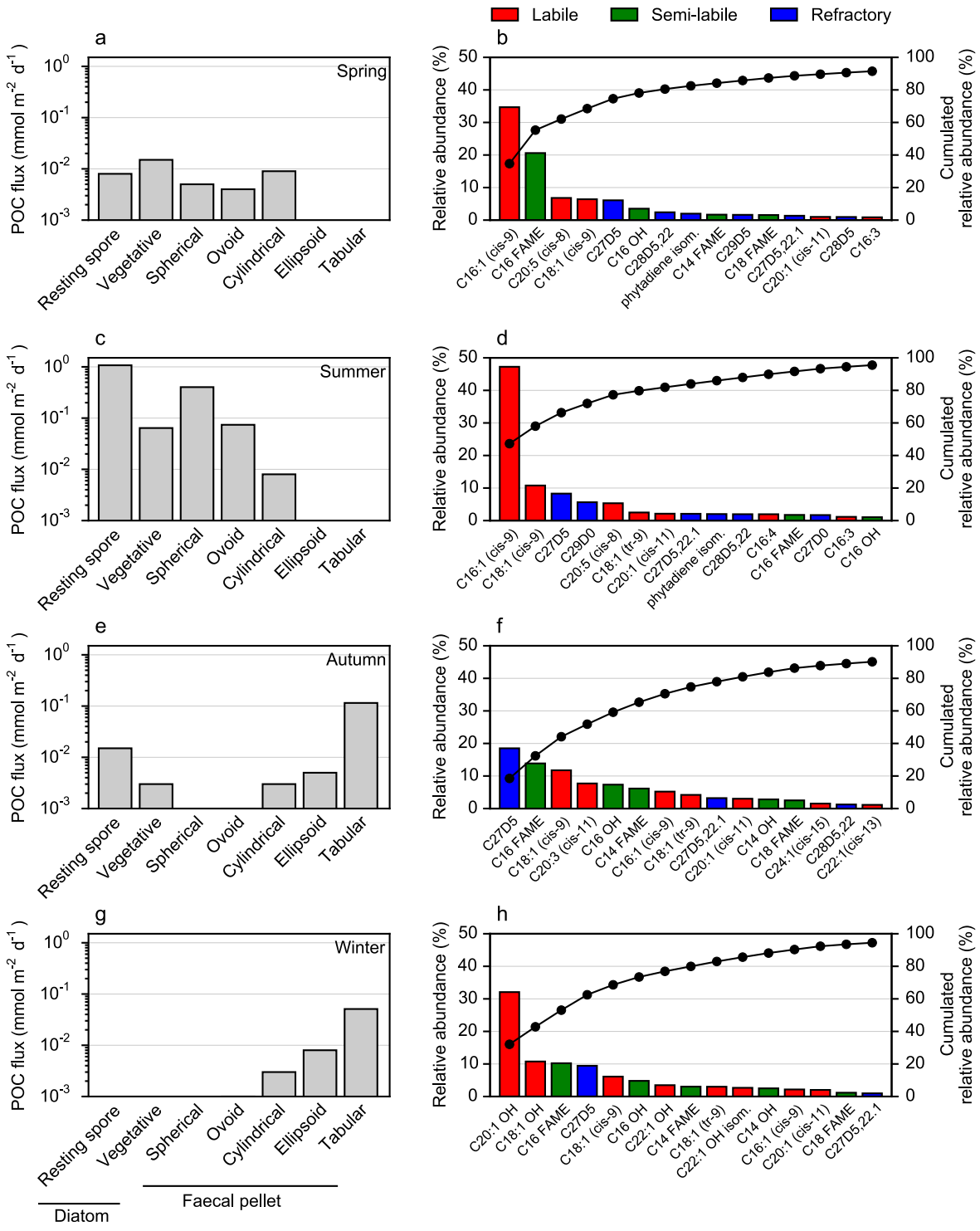

822

823 **Figure 4**

824