Annual particulate matter and diatom export in a high nutrient, low chlorophyll area of the Southern Ocean

M. Rembauville, I. Salter, F. Dehairs, J.-C. Miquel, S. Blain

Annual particulate matter and diatom export in a high nutrient, low chlorophyll area of the Southern Ocean

M. Rembauville[1,*], I. Salter[1,2], F. Dehairs[3], J.-C. Miquel[4] and S. Blain[1].

[1]Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire d'Océanographie Microbienne (LOMIC), Observatoire Océanologique, F-66650, Banyuls/mer, France

[2]Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Am Handelshafen 12, 27570 Bremerhaven, Germany

[3]Analytical, Environmental and Geo – Chemistry; Earth System Sciences Research Group, Vrije Universiteit Brussel, Belgium

[4]International Atomic Energy Agency, Environment Laboratories, 4, quai Antoine 1er, 98000 Monaco

[*]Corresponding author: rembauville@obs-banyuls.fr

Abstract

Upper ocean plankton assemblages are known to influence the export of carbon and biominerals from the mixed layer. However, relationships between plankton community structure and the magnitude and stoichiometry of export remain poorly characterized. We present data on biogeochemical and diatom export fluxes from the annual deployment of a sediment trap in a High Nutrient, Low Chlorophyll (HNLC) area upstream of the Kerguelen Plateau (KERFIX station). The weak and tidal-driven circulation provided favorable conditions for a quantitative analysis of export processes. Particulate organic carbon (POC) fluxes were highest in spring and summer. Biogenic silica (BSi) fluxes displayed similar seasonal patterns, although BSi:POC ratios were elevated in winter. *Fragilariopsis kerguelensis* dominated the annual diatom export assemblage (59.8 % of the total valve flux). We identified clusters of diatom species that were positively or negatively correlated to the BSi:POC ratio. Our results indicate that the differential role of certain diatom species for carbon and silicon export, previously identified from iron-fertilized productive areas, is also

28 valid in HNLC regimes. Although annual POC export below the mixed layer of the HNLC

29 site is two-fold lower that the one previously reported in a naturally iron-fertilized area of the

30 Kerguelen Plateau, the fraction of seasonal net community production exported is similar at

31 both sites (~ 1.5 %). These findings suggest that natural iron fertilization increases the

32 strength but not the efficiency of carbon export from the mixed layer.

33

Introduction

The Southern Ocean is the largest high nutrient, low chlorophyll (HNLC, Minas et al. 1986) area of the Global Ocean (Martin et al. 1990; Minas and Minas 1992). In open ocean areas of the Southern Ocean HNLC regime, low primary production is mainly attributable to iron limitation (Martin et al. 1990; de Baar et al. 1990; de Baar et al. 1995). However, in the vicinity of subantarctic islands and plateaus regions, iron inputs from shelf sediments and glacial melt represent a natural fertilization mechanism that can sustain long-lasting (several months) phytoplankton blooms (Blain et al. 2001; Blain et al. 2007; Pollard et al. 2007; Tarling et al. 2012). The fate of organic matter and carbon cycling within these blooms typically associated with strong air-to-sea CO_2 fluxes (Jouandet et al. 2008; Merlivat et al. 2015) have been addressed during multidisciplinary studies such as the KEOPS1 and KEOPS2 cruises near the Kerguelen Islands (Blain et al. 2008) , the CROZEX cruise around the Crozet islands (Pollard et al. 2009), and the DISCOVERY cruise near South Georgia (Tarling et al. 2012).

During the KEOPS cruises in spring and summer, short term measurement of carbon export using the ^{234}Th approach indicates a two-fold increase in carbon export in naturally fertilized waters compared to HNLC waters (Blain et al. 2007; Savoye et al. 2008; Planchon et al. 2015). However, an annual deployment of a moored sediment trap just below the mixed layer at the productive station A3 on the central Kerguelen Plateau (50°38 S − 72°02 E, Fig. 1) reported a low annual particulate organic carbon (POC) flux of 98.2 mmol m^{-2} yr^{-1} (Rembauville et al. 2015b). During the CROZEX study, ^{234}Th-derived export revealed similar patterns with a threefold higher export in the naturally fertilized area downstream of the Crozet Plateau when compared to the HNLC waters (Morris et al. 2007). Long-term moored sediment trap deployments (>3000 m) also revealed a twofold higher annual POC export in

60   the fertilized site when compared to the HNLC site, although POC fluxes were low (28.8 vs.

61   11.6 mmol m^{-2} yr^{-1}; Pollard et al., 2009).

62   Conceptual relationships between diatom community structure and carbon export have

63   been the subject of previous studies (Boyd and Newton 1995; Boyd and Newton 1999;

64   Quéguiner 2013). Detailed descriptions of diatom export assemblages from iron-fertilized

65   blooms in the Southern Ocean have highlighted the importance of diatom life cycle ecology

66   for the regulation of carbon and silicon export (Smetacek et al. 2004; Salter et al. 2007; Salter

67   et al. 2012; Smetacek et al. 2012; Assmy et al. 2013; Rembauville et al. 2015a). However,

68   despite significant levels of biomass production, low values of POC export have raised

69   questions concerning the efficiency of such systems to transfer carbon to depth through the

70   biological pump (Lam and Bishop 2007; Jacquet et al. 2011; Rembauville et al. 2015b) .

71   Indeed, the positive relationship between production and export efficiency observed in most

72   of the global ocean (Laws et al. 2011) appears to be invalid in the Southern Ocean (Maiti et

73   al. 2013). Furthermore, a recent global analysis comparing the fraction of microphytoplankton

74   with POC flux attenuation shows that highest attenuation coefficients occur in high latitude

75   regions (Guidi et al. 2015). These recent observations are consistent with the concept of high

76   biomass, low export (HBLE) regimes identified in certain regions of the Southern Ocean

77   (Lam and Bishop 2007), and thereafter at other locations of the global ocean (Lam et al.

78   2011). It has been suggested that in HBLE regimes, higher productivity does not necessarily

79   leads to higher carbon export but rather results in enhanced POC fragmentation,

80   remineralization (Obernosterer et al. 2008), and/or transfer to higher trophic levels (Huntley et

81   al. 1991). Certain regional studies support this scenario. For example, in a naturally fertilized

82   and diatom-dominated productive system downstream of South Georgia, highest zooplankton

83   biomass is associated with the lowest particle export efficiency (Cavan et al. 2015). Although

84   these snapshots offer intriguing insights into ecosystem function, they may be confounded by

4

85   the relatively short time-scales (days to weeks) characterizing the observations. Comparative

86   studies linking chemical fluxes to ecological vectors over seasonal and annual timescales

87   remain necessary to compare export efficiencies of HNLC and productive systems.

88   KERFIX (Kerguelen fixed station) was a five year observation program that ran from

89   1991 to 1995 (Jeandel et al. 1998) and was established as a component of the international

90   JGOFS program. The KERFIX station is located on the southwestern flank of the Kerguelen

91   Plateau (Fig. 1b). A key objective of the program was to describe the factors responsible for

92   low primary production in a region of the Antarctic Zone (AAZ) characterized by high

93   macronutrient concentrations. The monthly sampling program included hydrological variables

94   (Jeandel et al. 1998; Park et al. 1998), dissolved inorganic carbon and alkalinity (Louanchi et

95   al. 2001) as well as biological (Fiala et al. 1998; Razouls et al. 1998; Kopczyńska et al. 1998)

96   and geochemical parameters (Dehairs et al. 1996). These data were used to build and calibrate

97   numerical models to explain how the diatom spring bloom contributed to significant silicon

98   export despite an overall dominance of nanoplankton in these HNLC waters (Pondaven et al.

99   1998; Pondaven et al. 2000).

100   During the last two years of the KERFIX program (1993-1995), sediment traps were

101   deployed below the mixed layer with the aim of providing a coupled description of production

102   and export. Ternois et al. (1998) reported particulate organic carbon, hydrocarbon, sterol and

103   coccoliths export fluxes from a shallow sediment trap (175 m) over a 10-month time series

104   (April 1993 to January 1994). A high contribution of fresh (i.e., labile) marine organic

105   material was recorded during the summer and autumn months. During the winter months an

106   unresolved and complex mixture characterized the organic composition of particles and was

107   linked to zooplankton grazing. Despite these valuable insights, missing samples and position

108   of the sediment trap within the winter mixed layer (182 m, Park et al. 1998) prevented a

109   quantitative analysis of the export processes. A second sediment trap deployment was carried

110 out the following year at a slightly deeper position of 280 m covering a nearly complete

111 annual cycle. These samples provide a valuable opportunity to study the link between the

112 diatom flux assemblages and the intensity and stoichiometry of export in iron-limited HNLC

113 waters located 200 km upstream of the productive central Kerguelen Plateau.

114 In the present study, we report the biogeochemical fluxes (POC, particulate inorganic

115 carbon - PIC, biogenic silica - BSi) and diatom community composition of material collected

116 by a moored sediment trap deployed below the mixed layer in a low productivity area and

117 covering an entire annual cycle. Our aims are (1) to assess the reliability of the collected

118 fluxes by analyzing the physical characteristics of the deployment, (2) to investigate how

119 diatom community composition influences the magnitude of the POC flux and (3) examine

120 the seasonal export efficiency of this HNLC area in comparison to a more productive regime

121 on the central Kerguelen Plateau.

122

123 **Materials and methods**

124 **Sediment trap deployment and chemical analyses**

125 As part of the KERFIX program (Jeandel et al. 1998), a sediment trap was moored at the

126 HNLC station (50°40'S – 68°25'E), south of the Polar Front in the AAZ. The KERFIX

127 station is characterized by low phytoplankton biomass (Fiala et al. 1998; Kopczyńska et al.

128 1998) in comparison to the productive central Kerguelen Plateau (Fig. 1b). The sediment trap

129 (Technicap PPS5, 1 m^2 collecting area) was positioned at 280 m over a bottom depth of 2300

130 m. To prevent the intrusion of macrozooplankton and mesopelagic fish, the trap funnel was

131 equipped with a baffle (8 mm diameter cells) with an aspect ratio (height/diameter) of 6.2. A

132 current meter (Anderaa RCM7) was placed 20 m below the sediment trap and recorded

133 current speed, pressure and temperature with a 2 h interval. The sediment trap contained a 24-

134 sample carousel. Sample cups (280 mL) were filled with a preservative solution of hyper

135 saline seawater and 5 % formalin buffered to pH 8 with filtered (0.2 μm) sodium tetraborate.

136 The collection period was from the 19th February 1994 to the 22nd January 1995 (total = 337

137 days). Sampling intervals were programmed to reflect anticipated flux patterns with the

138 highest temporal resolution in spring and summer (7-10 days) and the lowest in winter (30

139 days). Following the recovery of the sediment trap, 50 mL of supernatant was withdrawn

140 from the sample and 1 mL of buffered preservative solution was added. Samples were sieved

141 through a 1.5 mm mesh and both fractions were examined under binocular microscope to

142 manually remove swimmers (organisms actively entering the trap). After the removal of

143 swimmers, both size fractions were combined and the samples were split into 1/8 aliquots

144 using a Folsom splitter (McEwen et al. 1954) with an error of <5 % (Sell and Evans 1982).

145 Prior to chemical analysis, wet aliquots were centrifuged and rinsed with milli-Q water

146 (10 minutes at 5000 rpm, three times) to remove excess salt and formalin. The supernatant

147 was withdrawn and the resulting pellet freeze-dried (FTS systems DURA DRY). Mass flux

148 was determined from the weight of the lyophilized pellet (Mettler-Toledo AE163 balance, 10

149 μg precision). For POC, 3-5 mg of freeze-dried pellet (Sartorius M3P balance, 1 μg precision)

150 was placed in silver cups and phosphoric acid (1 N) added in excess to dissolve $CaCO_3$. POC

151 content was measured with a CHN analyzer (Heraeus CHN-O-Rapid) calibrated with

152 acetanilide (Miquel et al. 1994). The precision derived from repeated measurements of carbon

153 on the acetanilide standard was 1.4 %. For BSi, a kinetic method (DeMaster 1981) was used

154 as described in Mosseri et al. (2005). Briefly, 5-10 mg of freeze-dried material was weighed

155 and placed in centrifuge tubes with 40 mL of ultrapure NaOH (0.2 N). The samples were

156 placed in a water bath at 95 °C and 200 μL of solution were removed after 1, 2, 3 and 4 h and

157 placed into scintillation vials and made up to 10 mL with milli-Q water. Silicic acid

158 concentrations were determined colorimetrically on a Skalar autoanalyser following (Aminot

159 and Kerouel 2007). The BSi content was determined by fitting a linear regression to silicic

160 acid concentration as a function of extraction time. The intercept of this relationship is taken

161 as BSi content without interference of silicon leaching from lithogenic material (DeMaster

162 1981). PIC was determined from direct measurement of calcium (Ca). 5 mg of freeze-dried

163 material was mineralized in Teflon vials by adding 0.5 mL of 65 % HNO_3 and 0.5 mL of 40

164 % HF. Samples were ultrasonicated and dried at 40°C overnight. This residue was dissolved

165 in 10 mL of 0.1 N HNO_3 and the calcium concentrations determined by coupled plasma-

166 optical emission spectrometry (ICP-OES, HORIBA Jobin Yvon 48 and 38). The flux for the

167 unsampled month (February 1995) was estimated from the mean flux of the time series and

168 used to estimate the annually integrated values POC, PIC and BSi fluxes.

169 **Slides preparation and diatom taxonomy**

170 Samples for diatom taxonomy were prepared using a micropaleontological oxidative method

171 as previously described in Romero et al. (1999). Briefly, a 1/8 wet aliquot was placed in a

172 beaker and oxidized with potassium permanganate (20 mL, 65 g L^{-1}), hydrochloric acid (50

173 mL, 37 %) and hydrogen peroxide (40 mL, 35 %) at 95 °C. Samples were then rinsed with

174 milli-Q water and centrifuged several times until the pH was equivalent to that of the milli-Q

175 water. Three slides were prepared per sample using a random settling method (Bárcena and

176 Abrantes 1998). Slides were observed under an inverted microscope with phase contrast

177 (Olympus BH2) at 400 and 1000 x magnification. A minimum of 400 valves were enumerated

178 per sample following Schrader and Gersonde (1978) and diatoms were identified to the

179 species level following Hasle and Syvertsen (1997). Diatom counts were not possible in the

180 last two sample cups (January 1995) due to the very low quantity of material.

181 Contrary to more recent sediment trap studies in which diatom counts were made

182 through direct observation of untreated samples (Salter et al. 2007; Salter et al. 2012;

183 Rembauville et al. 2015a; Rembauville et al. 2016a), at the time of the KERFIX program a

184 micropaleontological counting technique was used. The micropaleontological method was

185 originally developed for samples originating from sediment cores. The oxidation and multiple

186 centrifugation steps remove organic cell contents and separate diatom cells into valves and

187 girdle bands. Although these chemical oxidation steps aid in the detailed taxonomic

188 characterization of specimens, the destruction of organic matter prevents the distinction of full

189 and empty frustules and consequently the contribution of individual diatom species to total

190 POC export fluxes cannot be quantified (Rembauville et al. 2015a). Moreover the treatment

191 might selectively alter the lightly silicified species (Rembauville et al. 2015a), or lead to the

192 overestimation of some species with numerous girdle bands per cell such as *Dactyliosolen*

193 *antarcticus*. A cross validation of the two counting techniques would certainly be of interest at

194 this HNLC site. Unfortunately, however, there are no longer samples available to make such a

195 comparison. The biogeochemical and diatom taxonomy data are accessible at http://www.obs-

196 vlfr.fr/cd_rom_dmtt/OTHER/KERFIX/trapdata/.

197 **Numerical and statistical analyses**

198 To identify the major periods of current speed variations, current speed data was analyzed

199 using fast Fourier transform (FFT). The resulting power spectrum was compared to a red

200 noise, a theoretical signal in which the amplitude decreases with increasing frequency. The

201 red noise was considered as a null hypothesis and scaled to the power spectrum to identify

202 periods that differs significantly from a random distribution (Schulz and Mudelsee 2002).

203 To categorize the major diatom groups that were exported with similar seasonality, a

204 clustering analysis (Bray-Curtis distance, unweighted pair group method with arithmetic mean

205 – UPGMA agglomeration criteria) was performed on the relative abundance of diatom taxa

206 accounting for more than 1 % of the total annual diatom export (11 species). The association

207 of these major species with the BSi:POC ratio was studied using partial least square

208 regression (PLSR). The principle of PLSR is to decompose the predictors matrix (here the

209 valve fluxes of the 11 main diatom taxa) into few principal components and then perform a

210 regression of the response variable (here the BSi:POC ratio) on these components. A

211 significant advantage of PLSR is to avoid the weight of colinearity of the multiple predictors

212 which is a common feature of species assemblage data (Abdi 2010). Previous studies have

213 shown PLSR to be a useful statistical approach linking biological diversity to environmental

214 factors in the ocean (Salter et al. 2014a; Rembauville et al. 2015a). The PLSR was performed

215 on standardized variables (mean subtracted, divided by the standard deviation).

216

217 **Results**

218 **Hydrological context**

219 The trap depth gradually decreased by 4 meter (284 m to 280 m) from February to June 1994

220 and remained at 280 m until the recovery (Fig. 2a). No strong depth oscillation was observed

221 except during two short deepening events (4-6 m amplitude) that occurred in February and

222 September 1994. Temperature remained mostly constant between 1.8 and 2.2 °C except

223 during one short event from 20 to 30 March 1994 where temperature decreased to 1 °C (Fig.

224 2b). This event was not associated with any particular depth or current speed variation.

225 Current speed ranged from <1 to 30 cm s^{-1} and displayed a highly variable signal over short

226 time scales (Fig. 2c). There were no obvious seasonal patterns in current speed distribution

227 and 74 % of the current speed data was <12 cm s^{-1}.

228   The progressive vector diagram displayed numerous tidal ellipses over short

229 timescales (hours to days, Fig. 3a). The integrated displacement over one year corresponds to

230 a 450 km northward advection. Higher frequencies were observed for northwestward flow

231 when current speeds exceeded 20 cm s^{-1} (Fig. 3b). Conversely, the southwestward flow

232 displayed lower frequencies and was mainly characterized by speeds <10 cm s^{-1}. Six

233   significant peaks corresponding to tidal components were observed. Short timescale peaks

234   (6.2 h and 6.8 h period) corresponded to a combination of tidal components of longer periods.

235   The moon 2 (M2, 12.4 h period) tidal component was present, and long-term components (3 d

236   and 14 d period) were also observed.

237   **Biogeochemical fluxes**

238   Chlorophyll *a* concentrations started to increase in October 1993 from 0.2 µg L^{-1} to reach 1 µg

239   L^{-1} in mid December 1993 when mixed layer depth (MLD, data from was the shallowest (60

240   m, Fig. 4a). A significant proportion of the phytoplankton biomass (70 %) was located below

241   the MLD. The MLD gradually decreased to 185 m in August 1994 concomitantly with a

242   decrease in chlorophyll *a* to 0.2 µg L^{-1}. A second spring bloom occurred in November 1994

243   reaching a maximum of 1.2 µg L^{-1} in December and was also associated with a shoaling of the

244   MLD.

245   POC flux was highest in late summer (February 1994) following the sediment trap

246   deployment (0.9 mmol m^{-2} d^{-1}) and decreased to 0.10 - 0.25 mmol m^{-2} d^{-1} in autumn (Table 1,

247   Fig. 4b). Winter fluxes were negligible (<0.1 mmol m^{-2} d^{-1} from July to October 1994). A

248   small increase in POC flux of up to 0.25 mmol m^{-2} d^{-1} occurred concomitantly with the

249   phytoplankton bloom in November-December 1994. Annual POC export flux was estimated

250   at 51.6 mmol m^{-2} yr^{-1}. PIC fluxes were low in late summer (25 - 75 µmol m^{-2} d^{-1}, Table 1, Fig.

251   4b), negligible in winter, and increased to 50 – 160 µmol m^{-2} d^{-1} during the spring bloom

252   (November-December 1994). The annual PIC export flux was estimated at 7.7 mmol m^{-2} yr^{-1}.

253   BSi flux showed a similar seasonal pattern to POC with highest fluxes in late summer

254   (1 - 2 mmol m^{-2} d^{-1} in February – March 1994), moderate fluxes in autumn (~0.5 mmol m^{-2} d^{-}

255   ^{1}), and negligible fluxes in winter (Table 1, Fig. 4c). A small but noticeable increase was

256   observed during the spring bloom (up to 0.4 mmol m^{-2} d^{-1}). The BSi:POC molar ratio

257　　displayed a clear seasonal pattern with a value close to 2 in late summer, increasing to 3.9 in

258　　autumn. Winter values were <0.5, increasing to ~1.8 during the spring bloom. The annually

259　　integrated BSi:POC ratio (annual BSi flux divided by annual POC flux) was 2.2.

260　　**Diatom fluxes**

261　　The seasonal pattern of total diatom valve flux mirrored that of POC with the highest flux

262　　observed in the first sample cup (1.3×10^8 valve m^{-2} d^{-1}, Table 1, Fig. 5a), decreasing

263　　gradually in autumn to reach very low values in winter (1×10^6 valve m^{-2} d^{-1}). Total diatom

264　　valve flux increased again during the spring bloom to 3.5×10^7 valve m^{-2} d^{-1}.

265　　*Fragilariopsis kerguelensis* dominated the diatom export assemblage on an annual

266　　scale (59.8 %), with the highest relative contribution in winter (>70 % of the diatom

267　　assemblage in August). This species presented a notable export peak in summer (6×10^7

268　　valve m^{-2} d^{-1}, Fig. 5b) and lower values during spring (1×10^7 valve m^{-2} d^{-1}). Other diatom

269　　species displayed export peaks during both spring and summer such as *Thalassionema*

270　　*nitzschiodes* (16 % of the diatom community in November), *Fragilariopsis rhombica* (5 %),

271　　*Thalassiosira gracilis* (4 %), *Navicula directa* (6 %) and *Dactyliosolen antarcticus* (9 %). By

272　　contrast, certain species presented a preferential summer export peak such as *Chaetoceros*

273　　subgenus *Hyalochaete* resting spores (CRS, 10 % of the diatom assemblage in February),

274　　*Pseudo-nitzschia lineola* (10 %), *Pseudo-nitzschia heimii* (5 %), and *Chaetoceros socialis*

275　　(2.7 %).

276　　Two main clusters were identified based on the largest distance break after the first

277　　node of the dendrogram constructed with the diatom valve flux in each sediment trap sample

278　　cup (Fig. 6a). The coefficient of determination (R^2) of the PLSR model was 0.68. A first

279　　cluster was composed of *F. rhombica*, *F. kerguelensis*, *T. gracilis*, *N. directa*, *T. nitzschioides*

280　　and *D. antarcticus*. These species displayed two peaks in their export flux in late summer

281   1994 and spring 1995 (Fig. 5) and were positively correlated with the BSi:POC ratio (0.18 < β

282   < 0.5, Fig. 6b), except for *T. nitzschioides* (β = -0.03). A second cluster contained *F.*

283   *pseudonana*, *P-N. heimii*, *P.-N. lineola; T. oestrupuii*, and CRS. These species displayed a

284   clear mid-summer export peak in February 1994 and very low fluxes in spring 1995. They

285   were negatively correlated with the BSi:POC ratio (-0.18 < β < -0.05). Finally, *C. socialis*

286   constituted the outer branch of the dendrogram, displayed a clear mid-summer export peak

287   and was negatively correlated with the BSi:POC ratio (β = -0.23).

288

289   **Discussion**

290   **Hydrological context and sediment trap record reliability**

291   The mean temperature of ~2 °C observed over the course of the year is consistent with the

292   temperature of water masses just below the winter waters (WW) reported at the same station

293   (Park et al. 1998). The abrupt decrease in temperature to 1 °C at the end of March is unusual

294   considering the lowest recorded temperature of winter water (WW) is 1.8 °C (Park et al.

295   1998). Nevertheless, Park et al. (1998) reported the largest steric height negative anomaly

296   during the same period (February - March 1994). Such a major and abrupt change in water

297   mass circulation could entrain very cold WW northward and explain the observed temperature

298   decrease. Although the exact reason for this temperature change remains unresolved, it did not

299   affect the sediment trap depth and was not associated with any change in current speed and

300   therefore probably poorly affected the sediment trap collection efficiency. Current speed

301   variations were associated with tidal components (Fig. 3c). A similar finding was found on

302   the central Kerguelen Plateau, with a major contribution of the M2 tidal component

303   (Rembauville et al. 2015b). At KERFIX, the tidal components are more diverse and contain

304   components of diurnal and semi-diurnal waves. The additional complexity may arise from the

305   proximity of the plateau flank where most of the tidal energy is dissipated (Maraldi et al.

306   2011). Overall, the observations are entirely consistent with short-term observations of tidal-

307   driven water masses displacement (Park et al. 2008a) and emphasize the importance of tides

308   for circulation around the Kerguelen Plateau.

309   The KERFIX sediment trap deployment location was characterized by a major

310   northwestward flow. As the Antarctic Circumpolar Current encounters the Kerguelen Plateau,

311   most of the surface water continues an eastward flow over the central plateau, although deeper

312   currents appear to exhibit a northward inflection when they meet the western flank of the

313   plateau at the KERFIX location (Park et al. 2008b). The pseudo-Lagrangian view of the

314   progressive vector diagram is therefore consistent with the current understanding of

315   circulation in the study area. The progressive vector diagram (Fig. 3a) reflects the 450 km

316   northward displacement in one year which corresponds to advection with a mean speed of 1.4

317   cm s^{-1}. This is comparable to the range of sinking speeds reported for marine particles in the

318   region (0.01-1.1 cm s^{-1}, Laurenceau-Cornec et al. 2015) and thus advection should not have

319   transported particles far away from the overlying surface before they reach the shallow trap

320   depth (280 m). From July to November 1994, the flow is clearly westward and we cannot

321   rule-out a possible contribution from particles originating from the near central Kerguelen

322   Plateau. However, this contribution would be minor at annual scale because the POC flux

323   during the corresponding period is the lowest recorded (<0.05 mmol m^{-2} d^{-1}).

324   It is widely acknowledged that shallow sediment trap deployments are prone to

325   hydrodynamic artifacts (Gardner 1980; Buesseler et al. 2007). The low aspect ratio (1.7) and

326   conical funnel shape of the PPS5 could render this design more susceptible to hydrodynamic

327   artifacts (Hawley 1988; Buesseler et al. 2007). A current speed of 12 cm s^{-1} is often invoked

328   as an upper limit for the reliability of moored sediment trap (Baker et al. 1988). During the

329   KERFIX deployment, 74 % of the current speed data is below this threshold. However, some

330 current speeds increased episodically to 20 cm s^{-1} in February/March and October/November

331 1994. These two periods correspond to the highest and lowest POC fluxes, respectively.

332 Although the hydrological data generally suggest that the sediment trap was not subject to

333 major hydrodynamic biases, episodic events (~10 days) of current increase might have

334 impacted the sediment trap collection efficiency at short time scale (Gardner 1980; Baker et

335 al. 1988).

336   The sediment trap used in the present study was equipped with an 8 mm baffle (aspect

337 ratio of the baffle: 6.2). This design is typically considered to prevent the intrusion of large

338 organisms (e.g. fishes) into sediment traps, but has no effect on smaller swimmers feeding on

339 the trap funnel (Buesseler et al., 2007) or swimmers intrusion within the sampling cup

340 (Nodder and Alexander 1999). Although swimmers were removed before chemical analyzes,

341 unfortunately there is no record of swimmer abundance and diversity. These data would have

342 helped to address the potential impact of swimmers on trapping efficiency, and provided

343 additional information on the seasonal succession of biological communities (e.g. Matsuno et

344 al. 2014; Rembauville et al. 2015b). Unfortunately with the present dataset we cannot rule-out

345 a potential biological bias associated with the swimmers and we cannot explicitly address

346 trapping efficiencies as has been carried out in previous studies (Coppola et al. 2002;

347 Buesseler et al. 2010).

348   **Export seasonality and diatom export assemblage**

349 The annual record presented in this study covers 337 days from summer 1994 to summer

350 1995 and is therefore considered representative of the main seasonal transitions at the

351 KERFIX site. Both POC and BSi fluxes display clear late-summer maxima. It seems probable

352 that any export production originating from the 1993 phytoplankton bloom would have

353 occurred during the summer prior to the sediment trap deployment. The timing of the export

354 in spring 1994 is closely associated with the development of the spring phytoplankton bloom,

15

355   in contrast to the one month lag observed at the productive A3 station of the central

356   Kerguelen Plateau (Rembauville et al. 2015b). We previously attributed the temporal lag at

357   A3 to the formation and export of diatom resting spores that dominate POC flux (60-80 %)

358   during export events that occur 1 month later than surface chlorophyll *a* peaks (Rembauville

359   et al. 2015a). A similar time lag and export mechanism was also observed in the naturally

360   fertilized waters of South Georgia (Rembauville et al. 2016a). The coupling between

361   production and export at the KERFIX site would suggest that other export vectors aside from

362   diatom spore formation may be important in HNLC regimes.

363   CRS represent a minor contribution to the exported diatom community at the KERFIX

364   station (5.6 %), whereas they were the dominant component (70 %) at the productive A3

365   station (Rembauville et al. 2015a). The vegetative stages of *Chaetoceros Hyalochaete* are a

366   minor fraction of the mixed layer diatom assemblage at KERFIX (Fiala et al. 1998) where the

367   deep waters (2300 m) probably prevent the exported resting stage to be transported back in

368   the mixed layer to complete the life cycle (McQuoid and Hobson 1996). It was further

369   hypothesized that a strong decrease in silicic acid concentration in late summer in naturally

370   iron-fertilized areas could trigger diatom resting spore formation (Salter et al. 2012;

371   Rembauville et al. 2015a). The silicic acid concentration in the mixed layer in summer at

372   KERFIX never reaches values lower than 9 µmol L^{-1} (Jeandel et al. 1998) whereas it is almost

373   depleted (~1 µmol L^{-1}) over the central Kerguelen Plateau (Mosseri et al. 2008). These results

374   are consistent with the observation of a strict dominance of *Eucampia antarctica* var.

375   *antarctica* resting spores to the diatom export assemblage in the productive stations

376   downstream the Crozet Islands where silicic acid is depleted in summer, and negligible

377   contribution of resting spores in the upstream HNLC area (Moore et al. 2007; Salter et al.

378   2007).

379   The exported diatom assemblage at the KERFIX station was strictly dominated by *F.*

380   *kerguelensis* (59.8 %), consistent with its dominance in the mixed layer (Fiala et al. 1998;

381   Kopczyńska et al. 1998). *Fragilariopsis kerguelensis* typically dominates diatom export

382   assemblages in the vast HNLC areas of the Southern Ocean (Romero and Armand 2010;

383   Grigorov et al. 2014; Rigual-Hernández et al. 2015a,b), and it is the most abundant species in

384   the silica ooze under the Antarctic circumpolar current (Zielinski and Gersonde 1997). Its

385   strong and thick frustules, together with its ability to form long chains, might protect this

386   species from grazing pressure in the AAZ and contribute towards its ecological success

387   (Hamm et al. 2003; Smetacek et al. 2004; Crosta et al. 2005).

388   Clustering analysis delineates groups of diatom species that were exported with a

389   specific seasonality and the PLSR highlights the link between the timing of export of certain

390   diatom groups and the BSi:POC signature of export. Although correlation coefficients are

391   based on co-occurence and do not necessary imply causality, the observed relationships seem

392   consistent with the ecological characteristics of the diatom species. For example *F.*

393   *kerguelensis* and *T. gracilis* were present in export assemblages throughout the year with

394   peaks in spring and summer and the PLSR suggests a positive correlation between the flux of

395   these species and the BSi:POC ratio. This is consistent with the fact that *Fragilariopsis* is

396   frequently observed as empty frustules in both natural and artificial fertilization experiments

397   (Smetacek et al. 2004; Salter et al. 2012; Assmy et al. 2013). A detailed quantitative analysis

398   of exported diatom assemblages from the productive waters of the central Kerguelen Plateau

399   shows empty cells of *F. kerguelensis* and small centric species (comprising *T. gracilis*)

400   dominating spring export fluxes coinciding with the lowest POC flux and the highest

401   BSi:POC ratio (Rembauville et al. 2015a). These results suggest that these species with very

402   robust frustules predominantly contribute to the export of silicon (Smetacek et al. 2004;

403   Assmy et al. 2013). Other species displayed a clear mid-summer export peak and were

404   clustered together such as CRS and *Pseudo-Nitschia* spp. These two diatom groups were

405   found to be mostly exported as full cells in the productive area of the Kerguelen Plateau

406   (Rembauville et al. 2015a). Consistently with that, *Pseudo-nitzschia lineola*, and *Chaetoceros*

407   *Hyalochaete* were also positively associated with POC flux in a deeper (800 m) sediment trap

408   in the Polar Frontal Zone south of Tasmania (Rigual-Hernández et al. 2015a). *C. socialis*

409   displayed a clear mid-summer export peak and was also negatively correlated with the

410   BSi:POC ratio. This lightly silicified species is thought to contribute predominantly to

411   phytoaggregate formation (Alldredge et al. 1995) with a potentially important contribution to

412   carbon export at the end of phytoplankton blooms (Booth et al. 2002).

413   The phytoplankton community at KERFIX is dominated at annual scale by small

414   flagellates (2-10 µm) and mostly represented by Prasinophyceae and Cryptophyceae (Fiala et

415   al. 1998; Kopczyńska et al. 1998). Therefore, in contrast with a diatom-dominated system

416   such as the central Kerguelen Plateau, the seasonality of the BSi:POC ratio at KERFIX is

417   likely to be influenced by processes that are not quantified here (e.g. faecal pellet and/or non-

418   diatom phytoplankton contribution to POC flux). However, the PLSR suggests that the

419   diatom community structure remains an important ecological factor influencing the BSi:POC

420   export ratio. A precise quantification of the fraction of full and empty cells (Assmy et al.

421   2013), together with the contribution of non-diatom cells and faecal pellets is necessary to

422   fully quantify their relative contributions to POC flux (Rembauville et al. 2015a). Finally, the

423   use of modern techniques allowing the quantification of the BSi content at the cellular level

424   (e.g., Twining et al. 2004; Jungandreas et al. 2012) might help to refine the importance of

425   diatom community structure for the BSi:POC stoichiometry of export at HNLC sites.

426   Calcifying planktonic organisms were not quantified in the export assemblages as part

427   of the present study. Nevertheless, the seasonality of the PIC flux can be compared with the

428   abundance of calcifying communities in the mixed layer. The marked increase in

429　coccolithophore biomass in the mixed layer (Fiala et al. 1998; Kopczyńska et al. 1998) occurs

430　concomitantly with the highest PIC flux observed in the sediment trap (from November 1994

431　to January 1995). Pteropods are a minor component (<7 % of the mesozooplankton

432　abundance) of the zooplankton assemblage at KERFIX in summer (Carlotti et al. 2008) and

433　low foraminifera abundances are typical for the AAZ (Mortyn and Charles 2003; Bergami et

434　al. 2009; Lombard et al. 2011). Coccolithophore-derived $CaCO_3$ has been recently shown to

435　dominate (85 %) PIC export at the productive A3 station (Rembauville et al. 2016b). During

436　the 1993-1994 sediment trap deployment at KERFIX, Ternois et al. (1998) have reported the

437　highest coccolith export flux (>99 % contributed by *E. huxleyi*) in January 1994 at the same

438　period of the year than the highest PIC export we report in January 1995. These results

439　implies that coccolithophores might also strongly contribute to PIC export under HNLC

440　conditions, although a more detailed analysis of the exported calcifying plankton community

441　is required to confirm this hypothesis.

442　**Comparison with the iron-fertilized productive central Kerguelen Plateau**

443　　　　We carried out a comparison of water column and shallow sediment trap data from the

444　KERFIX (HNLC) and nearby A3 site (productive) in an attempt to elucidate the impact of

445　iron availability on production and export processes around the Kerguelen Plateau (Table 2).

446　The annual sediment trap records at KERFIX and A3 are separated by 17 years and may

447　themselves be influenced by inter annual variability and climate-driven, long-term trends

448　possibly associated with changes in the plankton community structure (Alvain et al. 2013;

449　Boyd et al. 2016, Davidson et al. 2016). However, there are no in situ data available at the two

450　stations with a sufficient time coverage to quantify such climate-driven changes (Henson et al.

451　2016). Furthermore, the sediment traps deployed at KERFIX and A3 were different models

452　(Technicap PPS5 and PPS3, respectively) that differ in their funnel shape and aspect ratio. We

453　cannot eliminate the possibility that these designs may have been subject to different

454 hydrodynamic and biological biases that alter the collection efficiency of sinking particles

455 (Hawley 1988; Buesseler et al. 2007). Nevertheless, the low and tidal-driven circulation

456 observed at both KERFIX and A3 (Rembauville et al. 2015b) should not result in large bias

457 when flux estimates from both stations are compared.

458   An upper limit of $1\mu g\ L^{-1}$ for chlorophyll *a* concentration has been suggested as a

459 threshold to define HNLC conditions (Tyrrell et al. 2005). Under this definition, the KERFIX

460 station lies in the upper limit of what is considered as HNLC conditions. The annual POC flux

461 at 300 m at KERFIX (52 mmol $m^{-2}\ yr^{-1}$) is in the same range as deep ocean POC fluxes

462 reported from other non-fertilized areas of the AAZ (33 mmol $m^{-2}\ yr^{-1}$ at 2200 m, Fischer et

463 al. 2002, 35 mmol $m^{-2}\ yr^{-1}$ at 1300 m, Tesi et al. 2012, 102 mmol $m^{-2}\ yr^{-1}$ at 2000 m Rigual-

464 Hernández et al. 2015b). This suggests that important processes determining the magnitude of

465 POC export in the AAZ occur in the upper layers of ocean.

466   One major difference between the two sites is a two-fold higher annual BSi:POC ratio

467 under HNLC conditions. This is similar to the 2-3.5 fold difference in BSi:POC ratio found in

468 deep sediment traps (>2000 m) between HNLC and iron-fertilized productive waters around

469 the Crozet Plateau (Salter et al. 2012). At KERFIX the maximum fluxes of *F. kerguelensis* are

470 one order of magnitude higher than at A3 and this species dominates the diatom export

471 assemblage (60 %) at this HNLC site compared to at A3 (10 %, Rembauville et al. 2015a). *F.*

472 *kerguelensis* is a strongly silicified species (Smetacek et al. 2004; Assmy et al. 2013) that

473 likely contributes to the higher BSi:POC export ratio on seasonal and annual time scales

474 (Rembauville et al. 2015a). Similar observations were made at Crozet where the fluxes of

475 heavily silicified and/or large species (*F. kerguelensis*, *C. pennatum* and *Dactyliosolen*

476 *antarcticus*) were higher under HNLC conditions (Salter et al. 2012). Although non-diatom

477 components may influence POC fluxes, it is apparent that iron limitation favors the ecological

20

478   selection of large and heavily silicified diatoms with a measurable and consistent effect on

479   BSi:POC export stoichiometry (Smetacek et al. 2004).

480   Annual PIC export is similar at the KERFIX and A3 stations (~7 mmol m^{-2} yr^{-1}). This

481   is in stark contrast to the Crozet Plateau where deep-ocean PIC fluxes were 7-10 times higher

482   at the iron-fertilized productive site (Salter et al. 2014b). These differences are likely related

483   to the position of the two plateaus relative to the Polar and Subantarctic Fronts. Indeed the

484   abundance of calcifying phyto- and zooplankton generally decreases south of the Polar Front

485   (e.g., Mortyn and Charles 2003; Hunt et al. 2008; Saavedra-Pellitero et al. 2014), leading to a

486   much lower PIC:POC export ratio (see a data compilation by Salter et al. 2014b).

487   Foraminifera are a dominant component of PIC fluxes at the Crozet Plateau north of the Polar

488   Front and pteropod aragonite fluxes are notably enhanced (Salter et al. 2014b). In contrast,

489   coccoliths of *Emiliania huxleyi* dominate the PIC export at A3 south of the Polar Front

490   (Rembauville et al. 2016b) and it is likely that they also contributed to PIC export at KERFIX

491   (Ternois et al. 1998). South of the Polar Front, the cosmopolitan species *E. huxleyi* dominates

492   the coccolithophore community composition (Saavedra-Pellitero et al. 2014; Winter et al.

493   2014). This species is known to prevail under low iron concentrations (Brand et al. 1983;

494   Muggli and Harrison 1997) and coccolithophore blooms are strongly temperature-dependant

495   in the high latitude ocean (Sadeghi et al. 2012). Therefore, the similarity in nitrate and

496   phosphate concentrations (Blain et al. 2015) and summer temperature may explain the

497   similarity of PIC fluxes mechanisms at both KERFIX and A3. These results support the idea

498   that the location of iron fertilization relative to the SAF and PF determines the magnitude of a

499   carbonate counter pump effect due to frontal zonation of calcifying plankton assemblages

500   (Salter et al. 2014b; Rembauville et al. 2016b).

501   The seasonal net community production (NCP, net primary production minus

502   heterotrophic respiration integrated during the productive period) derived from DIC budgets is

503   two-fold higher at A3 compared to KERFIX, although maximum primary production levels

504   are four-fold higher at A3 (Table 2). Similar to NCP, annual POC export is two-fold higher at

505   A3. Hence, the fraction of net community production exported annually from the mixed layer

506   is similar at the productive station A3 (1.5 %) and the HNLC station KERFIX (1.7 %).

507   However, it must be stressed that estimates of seasonal NCP rely on DIC distribution and are

508   associated with important uncertainties (Jouandet et al. 2008), and potentially strong inter

509   annual variability (Louanchi et al. 2001).

510   Despite the limitations outlined above our estimates suggest that the HNLC

511   environment exports a similarly low fraction of seasonal NCP (<10 %, assuming two-fold

512   uncertainty on both NCP and export) when compared to a productive iron-fertilized regime

513   (A3 station, Rembauville et al. 2015a). Previous short term estimates of production and export

514   have demonstrated the inverse relationship between primary production and export efficiency

515   in the Southern Ocean (Maiti et al. 2013). An artificial fertilization study concluded that iron

516   addition does not increase the export efficiency at short time scales (Lam and Bishop 2007).

517   Our findings support the notion that although natural iron fertilization in the Southern Ocean

518   increases carbon export out of the mixed layer (Blain et al. 2007; Pollard et al. 2009), it does

519   not appear to increase the efficiency the biological carbon export over annual timescales.

520   These results highlight the need to study the ecosystem processes responsible for the low

521   export efficiency to fully understand carbon pathways from primary production to export

522   (Huntley et al. 1991; Lam and Bishop 2007; Stukel et al. 2015; Le Moigne et al. 2016).

References

531 Abdi H (2010) Partial least squares regression and projection on latent structure regression (PLS Regression).
533 Wiley Interdisc Rev Comput Stat 2:97–106. doi: 10.1002/wics.51

534 Alldredge AL, Gotschalk C, Passow U, Riebesell U (1995) Mass aggregation of diatom blooms: Insights from a
535 mesocosm study. Deep Sea Res Part 2 Top Stud Oceanogr 42:9–27. doi: 10.1016/0967-0645(95)00002-
536 8

537 Alvain S, Le Quéré C, Bopp L, et al (2013) Rapid climatic driven shifts of diatoms at high latitudes. Remote
538 Sens Environ 132:195–201. doi: 10.1016/j.rse.2013.01.014

539 Aminot A, Kerouel R (2007) Dosage automatique des nutriments dans les eaux marines: méthodes en flux
540 continu. Ifremer, Plouzané, France

541 Assmy P, Smetacek V, Montresor M, et al (2013) Thick-shelled, grazer-protected diatoms decouple ocean
542 carbon and silicon cycles in the iron-limited Antarctic Circumpolar Current. Proc Natl Acad Sci
543 110:20633–20638. doi: 10.1073/pnas.1309345110

544 Baker ET, Milburn HB, Tennant DA (1988) Field assessment of sediment trap efficiency under varying flow
545 conditions. J Mar Res 46:573–592. doi: 10.1357/002224088785113522

546 Bárcena MA, Abrantes F (1998) Evidence of a high-productivity area off the coast of Málaga from studies of
547 diatoms in surface sediments. Mar Micropaleontol 35:91–103. doi: 10.1016/S0377-8398(98)00012-7

548 Bergami C, Capotondi L, Langone L, et al (2009) Distribution of living planktonic foraminifera in the Ross Sea
549 and the Pacific sector of the Southern Ocean (Antarctica). Mar Micropaleontol 73:37–48. doi:
550 10.1016/j.marmicro.2009.06.007

551 Blain S, Capparos J, Guéneuguès A, et al (2015) Distributions and stoichiometry of dissolved nitrogen and
552 phosphorus in the iron-fertilized region near Kerguelen (Southern Ocean). Biogeosciences 12:623–635.
553 doi: 10.5194/bg-12-623-2015

554 Blain S, Quéguiner B, Armand L, et al (2007) Effect of natural iron fertilization on carbon sequestration in the
555 Southern Ocean. Nature 446:1070–1074. doi: 10.1038/nature05700

556 Blain S, Quéguiner B, Trull T (2008) The natural iron fertilization experiment KEOPS (KErguelen Ocean and
557 Plateau compared Study): An overview. Deep Sea Res Part 2 Top Stud Oceanogr 55:559–565. doi:
558 10.1016/j.dsr2.2008.01.002

559 Blain S, Tréguer P, Belviso S, et al (2001) A biogeochemical study of the island mass effect in the context of the
560 iron hypothesis: Kerguelen Islands, Southern Ocean. Deep Sea Res Part 1 Oceanogr Res Pap 48:163–
561 187. doi: 10.1016/S0967-0637(00)00047-9

562 Booth BC, Larouche P, Bélanger S, et al (2002) Dynamics of Chaetoceros socialis blooms in the North Water.
563 Deep Sea Res Part 2 Top Stud Oceanogr 49:5003–5025. doi: 10.1016/S0967-0645(02)00175-3

564 Boyd PW, Dillingham PW, McGraw CM, et al (2016) Physiological responses of a Southern Ocean diatom to
565 complex future ocean conditions. Nature Clim Change 6:207–213. doi: 10.1038/nclimate2811

566 Boyd PW, Newton PP (1995) Evidence of the potential influence of planktonic community structure on the
567 interannual variability of particulate organic carbon flux. Deep Sea Res Part 1 Oceanogr Res Pap
568 42:619–639. doi: 10.1016/0967-0637(95)00017-Z

569 Boyd PW, Newton PP (1999) Does planktonic community structure determine downward particulate organic
570 carbon flux in different oceanic provinces? Deep Sea Res Part 1 Oceanogr Res Pap 46:63–91. doi:
571 10.1016/S0967-0637(98)00066-1

572 Brand LE, Sunda WG, Guillard RRL (1983) Limitation of marine phytoplankton reproductive rates by zinc,
573 manganese, and iron. Limnol Oceanogr 28:1182–1198. doi: 10.4319/lo.1983.28.6.1182

574 Buesseler KO, Antia AN, Chen M, et al (2007) An assessment of the use of sediment traps for estimating upper
575   ocean particle fluxes. J Mar Res 65:345–416.

576 Buesseler KO, McDonnell AMP, Schofield OME, et al (2010) High particle export over the continental shelf of
577   the west Antarctic Peninsula. Geophys Res Lett 37:L22606. doi: 10.1029/2010GL045448

578 Carlotti F, Thibault-Botha D, Nowaczyk A, Lefèvre D (2008) Zooplankton community structure, biomass and
579   role in carbon fluxes during the second half of a phytoplankton bloom in the eastern sector of the
580   Kerguelen Shelf (January–February 2005). Deep Sea Res Part 2 Top Stud Oceanogr 55:720–733. doi:
581   10.1016/j.dsr2.2007.12.010

582 Cavagna AJ, Fripiat F, Elskens M, et al (2015) Production regime and associated N cycling in the vicinity of
583   Kerguelen Island, Southern Ocean. Biogeosciences 12:6515–6528. doi: 10.5194/bg-12-6515-2015

584 Cavan EL, Le Moigne FAC, Poulton AJ, et al (2015) Zooplankton fecal pellets control the attenuation of
585   particulate organic carbon flux in the Scotia Sea, Southern Ocean. Geophys Res Lett 2014GL062744.
586   doi: 10.1002/2014GL062744

587 Coppola L, Roy-Barman M, Wassmann P, et al (2002) Calibration of sediment traps and particulate organic
588   carbon export using ^{234}Th in the Barents Sea. Mar Chem 80:11–26. doi: 10.1016/S0304-
589   4203(02)00071-3

590 Crosta X, Romero O, Armand LK, Pichon J-J (2005) The biogeography of major diatom taxa in Southern Ocean
591   sediments: 2. Open ocean related species. Palaeogeogr Palaeoclimatol Palaeoecol 223:66–92. doi:
592   10.1016/j.palaeo.2005.03.028

593 Davidson AT, McKinley J, Westwood K, et al (2016) Enhanced CO_2 concentrations change the structure of
594   Antarctic marine microbial communities. Mar Ecol Prog Ser 552:93–113. doi: 10.3354/meps11742

595 de Baar HJW, Buma AGJ, Nolting RF, et al (1990) On iron limitation of the Southern Ocean: Experimental
596   observations in the Weddell and Scotia Seas. Mar Ecol Prog Ser 65:105–122. doi: 10.3354/meps065105

597 de Baar HJW, de Jong JTM, Bakker DCE, et al (1995) Importance of iron for plankton blooms and carbon
598   dioxide drawdown in the Southern Ocean. Nature 373:412–415. doi: 10.1038/373412a0

599 Dehairs F, Jeandel C, Cattaldo T, et al (1996) Barium-barite as a tracer of export production: some information
600   from the water column. In: Ragueneau O (ed) Proceedings of the symposium OPALEO. Brest, pp 175–
601   192

602 DeMaster DJ (1981) The supply and accumulation of silica in the marine environment. Geochim Cosmochim
603   Acta 45:1715–1732. doi: 10.1016/0016-7037(81)90006-5

604 Fiala M, Kopczynska EE, Jeandel C, et al (1998) Seasonal and interannual variability of size-fractionated
605   phytoplankton biomass and community structure at station Kerfix, off the Kerguelen Islands,
606   Antarctica. J Plankton Res 20:1341–1356. doi: 10.1093/plankt/20.7.1341

607 Fischer G, Gersonde R, Wefer G (2002) Organic carbon, biogenic silica and diatom fluxes in the marginal winter
608   sea-ice zone and in the Polar Front Region: Interannual variations and differences in composition. Deep
609   Sea Res Part 2 Top Stud Oceanogr 49:1721–1745. doi: 10.1016/S0967-0645(02)00009-7

610 Gardner WD (1980) Field assessment of sediment traps. J Mar Res 38:41–52.

611 Grigorov I, Rigual-Hernandez AS, Honjo S, et al (2014) Settling fluxes of diatoms to the interior of the Antarctic
612   circumpolar current along 170°W. Deep Sea Res Part 1 Oceanogr Res Pap 93:1–13. doi:
613   10.1016/j.dsr.2014.07.008

614 Guidi L, Legendre L, Reygondeau G, et al (2015) A new look at ocean carbon remineralization for estimating
615   deepwater sequestration. Glob Biogeochem Cycles 29:1044–1059. doi: 10.1002/2014GB005063

616 Hamm CE, Merkel R, Springer O, et al (2003) Architecture and material properties of diatom shells provide
617   effective mechanical protection. Nature 421:841–843. doi: 10.1038/nature01416

618 Hasle GR, Syvertsen EE (1997) Chapter 2 - Marine Diatoms. In: Tomas CR (ed) Identifying Marine
619   Phytoplankton. Academic Press, San Diego, pp 5–385

620 Hawley N (1988) Flow in Cylindrical Sediment Traps. J Great Lakes Res 14:76–88. doi: 10.1016/S0380-
621   1330(88)71534-8

622 Henson SA, Beaulieu C, Lampitt R (2016) Observing climate change trends in ocean biogeochemistry: When
623   and where. Glob Chang Biol 22:1561–1571. doi: 10.1111/gcb.13152

624 Hunt BPV, Pakhomov EA, Hosie GW, Siegel V, Ward P, Bernard K (2008) Pteropods in Southern Ocean
625   ecosystems. Prog Oceanogr 78, 193–221. doi:10.1016/j.pocean.2008.06.001

626 Huntley ME, Lopez MD, Karl DM (1991) Top predators in the Southern ocean: A major leak in the biological
627   carbon pump. Science 253:64–66. doi: 10.1126/science.1905841

628 Jacquet SH., Lam PJ, Trull T, Dehairs F (2011) Carbon export production in the subantarctic zone and polar
629   front zone south of Tasmania. Deep Sea Res Part 2 Top Stud Oceanogr 58:2277–2292. doi:
630   10.1016/j.dsr2.2011.05.035

631 Jeandel C, Ruiz-Pino D, Gjata E, et al (1998) KERFIX, a time-series station in the Southern Ocean: A
632   presentation. J Mar Syst 17:555–569. doi: 10.1016/S0924-7963(98)00064-5

633 Jouandet MP, Blain S, Metzl N, et al (2008) A seasonal carbon budget for a naturally iron-fertilized bloom over
634   the Kerguelen Plateau in the Southern Ocean. Deep Sea Res Part 2 Top Stud Oceanogr 55:856–867.
635   doi: 10.1016/j.dsr2.2007.12.037

636 Jungandreas A, Wagner H, Wilhelm C (2012) Simultaneous measurement of the silicon content and
637   physiological parameters by FTIR spectroscopy in diatoms with siliceous cell walls. Plant Cell Physiol
638   53:2153–2162. doi: 10.1093/pcp/pcs144

639 Kopczyńska EE, Fiala M, Jeandel C (1998) Annual and interannual variability in phytoplankton at a permanent
640   station off Kerguelen Islands, Southern Ocean. Polar Biol 20:342–351. doi: 10.1007/s003000050312

641 Lam PJ, Bishop JKB (2007) High biomass, low export regimes in the Southern Ocean. Deep Sea Res Part 2 Top
642   Stud Oceanogr 54:601–638. doi: 10.1016/j.dsr2.2007.01.013

643 Lam PJ, Doney SC, Bishop JKB (2011) The dynamic ocean biological pump: insights from a global compilation
644   of particulate organic carbon, $CaCO_3$, and opal concentration profiles from the mesopelagic. Glob
645   Biogeochem Cycles 25:GB3009. doi: 10.1029/2010GB003868

646 Laurenceau-Cornec EC, Trull TW, Davies DM, et al (2015) Phytoplankton morphology controls on marine snow
647   sinking velocity. Mar Ecol Prog Ser 520:35–56. doi: 10.3354/meps11116

648 Laws EA, D'Sa E, Naik P (2011) Simple equations to estimate ratios of new or export production to total
649   production from satellite-derived estimates of sea surface temperature and primary production. Limnol
650   Oceanogr Methods 9:593–601. doi: 10.4319/lom.2011.9.593

651 Le Moigne FAC, Henson SA, Cavan E, et al (2016) What causes the inverse relationship between primary
652   production and export efficiency in the Southern Ocean? Geophys Res Lett 2016GL068480. doi:
653   10.1002/2016GL068480

654 Lombard F, Labeyrie L, Michel E, et al (2011) Modelling planktic foraminifer growth and distribution using an
655   ecophysiological multi-species approach. Biogeosciences 8:853–873. doi: 10.5194/bg-8-853-2011

656 Louanchi F, Ruiz-Pino DP, Jeandel C, et al (2001) Dissolved inorganic carbon, alkalinity, nutrient and oxygen
657   seasonal and interannual variations at the Antarctic Ocean JGOFS-KERFIX site. Deep Sea Res Part 1
658   Oceanogr Res Pap 48:1581–1603. doi: 10.1016/S0967-0637(00)00086-8

659   Maiti K, Charette MA, Buesseler KO, Kahru M (2013) An inverse relationship between production and export
660   efficiency in the Southern Ocean. Geophys Res Lett 40:1557–1561. doi: 10.1002/grl.50219

661   Maraldi C, Lyard F, Testut L, Coleman R (2011) Energetics of internal tides around the Kerguelen Plateau from
662   modeling and altimetry. J Geophys Res Oceans 116:C06004. doi: 10.1029/2010JC006515

663   Martin JH, Gordon RM, Fitzwater SE (1990) Iron in Antarctic waters. Nature 345:156–158. doi:
664   10.1038/345156a0

665   Matsuno K, Yamaguchi A, Fujiwara A, et al (2014) Seasonal changes in mesozooplankton swimmers collected
666   by sediment trap moored at a single station on the Northwind Abyssal Plain in the western Arctic Ocean.
667   J Plankton Res 36, 490–502. doi:10.1093/plankt/fbt092

668   McEwen GF, Johnson MW, Folsom TR (1954) A statistical analysis of the performance of the folsom plankton
669   sample splitter, based upon test observations. Arch Meteorol Geophys Biocl A 7:502–527. doi:
670   10.1007/BF02277939

671   McQuoid MR, Hobson LA (1996) Diatom Resting Stages. J Phycol 32:889–902. doi: 10.1111/j.0022-
672   3646.1996.00889.x

673   Merlivat L, Boutin J, Antoine D (2015) Roles of biological and physical processes in driving seasonal air–sea
674   CO_2 flux in the Southern Ocean: New insights from CARIOCA pCO_2. J Mar Syst 147:9–20. doi:
675   10.1016/j.jmarsys.2014.04.015

676   Minas H, Minas M (1992) Net community production in high nutrient-low chlorophyll waters of the tropical and
677   antarctic oceans - grazing vs iron hypothesis. Oceanol Acta 15:145–162.

678   Minas HJ, Minas M, Packard TT (1986) Productivity in upwelling areas deduced from hydrographic and
679   chemical fields. Limnol Oceanogr 31:1182–1206. doi: 10.4319/lo.1986.31.6.1182

680   Miquel JC, Fowler SW, La Rosa J, Buat-Menard P (1994) Dynamics of the downward flux of particles and
681   carbon in the open northwestern Mediterranean Sea. Deep Sea Res Part 1 Oceanogr Res Pap 41:243–
682   261. doi: 10.1016/0967-0637(94)90002-7

683   Moore CM, Hickman AE, Poulton AJ, et al (2007) Iron–light interactions during the CROZet natural iron bloom
684   and EXport experiment (CROZEX): II—Taxonomic responses and elemental stoichiometry. Deep Sea
685   Res Part 2 Top Stud Oceanogr 54:2066–2084. doi: 10.1016/j.dsr2.2007.06.015

686   Morris, P.J., Sanders, R., Turnewitsch, R., Thomalla, S., (2007) [234]Th-derived particulate organic carbon export
687   from an island-induced phytoplankton bloom in the Southern Ocean. Deep Sea Res Part 2 Top Stud
688   Oceanogr 54:2208–2232. doi:10.1016/j.dsr2.2007.06.002

689   Mortyn PG, Charles CD (2003) Planktonic foraminiferal depth habitat and δ18O calibrations: Plankton tow
690   results from the Atlantic sector of the Southern Ocean. Paleoceanography 18:1037. doi:
691   10.1029/2001PA000637

692   Mosseri J, Quéguiner B, Armand L, Cornet-Barthaux V (2008) Impact of iron on silicon utilization by diatoms
693   in the Southern Ocean: A case study of Si/N cycle decoupling in a naturally iron-enriched area. Deep
694   Sea Res Part 2 Top Stud Oceanogr 55:801–819. doi: 10.1016/j.dsr2.2007.12.003

695   Mosseri J, Quéguiner B, Rimmelin P, et al (2005) Silica fluxes in the northeast Atlantic frontal zone of Mode
696   Water formation (38°–45°N, 16°–22°W) in 2001–2002. J Geophys Res Oceans 110:C07S19. doi:
697   10.1029/2004JC002615

698   Muggli DL, Harrison PJ (1997) Effects of iron on two oceanic phytoplankters grown in natural NE subarctic
699   pacific seawater with no artificial chelators present. J Exp Mar Biol Ecol 212:225–237. doi:
700   10.1016/S0022-0981(96)02752-9

701   Nodder SD, Alexander BL (1999) The effects of multiple trap spacing, baffles and brine volume on sediment
702   trap collection efficiency. J Mar Res 57:537–559. doi: 10.1357/002224099764805183

703   Obernosterer I, Christaki U, Lefèvre D, et al (2008) Rapid bacterial mineralization of organic carbon produced
704   during a phytoplankton bloom induced by natural iron fertilization in the Southern Ocean. Deep Sea
705   Res Part 2 Top Stud Oceanogr 55:777–789. doi: 10.1016/j.dsr2.2007.12.005

706   Park Y-H, Charriaud E, Pino DR, Jeandel C (1998) Seasonal and interannual variability of the mixed layer
707   properties and steric height at station KERFIX, southwest of Kerguelen. J Mar Syst 17:571–586. doi:
708   10.1016/S0924-7963(98)00065-7

709   Park Y-H, Fuda J-L, Durand I, Naveira Garabato AC (2008a) Internal tides and vertical mixing over the
710   Kerguelen Plateau. Deep Sea Res Part 2 Top Stud Oceanogr 55:582–593. doi:
711   10.1016/j.dsr2.2007.12.027

712   Park Y-H, Roquet F, Durand I, Fuda J-L (2008b) Large-scale circulation over and around the Northern
713   Kerguelen Plateau. Deep Sea Res Part 2 Top Stud Oceanogr 55:566–581. doi:
714   10.1016/j.dsr2.2007.12.030

715   Planchon F, Ballas D, Cavagna A-J, et al (2015) Carbon export in the naturally iron-fertilized Kerguelen area of
716   the Southern Ocean based on the [234]Th approach. Biogeosciences 12:3831–3848. doi: 10.5194/bg-12-
717   3831-2015

718   Pollard R, Sanders R, Lucas M, Statham P (2007) The Crozet natural iron bloom and export experiment
719   (CROZEX). Deep Sea Res Part 2 Top Stud Oceanogr 54:1905–1914. doi: 10.1016/j.dsr2.2007.07.023

720   Pollard RT, Salter I, Sanders RJ, et al (2009) Southern Ocean deep-water carbon export enhanced by natural iron
721   fertilization. Nature 457:577–580. doi: 10.1038/nature07716

722   Pondaven P, Fravalo C, Ruiz-Pino D, et al (1998) Modelling the silica pump in the Permanently Open Ocean
723   Zone of the Southern Ocean. J Mar Syst 17:587–619. doi: 10.1016/S0924-7963(98)00066-9

724   Pondaven P, Ruiz-Pino D, Fravalo C, et al (2000) Interannual variability of Si and N cycles at the time-series
725   station KERFIX between 1990 and 1995 – a 1-D modelling study. Deep Sea Res Part 1 Oceanogr Res
726   Pap 47:223–257. doi: 10.1016/S0967-0637(99)00053-9

727   Quéguiner B (2013) Iron fertilization and the structure of planktonic communities in high nutrient regions of the
728   Southern Ocean. Deep Sea Res Part 2 Top Stud Oceanogr 90:43–54. doi: 10.1016/j.dsr2.2012.07.024

729   Razouls S, Réau GD, Guillot P, et al (1998) Seasonal abundance of copepod assemblages and grazing pressure
730   in the Kerguelen Island area (Southern Ocean). J Plankton Res 20:1599–1614. doi:
731   10.1093/plankt/20.8.1599

732   Rembauville M, Blain S, Armand L, et al (2015a) Export fluxes in a naturally iron-fertilized area of the Southern
733   Ocean – Part 2: Importance of diatom resting spores and faecal pellets for export. Biogeosciences
734   12:3171–3195. doi: 10.5194/bg-12-3171-2015

735   Rembauville M, Manno C, Tarling GA, et al (2016a) Strong contribution of diatom resting spores to deep-sea
736   carbon transfer in naturally iron-fertilized waters downstream of South Georgia. Deep Sea Res Part 1
737   Oceanogr Res Pap 115:22–35. doi: 10.1016/j.dsr.2016.05.002

738   Rembauville M, Meilland J, Ziveri P, et al (2016b) Planktic foraminifer and coccolith contribution to carbonate
739   export fluxes over the central Kerguelen Plateau. Deep Sea Res Part 1 Oceanogr Res Pap 111:91–101.
740   doi: 10.1016/j.dsr.2016.02.017

741   Rembauville M, Salter I, Leblond N, et al (2015b) Export fluxes in a naturally iron-fertilized area of the
742   Southern Ocean – Part 1: Seasonal dynamics of particulate organic carbon export from a moored
743   sediment trap. Biogeosciences 12:3153–3170. doi: 10.5194/bg-12-3153-2015

744   Rigual-Hernández AS, Trull TW, Bray SG, et al (2015a) Latitudinal and temporal distributions of diatom
745   populations in the pelagic waters of the Subantarctic and Polar Frontal zones of the Southern Ocean and
746   their role in the biological pump. Biogeosciences 12:5309–5337. doi: 10.5194/bg-12-5309-2015

747 Rigual-Hernández AS, Trull TW, Bray SG, et al (2015b) Seasonal dynamics in diatom and particulate export
748   fluxes to the deep sea in the Australian sector of the southern Antarctic Zone. J Mar Syst 142:62–74.
749   doi: 10.1016/j.jmarsys.2014.10.002

750 Romero OE, Armand L (2010) Marine diatoms as indicators of modern changes in oceanographic conditions. In:
751   Smol J, Stoermer E (ed) The diatoms: applications for the environmental and earth sciences. Cambridge
752   University Press, Cambridge, pp 373-400. doi:10.1017/CBO9780511763175.021

753 Romero OE, Lange CB, Fisher G, et al (1999) Variability in export prodution documented by downward fluxes
754   and species composition of marine planktonic diatoms: observations from the tropical and equatorial
755   Atlantic. In: Fischer G, Wefer G (ed) The use of proxies in paleoceanography, examples from the South
756   Atlantic, Springer, Berlin, pp 365–392. doi:10.1007/978-3-642-58646-0_14

757 Saavedra-Pellitero M, Baumann K-H, Flores J-A, Gersonde R (2014) Biogeographic distribution of living
758   coccolithophores in the Pacific sector of the Southern Ocean. Mar Micropaleontol 109:1–20. doi:
759   10.1016/j.marmicro.2014.03.003

760 Sadeghi A, Dinter T, Vountas M, et al (2012) Remote sensing of coccolithophore blooms in selected oceanic
761   regions using the PhytoDOAS method applied to hyper-spectral satellite data. Biogeosciences 9:2127–
762   2143. doi: 10.5194/bg-9-2127-2012

763 Salter I, Galand PE, Fagervold SK, et al (2014a) Seasonal dynamics of active SAR11 ecotypes in the
764   oligotrophic Northwest Mediterranean Sea. ISME J. doi: 10.1038/ismej.2014.129

765 Salter I, Kemp AES, Moore CM, et al (2012) Diatom resting spore ecology drives enhanced carbon export from
766   a naturally iron-fertilized bloom in the Southern Ocean. Glob Biogeochem Cycles 26:GB1014. doi:
767   10.1029/2010GB003977

768 Salter I, Lampitt RS, Sanders R, et al (2007) Estimating carbon, silica and diatom export from a naturally
769   fertilised phytoplankton bloom in the Southern Ocean using PELAGRA: A novel drifting sediment trap.
770   Deep Sea Res Part 2 Top Stud Oceanogr 54:2233–2259. doi: 10.1016/j.dsr2.2007.06.008

771 Salter I, Schiebel R, Ziveri P, et al (2014b) Carbonate counter pump stimulated by natural iron fertilization in the
772   Polar Frontal Zone. Nat Geosci 7:885–889. doi: 10.1038/ngeo2285

773 Savoye N, Trull TW, Jacquet SHM, et al (2008) ^{234}Th-based export fluxes during a natural iron fertilization
774   experiment in the Southern Ocean (KEOPS). Deep Sea Res Part 2 Top Stud Oceanogr 55:841–855. doi:
775   10.1016/j.dsr2.2007.12.036

776 Schrader HJ, Gersonde R (1978) Diatoms and silicofagellates. Micropaleontological counting methods and
777   techniques: an exercise on an eight metres section of the Lower Pliocene of Capo Rosello, Sicily.
778   Utrecht Micropaleontol Bull 129–176.

779 Schulz M, Mudelsee M (2002) REDFIT: Estimating red-noise spectra directly from unevenly spaced
780   paleoclimatic time series. Comput Geosci 28:421–426. doi: 10.1016/S0098-3004(01)00044-9

781 Sell DW, Evans MS (1982) A statistical analysis of subsampling and an evaluation of the Folsom plankton
782   splitter. Hydrobiologia 94:223–230. doi: 10.1007/BF00016403

783 Smetacek V, Assmy P, Henjes J (2004) The role of grazing in structuring Southern Ocean pelagic ecosystems
784   and biogeochemical cycles. Antarct Sci 16:541–558. doi: 10.1017/S0954102004002317

785 Smetacek V, Klaas C, Strass VH, et al (2012) Deep carbon export from a Southern Ocean iron-fertilized diatom
786   bloom. Nature 487:313–319. doi: 10.1038/nature11229

787 Stukel MR, Asher E, Couto N, et al (2015) The imbalance of new and export production in the western Antarctic
788   Peninsula, a potentially "leaky" ecosystem. Glob Biogeochem Cycles 29:2015GB005211. doi:
789   10.1002/2015GB005211

790   Tarling GA, Ward P, Atkinson A, et al (2012) DISCOVERY 2010: Spatial and temporal variability in a dynamic
791   polar ecosystem. Deep Sea Res Part 2 Top Stud Oceanogr 59–60:1–13. doi: 10.1016/j.dsr2.2011.10.001

792   Ternois Y, Sicre M-A, Boireau A, et al (1998) Hydrocarbons, sterols and alkenones in sinking particles in the
793   Indian Ocean sector of the Southern Ocean. Org Geochem 28:489–501. doi: 10.1016/S0146-
794   6380(98)00008-4

795   Tesi T, Langone L, Ravaioli. M, et al (2012) Particulate export and lateral advection in the Antarctic Polar Front
796   (Southern Pacific Ocean): one-year mooring deployment. J Mar Syst 105–108:70–81. doi:
797   10.1016/j.jmarsys.2012.06.002

798   Twining BS, Baines SB, Fisher NS (2004) Element stoichiometries of individual plankton cells collected during
799   the Southern Ocean Iron Experiment (SOFeX). Limnol Oceanogr 49:2115–2128. doi:
800   10.4319/lo.2004.49.6.2115

801   Tyrrell T, Merico A, Waniek JJ, et al (2005) Effect of seafloor depth on phytoplankton blooms in high-nitrate,
802   low-chlorophyll (HNLC) regions. J Geophys Res Biogeosci 110:G02007. doi: 10.1029/2005JG000041

803   Winter A, Henderiks J, Beaufort L, et al (2014) Poleward expansion of the coccolithophore Emiliania huxleyi. J
804   Plankton Res 36:316–325. doi: 10.1093/plankt/fbt110

805   Zielinski U, Gersonde R (1997) Diatom distribution in Southern Ocean surface sediments (Atlantic sector):
806   Implications for paleoenvironmental reconstructions. Palaeogeogr Palaeoclimatol Palaeoecol 129:213–
807   250. doi: 10.1016/S0031-0182(96)00130-7

Figures legends

809 **Fig. 1:** a) Location of the sediment trap studies in the Southern Ocean for which export fluxes

810 of particulate organic matter and diatom are reported over a complete annual cycle. b) Map of

811 the Kerguelen Plateau showing the location of annual sediment trap deployments at the

812 KERFIX station (this study) and A3 station (Rembauville et al. 2015a,b). Grey scale

813 corresponds to a 15-year climatology (1997-2013) of satellite-derived chlorophyll *a*

814 (Globcolour). The dashed line represents a 0.5 µg L^{-1} value and highlights difference between

815 the productive central Kerguelen Plateau and HNLC area to the West. The black contour line

816 represents the 1000 m isobath and the arrow denotes the approximate Polar Front (PF)

817 location.

818 **Fig. 2:** Hydrological properties recorded by the moored instruments deployed on the sediment

819 trap mooring: a) Trap depth variation, b) temperature and c) current speed. Grey lines are raw

820 data, black lines are filtered data using a moving average with a 2 days window.

821 **Fig. 3:** Hydrodynamics at the sediment trap deployment location. a) Progressive vector

822 diagram showing water displacement integrated over the sediment trap deployment period.

823 The first day of each month is shown by a circle. b) Wind rose plot of current speed and

824 direction. Grey circles are the probability distribution drawn every 2 % from 0 to 10 %. c)

825 Power spectrum resulting from the spectral analysis of the current speed. Dotted line

826 represents 99 % probability threshold for a random red noise distribution.

827 **Fig. 4:** Phytoplankton biomass and particulate export. a) Chlorophyll *a* concentration in the

828 upper 300 m at the KERFIX station, original monthly measurements are shown by black dots,

829 redrawn from Fiala et al. (1998). Dotted line denotes the mixed layer depth from Park et al.

830 (1998). b) Particulate organic carbon (POC) and inorganic carbon (PIC) fluxes recoded by the

831   sediment trap at 280 m. c) Biogenic silica (BSi) and BSi:POC molar ratio of the exported

832   particles.

833   **Fig. 5:** Diatom export fluxes measured in the sediment trap. a) Total diatom valve flux and b)-

834   l) diatom valve flux for species accounting for >1 % of the annually-integrated diatom valve

835   flux (grey bars). Numbers in bracket refer to the relative contribution of each species to total

836   diatom valves following integration over the entire deployment period. The relative

837   contribution of each species to the diatom assemblage is shown by dots and lines. CRS:

838   *Chaetoceros* subgenus *Hyalochaete* resting spores.

839   **Fig. 6:** Clustering of diatom species and association with the BSi:POC ratio. a) Dendrogram

840   based on diatom valve flux (Bray-curtis distance, UPGMA aggregation) for diatom species

841   contributing to >1 % of the total annual valve export. b) Correlation coefficients (β) from a

842   PLSR between the diatom valve fluxes and the BSi:POC molar ratio ($R^2 = 0.68$, analysis

843   performed on standardized variables).