

1 **Pigments, elemental composition (C, N, P, Si) and**
2 **stoichiometry of particulate matter, in the naturally iron**
3 **fertilized region of Kerguelen in the Southern Ocean**

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16
17 **Abstract**

18 The particulate matter distribution and phytoplankton community structure of the iron-
19 fertilized Kerguelen region were investigated in early austral spring (October-November
20 2011) during the KEOPS2 cruise. The iron-fertilized region was characterized by a complex
21 mesoscale circulation resulting in a patchy distribution of particulate matter. Integrated
22 concentrations over 200 m ranged from 72.2 to 317.7 mg m⁻² for chlorophyll *a*, 314 to
23 744 mmol m⁻² for biogenic silica (BSi), 1,106 to 2,268 mmol m⁻² for particulate organic
24 carbon, 215 to 436 mmol m⁻² for particulate organic nitrogen, and 29.3 to 39.0 mmol m⁻² for
25 particulate organic phosphorus. Three distinct high biomass areas were identified: the coastal
26 waters of Kerguelen Islands, the easternmost part of the study area in the Polar Front Zone,
27 and the southeastern Kerguelen Plateau. As expected from previous artificial and natural iron-
28 fertilization experiments, the iron-fertilized areas were characterized by the development of

1 large diatoms revealed by BSi size-fractionation and HPLC pigment signatures, whereas the
2 iron-limited reference area was associated to a low biomass dominated by a mixed
3 (nanoflagellates and diatoms) phytoplankton assemblage. A major difference from most
4 previous artificial iron fertilization studies was the observation of much higher Si:C, Si:N, and
5 Si:P ratios (respectively 0.31 ± 0.16 , 1.6 ± 0.7 and 20.5 ± 7.9) in the iron-fertilized areas
6 compared to the iron-limited reference station (respectively 0.13, 1.1, 5.8). A second
7 difference is the patchy response of the elemental composition of phytoplankton communities
8 to large scale natural iron fertilization. Comparison to the previous KEOPS1 cruise also
9 allowed to address the seasonal dynamics of phytoplankton bloom over the southeastern
10 plateau. From POC, PON, and BSi evolutions, we showed that the elemental composition of
11 the particulate matter also varies at the seasonal scale. This temporal evolution followed
12 changes of the phytoplankton community structure as well as major changes in the nutrient
13 stocks progressively leading to silicic acid exhaustion at the end of the productive season.

14 Our observations suggest that the specific response of phytoplankton communities under
15 natural iron fertilization is much more diverse than what has been regularly observed in
16 artificial iron fertilization experiments and that the elemental composition of the bulk
17 particulate matter reflects phytoplankton taxonomic structure rather than being a direct
18 consequence of iron availability.

19

20 **1 Introduction**

21 Considered as the largest High Nutrient Low Chlorophyll (HNLC) region in the world, the
22 Southern Ocean is characterized by low phytoplankton productivity despite nutrient-rich
23 waters (Martin et al., 1991; Sarmiento et al., 2004). The “Iron Hypothesis” is now largely
24 acknowledged to explain this paradox. Martin et al. (1990) estimated that new production
25 could be enhanced about 30-fold under iron-replete conditions and could thus stimulate the
26 export of carbon (C) to the deep ocean by fixing atmospheric CO₂. This hypothesis motivated
27 several artificial iron (Fe) enrichment experiments in different HNLC areas all over the world
28 (Boyd et al., 1999; Takeda, 1998; de Baar et al., 2005; Boyd, 2007; Smetacek et al., 2012).
29 All these studies confirmed that addition of Fe stimulated phytoplankton growth but only one
30 postulated an enhanced C sequestration on the sea floor (Smetacek et al., 2012). This could

1 result from experimental artifacts, and especially from the shorter duration of experiments
2 compared to that of vertical export processes.

3 To overcome those experimental constraints, the concept of “natural fertilization laboratory”
4 was coined by Blain et al. (2007). The objective was to investigate the response of ecosystem
5 functioning and biogeochemical cycles in a naturally iron-fertilized system by comparison
6 with a nearby typical HNLC environment. In the early 2000s, five projects addressed this
7 concept in different regions of the Southern Ocean: the Kerguelen Ocean and Plateau
8 compared Study (KEOPS1) (Blain et al., 2007), the CROZet natural iron bloom and EXport
9 experiment (CROZEX) (Pollard et al., 2009), the Blue Water Zone (BWZ) program (Zhou et
10 al., 2010; 2013), the Discovery 2010 cruises (Tarling et al., 2012), and the Dynamic Light on
11 Fe limitation (DynaLiFe) project (Arrigo and Alderkamp, 2012). Each of these studies
12 focused on recurrent seasonal blooming regions characterized by large bathymetric
13 discontinuities (such as ridges, islands and/or submarine plateaus) and strong hydrodynamic
14 forcings (especially geostrophic fronts), which together interact and generate natural iron
15 inputs to surface waters. The natural iron enrichment experiments consistently verified an
16 enhanced efficiency of C export within the naturally Fe-fertilized systems which was
17 approximately 3-times higher than in the surrounding Fe-limited areas (Morris and Charette,
18 2013). However, some gaps still persist regarding the understanding of the factors controlling
19 the dynamics of phytoplankton blooms in naturally Fe-fertilized systems of the Southern
20 Ocean.

21 Previous studies in the literature have documented the influence of iron on both the structure
22 and the elemental ratios of phytoplankton communities. The phytoplankton community
23 structure is known to directly impact the fate of carbon through sinking rates depending on
24 various factors such as cell size, ballast minerals, transparent exopolymers (TEP), or
25 (re)packaging in zooplankton fecal pellets (Margalef, 1965; Falkowski et al., 2003; Legendre
26 and Le Fèvre, 1989; Armstrong et al., 2009). Artificial and natural iron-fertilization
27 experiments evidenced the preferential development of large diatoms (> 20 µm) under iron-
28 replete conditions (Hutchins and Bruland, 1998; Takeda, 1998; Hare et al., 2005; Armand et
29 al., 2008; Timmermans et al., 2008). In a recent review paper, Quéguiner (2013) proposed a
30 conceptual general scheme for phytoplankton development in naturally Fe-fertilized systems
31 where phytoplankton are separated into two groups occupying different niches in the water
32 column according to their adaptation to limiting proximal factors (iron, silicic acid, and light)

1 and their resistance to grazing by micro- and mesozooplankton. Diatoms are responsible for
2 more than 40 % of the global oceanic primary production (Nelson et al., 1995). Large diatoms
3 favor the export and sequestration of carbon (Nelson et al., 1995; Buesseler, 1998). Diatom
4 growth can be controlled by silicic acid (H_4SiO_4) availability, an essential nutrient for the
5 formation of diatom frustules. Together Fe and H_4SiO_4 could be co-limiting (Dugdale et al.,
6 1995) and could directly alter the stoichiometry of biogenic matter by influencing the uptake
7 rates of major elements. Both artificial and natural iron-fertilization experiments reported
8 higher Si:C, Si:N and Si:P ratios under Fe-stress compared to Fe-replete conditions (Hutchins
9 and Bruland, 1998; Franck et al., 2000; Moore et al., 2007). Thus, Fe limitation seemed to
10 promote the development of more heavily silicified diatoms by strongly enhancing the Si
11 compared to C and N uptake rates (de Baar et al., 1997; Firme et al., 2003). However, some
12 exceptions were soon documented. For example, Hutchins et al. (1998) observed that Fe
13 could sometimes limit phytoplankton growth without changing the Si:C and Si:N ratios. The
14 control of phytoplankton elemental ratios in response to iron availability therefore remains
15 poorly understood, which clearly calls for new observations.

16 During the first KEOPS cruise (KEOPS1), conducted in January-February 2005, the impact of
17 iron on H_4SiO_4 and nitrate (NO_3^-) utilization by diatoms was investigated in the southeastern
18 part of the naturally iron-fertilized Kerguelen Plateau (Mosseri et al., 2008; Timmermans et
19 al., 2008). In this area, an annual bloom of diatoms depleting dissolved inorganic carbon
20 (DIC) in surface waters (Jouandet et al., 2008) is sustained by continuous iron inputs at the
21 surface thanks to the enhanced vertical inputs of iron-rich deep waters from the plateau (Blain
22 et al., 2007; Park et al., 2008a). Unexpectedly, Mosseri et al. (2008) reported moderate
23 differences in elemental ratios (Si:C:N) of the particulate matter between Fe-fertilized waters
24 and HNLC waters. This observation was attributed to the combined effects of the presence of
25 an already decaying diatom bloom over the plateau, and the presence of heavily silicified
26 diatoms in HNLC waters. H_4SiO_4 :DIC and H_4SiO_4 : NO_3^- elemental uptake ratios of the
27 natural diatom community of the plateau were close to 0.13 and 1 respectively, as expected
28 for diatoms growing in nutrient-replete conditions (Hutchins and Bruland, 1998; Takeda,
29 1998). However, the high NO_3^- concentrations in surface waters compared to H_4SiO_4
30 depletion at the end of the bloom suggested a strong decoupling between the seasonal
31 consumption of these two nutrients. According to Mosseri et al. (2008), this could be due to
32 differential remineralisation between Si and N and by the capacity of diatoms to grow

1 preferentially on ammonium, thereby preventing the complete utilization of the winter NO_3^-
2 stock. In the context of the “silicic acid leakage hypothesis” of Matsumoto et al. (2002), this
3 unexpected decoupling between H_4SiO_4 and NO_3^- consumptions, if extended over the entire
4 Permanently Open Ocean Zone (POOZ) of the Southern Ocean, could have large implications
5 at global scale in the control of low latitude productivity and phytoplankton assemblages
6 (Sarmiento et al., 2004). Moreover, understanding this decoupling is of critical importance to
7 assess the efficiency of Fe fertilization in terms of DIC uptake at regional and global scales.

8 In order to follow up on KEOPS1 observations, the second KEOPS cruise (KEOPS2) was
9 conducted in the naturally iron-fertilized region of Kerguelen Plateau (KP) during austral
10 spring (October-November) 2011. Focused east of the Kerguelen Islands (KI), the study
11 investigated the biogeochemical cycles and phytoplankton community structures in contrasted
12 environments differently impacted by iron availability and mesoscale activity. In this paper,
13 we examine the particulate matter distribution in relation to the phytoplankton community
14 structure in these contrasted environments. By combining KEOPS1 data corresponding to the
15 late stage of the bloom, the temporal evolution of phytoplankton community over the KP will
16 be documented during the entire blooming period. The aim is to assess the seasonal degree of
17 coupling between C, N, P, and Si cycles to better understand the seasonal dynamics of
18 phytoplankton blooms in naturally Fe-fertilized region. The use of lithogenic silica as a proxy
19 for lithogenic matter is discussed to track potential sources of Fe in the KP region.

20 **2 Method**

21 **2.1 Sampling strategy**

22 The KEOPS2 cruise was conducted in austral spring from October 10th to November 20th
23 2011 aboard the R/V Marion Dufresne (TAAF/IPEV). This research project was focused east
24 of the KP which is characterized by the passage of the Polar Front (PF), as illustrated in
25 Fig. 1. The KP region is surrounded by the Antarctic Circumpolar Current (ACC) whose main
26 branch circulates to the north of the plateau (Park et al., 2008b). A southern branch of the
27 ACC circulates to the south of Kerguelen Islands to further join a branch of the Fawn Trough
28 Current (FTC). The FTC has a main northeast direction, but a minor branch splits away
29 northwestward to rejoin the eastern side of the KP (Park et al., 2008b). These particular
30 hydrographic features generate contrasted environments which are differently impacted by

1 iron availability and mesoscale activity. Among these contrasted environments, KEOPS2
2 focused on the northeastern Kerguelen bloom (E stations), the eastern bloom (F-L and F-S
3 stations) in the Polar Front Zone (PFZ), and the southeastern KP bloom (A3 station). The
4 latter was visited twice (A3-1 in October and A3-2 in November) at a reference station that
5 had been already studied during the KEOPS1 cruise. For comparison, the station R2 was
6 considered as representative of the HNLC off-plateau area. A temporal evolution study of the
7 northeastern Kerguelen bloom was led on the complex recirculation system located in a
8 stationary meander of the PF. This site (referred as stations E including E-1, E-2, E-3, E-4E
9 and E-5) was visited five times in the course of the cruise. Across this complex system, two
10 transects were sampled to get a detailed description of the biogeochemical parameters of the
11 eastern Kerguelen area. The first transect, oriented south to north (TNS), was sampled from
12 21 to 23 October; the second transect, oriented west to east (TEW), was sampled from 31
13 October to 02 November.

14 Seawater samples were collected using a Seabird *SBE 911-plus* CTD unit mounted on a 24
15 12-L bottles rosette. A total of 30 different stations were sampled for analysis of particulate
16 (biogenic and lithogenic) silica, particulate organic matter (carbon, nitrogen and phosphorus)
17 and biomarker pigments. Sampling was performed at 6 to 24 depths over the water column
18 and covered a wide range of bottom depths from 84 m to 2,786 m above and off-plateau
19 respectively.

20 **2.2 Biogenic and lithogenic silica stocks**

21 For particulate silica analyses, size fractionation was performed by filtering 2-L seawater onto
22 stacked 0.8 and 20 μm Nucleopore® polycarbonate filters simultaneously. Samples were
23 folded in 4 and stored in Eppendorf vials, dried overnight at 60°C before being closed and
24 stored at room temperature. Biogenic silica (BSi) and lithogenic silica (LSi) were measured
25 following the triple extraction procedure described by Ragueneau et al. (2005). Dried filters
26 were digested two times at 95°C for 45 mn with an analysis of both Si and Al concentrations
27 at each step. In order to correct BSi for LSi contamination, particulate aluminum was
28 measured in parallel by the Lumogallion fluorescence method of Hydes and Liss (1976)
29 adapted by Howard et al. (1986). After the double alkaline digestion, a third extraction in
30 2.9 mol L⁻¹ hydrofluoric acid was performed on dried filters during 48h. Blank values were
31 1.0 ± 0.2 nmol L⁻¹ for BSi, 16 ± 7 nmol L⁻¹ for LSi and 24 ± 9 nmol L⁻¹ for particulate Al.

1 This implied detection limits, defined by the sum of the average blank value plus three times
2 the standard deviation of the blanks, of 1.6 nmol L^{-1} , 37 nmol L^{-1} and 51 nmol L^{-1} for BSi ,
3 LSi and particulate Al respectively. For some samples, Al concentrations analyzed after the
4 second NaOH extraction were inferior to the detection limit. These samples were also
5 characterized by the lowest LSi concentrations. The correction of the lithogenic interference is
6 only valid considering that Al content of diatom frustules is negligible as compared to that of
7 LSi (Schlüter and Rickert, 1998). According to Ragueneau et al. (2005), in the case of low
8 LSi concentrations, as in open ocean waters, the interference of diatom Al may overestimate
9 LSi concentrations. For these reasons, we decided not to apply the Al correction for samples
10 with Al concentrations below the quantification limit, defined by the sum of the average blank
11 value plus ten times the standard deviation of the blanks (114 nmol L^{-1}). This concerns
12 especially off-plateau stations far from the influence of Kerguelen Islands.

13 **2.3 Particulate organic carbon (POC), nitrogen (PON) and phosphorus (POP)**

14 For POC and PON measurements, 1-L seawater samples were collected. For POP
15 measurements 0.5-L seawater samples were collected. Samples were filtered onboard on 25-
16 mm Whatman GF/F filters (precombusted at 450°C) and stored in precombusted glass vial.
17 Filters were dried several days at 60°C , then sealed with an aluminium cap and stored at room
18 temperature. In order to remove inorganic carbon, POC/PON filters were acidified with
19 fuming HCl. Finally, POC and PON concentrations were determined using the combustion
20 method of Strickland and Parsons (1972) on an EA 2400 CHN Analyzer. POP filters were
21 digested following the wet oxidation method described by Pujo-Pay and Raimbault (1994).
22 Extracts were clarified through $0.2\text{-}\mu\text{m}$ Nucleopore® polycarbonate filters before being
23 analyzed on a 3-SEAL autoanalyzer. Blanks were $1.27 \pm 0.26 \mu\text{mol L}^{-1}$ for POC,
24 $0.06 \pm 0.02 \mu\text{mol L}^{-1}$ for PON and $0.011 \pm 0.005 \mu\text{mol L}^{-1}$ for POP. The detection limits,
25 defined as above, were 2.05 and $0.12 \mu\text{mol L}^{-1}$ for POC and PON and $0.026 \mu\text{mol L}^{-1}$ for POP.
26 Most samples collected below 100 m showed POC concentrations inferior to the
27 quantification limit ($3.87 \mu\text{mol L}^{-1}$). To compare integrated concentrations of particulate
28 matter over the same depth (200 m), we decided to estimate these low POC concentrations as
29 the minimum detectable concentration ($2.05 \mu\text{mol L}^{-1}$). This approximation seems reasonable
30 considering that PON and POP standing stocks were mostly concentrated in the upper 100 m.

1 2.4 Pigment measurements

2 For pigment analyses, seawater samples were filtered through 25-mm Whatman GF/F filters.
3 The filtered volumes varied from 1-L to 2.2-L according to the charge in particles. Filters
4 were then placed in cryotubes and stored in liquid nitrogen. In the laboratory, pigments were
5 extracted and analyzed following the procedure of Van Heukelem and Thomas (2001)
6 modified by Ras et al. (2008). Filters were extracted in 3-mL methanol (100 %) for 2h at
7 -20°C. The extracts were then vacuum-filtered onto Whatman GF/F filters. Within 24h of
8 extraction, extracts were analyzed by High Performance Liquid Chromatography (HPLC)
9 with a complete Agilent Technologies 1200 series system. Separation of pigments was
10 performed by means of a reversed phase C8 Zorbax Eclipse XDB column (3×150 mm;
11 3.5 µm particle size). Concentrations were calculated from the peak area obtained by diode
12 array detection at 450 nm for carotenoids, chlorophylls *c* and *b*, 667 nm for chlorophyll *a* and
13 derived pigments and 770 nm for bacteriochlorophyll *a*. An internal standard correction
14 (Vitamine E acetate, Sigma) and external calibration standards (provided by DHI Water and
15 Environment in Denmark) were applied for calculations of pigment concentrations. This
16 method enabled detection of 25 pigments with low detection limits (varying from 0.1 ng L⁻¹
17 for chlorophyll *b* to 0.4 ng L⁻¹ for chlorophyll *a* and alloxanthin, considering a filtered volume
18 of 1-L of seawater). Following the methods of Claustre (1994) and Vidussi et al. (2001)
19 modified by Uitz et al. (2006), seven diagnostic pigments were used as biomarkers of specific
20 phytoplankton taxa to assess the contribution of three pigment-based size classes (micro-,
21 nano-, and picophytoplankton) to the total phytoplankton biomass. The seven pigments are
22 fucoxanthin (Fuco), peridinin (Peri), alloxanthin (Allo), 19'-butanoyloxyfucoxanthin (19'BF),
23 19'-hexanoyloxyfucoxanthin (19'HF), zeaxanthin (Zea), and total chlorophyll *b* (TChl *b*).
24 Microphytoplankton (> 20 µm) is associated to Fuco and Peri pigments. Nanophytoplankton
25 (2-20 µm) is associated to Allo, 19'BF and 19'HF pigments. Picophytoplankton (< 2 µm) is
26 associated to Zea and TChl *b* pigments.

1 3 Results

2 3.1 Phytoplankton pigments: biomass and community composition

3 3.1.1 Spatial variability over the study area

4 The study area was characterized by an heterogeneous distribution of vertically integrated
5 chlorophyll *a* concentrations (Chl *a*, in Fig. 2a). It is important to keep in mind that this
6 overview of the study area was also influenced by the rapid temporal evolution of the
7 phytoplankton blooms. The TNS transect and station A3-1 were sampled at the start of the
8 bloom, ten days before sampling the TEW transect including stations F-L and F-S. Satellite
9 images (d'Ovidio et al., 2012) revealed that during the TEW transect, the bloom was rapidly
10 developing with a large spatial heterogeneity.

11 The lowest integrated Chl *a* concentrations were found at the off-plateau stations R2
12 (39.0 mg m⁻²) and TNS-1 (52.1 mg m⁻²). Maximum concentrations were observed at TEW-7
13 (223.0 mg m⁻²) and F-L (353.8 mg m⁻²), evidencing a very high phytoplankton biomass in the
14 PFZ. The Polar Front clearly isolated these very high Chl *a* waters from comparatively lower
15 Chl *a* southern waters (ranging from 100.0 to 187.7 mg m⁻²).

16 In the same way, the study area was characterized by an heterogeneous distribution of
17 phytoplankton communities as revealed by pigment biomarkers (Figs. 2b, 2c and 2d). The
18 phytoplankton community was mainly dominated by microphytoplankton (representing on
19 average 83 % of total Chl *a* biomass) all over the study area. The microphytoplankton
20 contribution was however clearly lower at stations R2 and TNS-1 (47 and 39 % of total Chl *a*
21 biomass respectively) due to a higher proportion of nanophytoplankton (39 and 41 % of total
22 Chl *a* biomass respectively). Stations TNS-1 and TNS-2 also departed from this general trend
23 by exhibiting a higher picophytoplankton contribution (~20 % of total Chl *a* biomass) as
24 compared to the other stations (<10 % of total Chl *a* biomass).

25 Chl *a* : Fuco ratios (2.3 ± 0.4 ; data not shown) were within the typical range of values (1.1 to
26 2.3) for diatoms (Wright and Jeffrey, 1987; Tester et al., 1995; Ediger et al., 2001) except for
27 the off-plateau stations R2 and TNS-1, where higher ratios (4.3 ± 0.8) were found.
28 Fucoxanthin is the dominant biomarker for diatoms but is also found in some
29 prymnesiophytes (e.g. *Phaeocystis* sp.), chrysophytes (e.g. silicoflagellates such as *Dictyocha*
30 sp.) and dinoflagellates. The very low concentrations in 19'BF, 19'HF and peridinin at all

1 stations (ranging from 0.8 to 9.7, 1.9 to 12.8 and 0.4 to 3.2 mg m⁻² respectively) compared to
2 fucoxanthin (20.9 to 160.2 mg m⁻²) clearly evidence the dominance of diatoms over the other
3 classes of phytoplankton all over the study area, except at R2 and TNS-1. At these stations,
4 Chl *a* : 19'BF (12.0 ± 1.4), and Chl *a* : 19'HF (4.4 ± 0.1) ratios were the lowest of the study
5 area, reflecting the higher contribution of nanoflagellates to the phytoplankton community
6 (data not shown).

7 3.1.2 Vertical distributions along transects TNS and TEW

8 The vertical distribution of Chl *a* along transects TNS and TEW are presented in Fig. 3 and
9 Fig. 4 respectively. For both transects, the higher concentrations (> 0.5 mg m⁻³) were
10 restricted to the upper 150 m and were clearly dominated by microphytoplankton
11 communities.

12 At the beginning of the bloom, Chl *a* concentrations ranged from 0.5 to 1.5 mg m⁻³ in the
13 upper 100 m from TNS-3 to TNS-6 and in the upper 180 m from TNS-7 to TNS-10 following
14 the mixed layer depth (Fig. 3). North of the PF, Chl *a* concentrations were lower reaching 0.6
15 mg m⁻³ in the upper 60 m at TNS-2 and 0.3 mg m⁻³ over 200 m depth at TNS-1. TNS-1 was
16 very different from the rest of the transect with higher contributions of nanophytoplankton
17 over 150 m (20 to 50 % contribution to total biomass depending on depth; Fig. 5). Ten days
18 later, higher phytoplankton biomasses (up to 5.0 mg m⁻³) were observed in the PF area
19 between TEW-7 and TEW-8 (Fig. 4). Vertical profiles clearly evidenced the PF influence
20 which isolated very high Chl *a* waters to the north from comparatively lower Chl *a* waters to
21 the south. The coastal station TEW-1 was also characterized by very high Chl *a*
22 concentrations within the first 40 m (up to 4.7 mg m⁻³). As shown by satellite images
23 (d'Ovidio et al., 2012), TEW-1 already supported a large phytoplankton bloom before the
24 beginning of the cruise, likely due to precocious favorable growth conditions in the coastal
25 zone. The latter was separated from the off-plateau waters by the southern branch of the PF
26 circulating along the shelf-break between TEW-3 and TEW-4. The PF signature along the
27 shelf break was defined by lower Chl *a* concentrations (< 1.0 mg m⁻³). Maximum
28 concentrations in fucoxanthin (2.0 to 2.5 mg m⁻³) were similarly found for both the eastern
29 area north of the PF and at station TEW-1, indicating the dominance by diatoms (Fig. 6). The
30 core of the TEW transect (TEW-4 to TEW-6) was characterized by Chl *a* concentrations
31 ranging from 1.0 to 1.5 mg m⁻³ at the surface and a significant increase of the

1 nanophytoplankton contribution to the total biomass (20 to 30 %; Fig. 6). An increased
2 grazing activity was evidenced at TEW-7 and TEW-8 by relatively higher concentrations in
3 phaeopigments (Phaeo); the ratio of Phaeo to Chl *a* was indeed higher (0.3) at these sites as
4 compared to all other stations (< 0.1 ; data not shown).

5 3.1.3 Temporal evolution at contrasted productive stations

6 No clear temporal evolution of the phytoplankton biomass could be evidenced in the complex
7 system of recirculation located in the stationary meander of the PF, as demonstrated by the
8 integrated Chl *a* concentrations (ranging between 98.2 and 129.0 mg m⁻²) from the first (E-1)
9 to the last (E-5) visit in Fig. 7.

10 Stations E-4W and A3 were visited two times (Fig. 7). The largest phytoplankton
11 development was observed at the KP reference station A3, where Chl *a* concentrations have
12 increased 3.5-fold over one month (from 106.2 mg m⁻² in October, A3-1 visit, to 371.7 mg m⁻²
13 in November, A3-2 visit). This evolution was accompanied by an increase of the
14 Phaeo : Chl *a* ratio (from < 0.1 to 0.3), reflecting a higher grazing activity at the second visit
15 (data not shown).

16 Station E-4W was characterized by a moderate evolution compared to A3, likely due to the
17 shorter period of time between the two sampling periods (6 days compared to 27 days). Chl *a*
18 concentrations increased about 2-fold from 131.2 to 249.8 mg m⁻² between the two visits.

19 For A3 station and E stations, the temporal evolution of chlorophyll biomass was mainly due
20 to the development of a microphytoplankton community largely dominated by diatoms. At
21 these stations, integrated nano- and picophytoplankton biomasses, determined using
22 diagnostic pigments, were very low and nearly constant all over the course of the cruise
23 (respectively 14.4 ± 3.7 and 4.6 ± 1.7 mg m⁻²; Fig. 7).

24 3.2 Biogenic silica and particulate organic matter

25 3.2.1 Spatial variability over the study area

26 The study area was characterized by an heterogeneous distribution of biogenic silica (BSi)
27 and particulate organic carbon (POC), nitrogen (PON) and phosphorus (POP) (Fig. 8). The
28 lowest vertically integrated concentrations of BSi, POC, and PON were measured at the off-
29 shore stations R2 and TNS-1 with integrated values over 200 m of 88.6 mmol Si m⁻², 610.5

1 mmol C m⁻², and 78.1 mmol N m⁻² respectively. The lowest concentrations of POP were
2 evidenced at the station TEW-3 (8.9 mmol P m⁻² over 200 m). The highest concentrations
3 were observed between TEW-7 and TEW-8 (250.4 to 377.6 mmol Si m⁻² for BSi, 1,200 to
4 1,875 mmol C m⁻² for POC, 214.7 to 354.4 mmol N m⁻² for PON, 29.5 to 39.0 mmol P m⁻² for
5 POP), confirming the very high phytoplankton biomass of the PF area. North of the KP, the
6 distribution of BSi, POC, PON and POP was influenced by the passage of the PF which
7 isolated northern waters characterized by low particulate matter concentrations from southern
8 waters characterized by high particulate matter concentrations. This feature is especially
9 highlighted for BSi concentrations (Table 1).

10 3.2.2 Vertical distribution along transects TNS and TEW

11 At the beginning of the bloom, along the TNS transect, POC, PON and POP concentrations
12 were low at all stations (< 12 μmol C L⁻¹, < 1.5 μmol N L⁻¹ and < 0.16 μmol P L⁻¹
13 respectively; Fig. 9). For BSi concentrations, two contrasted areas were observed on either
14 side of the PF, with southern waters richer (1.29 to 3.14 μmol Si L⁻¹) than northern waters
15 (0.08 to 1.05 μmol Si L⁻¹).

16 Along the TEW transect (Fig. 10), ten days later, the vertical distributions of BSi and
17 particulate organic matter clearly followed the same pattern as Chl *a*. The highest BSi, POC,
18 PON and POP concentrations were observed at both the coastal station TEW-1 at the surface
19 (2.77 to 5.87 μmol Si L⁻¹, 5.50 to 16.3 μmol C L⁻¹, 1.00 to 2.82 μmol N L⁻¹, and 0.15 to
20 0.22 μmol P L⁻¹ respectively) and in the PF area between TEW-7 and TEW-8 down to 50 m
21 depth (2.85 to 5.42 μmol Si L⁻¹, 10.1 to 31.9 μmol C L⁻¹, 2.42 to 5.89 μmol N L⁻¹, 0.23 to
22 0.81 μmol P L⁻¹ respectively). The core of the transect (TEW-3 to TEW-6) was characterized
23 by lower particulate matter concentrations (0.51 to 2.91 μmol Si L⁻¹, 3.93 to 11.4 μmol C L⁻¹,
24 0.42 to 2.21 μmol N L⁻¹ and 0.01 to 0.19 μmol P L⁻¹). As noticed for Chl *a* in this area, higher
25 BSi concentrations (2.32 to 2.91 μmol Si L⁻¹) were observed at TEW-4 down to 100 m depth.
26 Standing out of Chl *a* and particulate organic matter distributions, a well-defined deep BSi
27 maximum (2.00 ± 0.10 μmol Si L⁻¹) was found at 300 m at TEW-5.

28 For both transects, the vertical distribution of BSi strongly paralleled that of fucoxanthin
29 (Fig. 3), confirming the dominance of diatoms in the phytoplankton communities of the
30 Kerguelen region. Size-fractionation of BSi can bring information on the sizes of the diatoms
31 even though the presence of debris can alter this information. Nano-sized fraction of BSi (0.8

1 to 20 μm) can then correspond to the presence of small diatom species or fragments of
2 diatoms. Micro-sized fraction of BSi ($> 20 \mu\text{m}$) indicates the presence of large siliceous
3 phytoplankton which could represent both large diatoms cells and large colonies of diatoms.
4 In the Kerguelen region, size fractionation of BSi (Fig. 11) revealed the major role played by
5 large ($> 20 \mu\text{m}$) siliceous phytoplankton which accounted for $> 60 \%$ of total BSi at all
6 productive stations over different depths according to the location: down to 200 m at TEW-4,
7 A3-2, and E (E-1 to E-5) stations (typical vertical profile represented by station TEW-4 in
8 Fig. 11a), down to 100 m at E-4W and in the PF area (represented by F-L vertical profile in
9 Fig. 11b), and down to 40 m at TEW-1 (data not shown). The relative contribution of the two
10 size classes was mainly driven by the evolution of the large size fraction over these different
11 depths, as the small size fraction concentrations remained fairly constant around
12 $190 \text{ mmol Si m}^{-2}$. As a consequence, the nano-sized diatoms (0.8 to $20 \mu\text{m}$) were dominant at
13 the low productive stations (R2, TNS-1, TNS-2, TEW-2, TEW-3, TEW-5 and TEW-6; typical
14 vertical profile illustrated by station R2 in Fig. 11c) and everywhere below 200 m except at
15 station TEW-5 (Fig. 11d). The latter station showed an increasing contribution of the micro-
16 sized fraction ($> 20 \mu\text{m}$) to total siliceous biomass with depth (ranging from 23 % at the
17 surface and 60 % between 300 and 400 m). This unusual feature coincided with the deep BSi
18 maximum mentioned above.

19 3.2.3 Temporal evolution at contrasted productive stations

20 Slight increases in BSi (Fig. 12) and particulate organic matter (data not shown)
21 concentrations were observed in the recirculation system (stations E). From the first (E-1) to
22 the third visit (E-3), integrated concentrations over 200 m were relatively constant (average:
23 $308.2 \pm 23.6 \text{ mmol Si m}^{-2}$ for BSi, $1,065 \pm 51 \text{ mmol C m}^{-2}$ for POC, $195.6 \pm 11.6 \text{ mmol N m}^{-2}$
24 for PON and $13.5 \pm 1.6 \text{ mmol P m}^{-2}$ for POP). Values then increased at the two last visits
25 (E-4E and E-5), reaching $410.7 \pm 23.1 \text{ mmol Si m}^{-2}$, $1,651 \pm 26 \text{ mmol C m}^{-2}$,
26 $231.5 \pm 31.0 \text{ mmol N m}^{-2}$ and $28.5 \pm 5.9 \text{ mmol P m}^{-2}$. In addition, vertical profiles revealed
27 that BSi and particulate organic matter were concentrated in a shallow layer (from the surface
28 down to 100 m depth) during these two last visits (data not shown).

29 As mentioned for Chl *a*, the largest phytoplankton development was observed at A3 with
30 increasing concentrations of BSi (from 163.5 to $713.3 \text{ mmol Si m}^{-2}$), POC (from 1,259 to
31 $2,267 \text{ mmol C m}^{-2}$), PON (from 137.9 to $435.9 \text{ mmol N m}^{-2}$), and POP (from 9.7 to

1 29.3 mmol P m⁻²) between A3-1 and A3-2 visits (Fig. 12, data not shown for POC, PON and
2 POP concentrations). On the first visit of E-4W, the situation was already characterized by
3 high BSi, POC, PON, and POP concentrations over 100 m depth (up to 3.83, 20.0, 3.60,
4 0.27 μmol L⁻¹ respectively). The temporal evolution between the two visits was still
5 considerable with integrated concentrations varying from 379.5 to 744.2 mmol m⁻² for BSi,
6 1,162 to 1,598 mmol m⁻² for POC, from 288.2 to 354.1 mmol m⁻² for PON, and from 21.5 to
7 32.6 mmol m⁻² for POP.

8 The temporal evolution of particulate matter in the meander of the PF and at stations A3 and
9 E-4W evidenced a significant growth of the siliceous phytoplankton community since the
10 beginning of the cruise. As a general trend, the large size fraction (> 20 μm) was overall
11 contributing to around 60 % of integrated BSi stocks in the surface productive layer, with the
12 exception of stations R2 and E-3 where the small size fraction (0.8 to 20 μm) was slightly
13 dominant (respectively accounting for 59.4 % and 52.5 % of above mentioned integrated BSi
14 stocks). However, it is particularly important to notice that the BSi stocks located between
15 200 and 400 m, which may reflect the communities sinking out of the surface layer, were
16 always dominated by the nano-sized particles (ranging from 61.4 to 86.1 % of BSi stocks
17 integrated from 200 to 400 m depths).

18 **3.3 Elemental ratios of particulate matter**

19 The elemental ratios in the upper 200 m are presented as six clusters of stations (Fig. 13),
20 grouped in function of biomass, elemental ratios and phytoplankton community structure
21 reported for each station. The objective of this clustering is to provide an overview of the
22 distribution of elemental ratios over the study area to highlight some spatial and temporal
23 patterns. Each cluster of stations includes systems with different environmental dynamics.
24 Mann-Whitney tests were then performed on these six clusters for each elemental ratio (Si:C,
25 Si:N, Si:P, C:N, C:P and N:P) to determine the clusters that were significantly different from
26 each other at the 95% confidence level (Fig. 13). The six clusters of stations corresponded to:
27 (1) the lowest biomass stations including the off-plateau stations R2 and TNS-1, and A3-1 at
28 the start of the bloom, (2) the moderate productive stations north of the PF (TNS-2, TEW-2,
29 TEW-3), (3) the high biomass stations in the PFZ (TEW-7, TEW-8, F-L, F-S), (4) the high
30 biomass stations south of the PF (A3-2, E-4W, E-4W2), (5) the moderate biomass stations

1 south of the PF (TNS-3 to TNS-10 , E-1 to E-5, TEW-4 to TEW-6), (6) the coastal station
2 TEW-1.

3 The lowest Si:C, Si:N and Si:P ratios were observed at the lowest biomass stations (cluster
4 (1)) of the study area in the upper 200 m (respectively 0.11 ± 0.07 , 0.67 ± 0.43 and 9.6 ± 6.4).
5 Except for cluster (1), Si:C, Si:N and Si:P ratios were always higher than the typical values
6 for nutrient-replete diatoms (Brzezinski, 1985). The highest average values were observed at
7 the coastal station TEW-1 in the upper 70 m (cluster (6)) reaching 0.70 ± 0.25 for Si:C,
8 2.59 ± 0.40 for Si:N and 34.4 ± 6.6 for Si:P. The other stations located north of the PF or in
9 the PFZ (clusters (2) and (3)) were characterized by lower average Si:C, Si:N and Si:P molar
10 ratios (respectively 0.28 ± 0.01 , 1.32 ± 0.13 , 16.0 ± 2.6) than the stations south of the PF
11 (respectively 0.35 ± 0.01 , 1.75 ± 0.05 , 24.9 ± 4.3). This observation agreed with statistical
12 tests: the clusters of the stations north of the PF were statistically different from the other
13 clusters south of the PF (Fig. 13).

14 Except for the lowest biomass stations (cluster (1)), C:N and C:P ratios were relatively
15 constant (reaching average values of 5.1 ± 1.4 and 73.0 ± 35.4 respectively) and lower than
16 the Redfield et al. (1963) ratios. N:P ratios were close to the Redfield's ratio all over the study
17 area (average: 14.4 ± 6.3) except for the stations located in the PFZ (cluster (3)). These
18 stations were characterized by lower C:P ($48.1.7 \pm 18.0$) and N:P (10.5 ± 3.3) ratios than the
19 rest of the study area. The Mann-Whitney test did not evidence any significant difference
20 between the median of the six clusters for C:P and N:P ratios. For C:N ratios, only the low
21 biomass stations were significantly different from the other stations at the 95 % confidence
22 level.

23 Over the course of the cruise, the development of diatoms was evidenced between the first
24 (A3-1) and the second visits (A3-2) at A3 with Si:C and Si:N ratios increasing respectively
25 from 0.14 ± 0.06 to 0.32 ± 0.06 and 0.87 ± 0.25 to 1.66 ± 0.24 (data not shown). Significant
26 increases in Si:C and Si:N were also observed at E-4W from the first (0.29 ± 0.12 for Si:C
27 and 1.25 ± 0.62 for Si:N) to the second visit (0.39 ± 0.07 for Si:C and 2.06 ± 0.15 for Si:N).
28 Moderate increases were shown for Si:P ratio both at A3 (from 17.3 ± 2.9 to 19.6 ± 6.7) and
29 E-4W (from 18.3 ± 4.4 to 19.4 ± 6.3). At E-4W, a slight decrease was evidenced from the first
30 to the second visit for C:N (from 5.5 ± 0.5 to 5.0 ± 0.5), C:P (from 76.3 ± 12.3 to 71.7 ± 25.7)
31 and N:P (from 17.1 ± 6.0 to 12.9 ± 1.9). At A3, higher decrease was observed from the first to

1 the second visit for C:N (from 8.8 ± 3.5 to 5.3 ± 0.2), C:P (from 148.9 ± 47.2 to 65.9 ± 32.8)
2 and N:P (from 20.9 ± 3.1 to 11.4 ± 5.2).

3 **3.4 Lithogenic silica**

4 Lithogenic silica is a good proxy to track the transport of lithogenic material (and indirectly
5 Fe) from terrestrial erosion, aeolian dust deposition or sediment resuspension to the water
6 column (Quéguiner et al., 1997). Over the entire study area, LSi concentrations did not exceed
7 $0.11 \mu\text{mol L}^{-1}$ throughout most of the water column, except at stations subjected to continental
8 influence (Fig. 14). The highest LSi values were observed at the coastal station TEW-1
9 (average: $1.31 \pm 0.14 \mu\text{mol L}^{-1}$) and at station A3 near the bottom ($1.34 \pm 0.07 \mu\text{mol L}^{-1}$). In
10 addition, compared to surrounding waters, station A3 was characterized by relatively higher
11 concentrations down to 300 m (values $> 0.15 \mu\text{mol L}^{-1}$). This feature was also observed at the
12 second visit A3-2 (Fig. 15). The lowest LSi concentrations were found at TNS-1 with values
13 $< 0.01 \mu\text{mol L}^{-1}$ over the first 400 m (Fig. 14). As expected, concentrations were low at
14 station R2 (Fig. 15), located far from any continental influence ($< 0.04 \mu\text{mol L}^{-1}$ in the upper
15 100 m), although a maximum was reported at 500 m ($0.12 \mu\text{mol L}^{-1}$). Inside the meander of
16 the PF (stations E), LSi concentrations were lower than $0.10 \mu\text{mol L}^{-1}$ but local maximums
17 (0.12 to $0.13 \mu\text{mol L}^{-1}$) between 600 and 700 m were noticed at the first (E-1), the fourth (E-
18 4E) and the last visit (E-5) (and likely E-2, although data are missing to confirm it). High LSi
19 concentrations were also observed at E-4W at 75 m and 400 m (0.23 and $0.12 \mu\text{mol L}^{-1}$
20 respectively) only during the second visit. Along the transect TEW, LSi concentrations were
21 higher in the PFZ reaching values higher than $0.11 \mu\text{mol L}^{-1}$ over the water column at TEW-8.
22 As a general trend, LSi was mainly composed of small particles (from 0.8 to 20 μm) over the
23 water column, representing in average 59.5 % of total LSi. However, local maximums
24 observed at A3-2 (50 m), F-L (300 m), E-4W2 (75 and 400 m) and E-5 (600 m) were
25 associated to large particles ($> 20 \mu\text{m}$), accounting for 65.2 to 86.5 % of the total LSi.

26 **4 Discussion**

27 **4.1 The Kerguelen Plateau region: a mosaic of biogeochemical environments**

28 The biogeochemical characteristics of the water masses northeast of the Kerguelen Islands
29 have already been documented by Blain et al. (2001) in early spring (October 1995). They

1 highlighted the complex mesoscale structure of water masses which generated contrasting
2 biogeochemical environments above the KP. The particular mesoscale circulation is directly
3 impacted by the topography of the KP and the presence of the PF pathway isolating warm
4 northern subantarctic surface waters from cold southern Antarctic Surface Water (AASW)
5 (Park and Gamberoni, 1997). Similar circulation patterns (Park et al., this volume; Zhou et al.,
6 this volume) were observed during the KEOPS2 cruise. This is probably partly for that reason
7 that a mosaic of biogeochemical conditions was also encountered.

8 Coastal waters (corresponding to stations TEW-1 and TEW-2) were characterized by a large
9 diatom bloom and high LSi concentrations, evidencing strong lithogenic material inputs
10 (including iron) from the plateau.

11 A strong shelf front isolated these warmer coastal waters ($> 2.4^{\circ}\text{C}$) from the cold (2.3°C) PF
12 water tongue containing low Chl *a* and BSi concentrations. Blain et al. (2001) associated this
13 water tongue (corresponding to station TEW-3 in our study) to an intrusion of AASW where
14 phytoplankton growth was limited by an unfavorable light-mixing regime. Indeed, TEW-3
15 showed the deepest mixed layer depth (95 m) of the west-east transect, but unfortunately
16 photosynthetic parameters were not determined precluding any conclusion about the light
17 limitation hypothesis. Grazing pressure could also be another limiting factor for
18 phytoplankton growth. However, zooplankton biomass was too low at TEW-3 (Carlotti et al.,
19 this volume) to explain the low Chl *a* and BSi concentrations.

20 By contrast, a productive, high-biomass system was found in the eastern area in the PF
21 between TEW-7 and TEW-8. This area was characterized by a shallow mixed layer (down to
22 50 m), likely providing favorable light conditions for diatom growth. Despite being far from
23 the plateau, these stations showed sufficient iron concentrations ($\sim 0.2 \text{ nmol L}^{-1}$ over 50 m;
24 Qu  rou   et al., this volume) to support phytoplankton growth. Significant iron could be
25 supplied by the transport of Fe-rich deep waters from the KP to the northwestern Kerguelen
26 Abyssal Plain east of the KP (Zhou et al., this volume), but also from the coastal area by
27 lateral advection driven by the subantarctic surface water eastward flow north of the PF
28 (Bucciarelli et al., 2001). Potential sources of iron will be discussed in paragraph 4.4.

29 The largest diatom development was observed over the southeast KP at the reference station
30 A3 (during the second visit) with the highest Chl *a* and BSi concentrations reported during the
31 cruise. This station also evidenced high LSi concentrations near the bottom suggesting

1 lithogenic material inputs from the plateau sediments. Indeed, one major conclusion of
2 KEOPS1 was that the long-lasting diatom bloom above the plateau was maintained by the
3 continuous supply to the surface mixed layer of iron and nutrients. The latter originated from
4 below due to an enhanced tidally-induced vertical mixing associated to a weak mean residual
5 circulation resulting in a long retention time for nutrients and trace elements (Blain et al.,
6 2007; Park et al., 2008a). On a longer time-scale, it was assumed that iron supply to A3
7 originated from horizontal advection from the extensive shoal around the Heard/Mc Donald
8 Islands (Park et al., 2008a). East of the KP, this northward circulation along the topography
9 could also lead to a partial export of the plateau bloom. This feature was supported by the
10 observation of similar biogeochemical properties at station A3 and at the eastern flank
11 (corresponding to station E-4W for the two visits) of the KP. The E-4W station evidenced the
12 same range of values as A3 in terms of BSi, POC, PON, and POP concentrations and quite
13 similar diatom community compositions mainly dominated by *Chaetoceros Hyalochaete*,
14 *Thalassiosira*-like (pending SEM determination) and *Pseudo-nitzschia* spp. (Lasbleiz et al., in
15 prep.). Furthermore, the assemblages in sediments at these two sites were similarly composed
16 of *Eucampia antarctica*, *Dactyliosolen antarctica*, *Fragilariopsis kerguelensis*, *Chaetoceros*
17 resting spores, *Rhizosolenia* spp. as well as an uncommon species, *Thalassiosira decipiens*,
18 not observed anywhere else over the study area (Wilks, 2013). The northward export of part
19 of the southeast KP bloom also serves as a good explanation to the higher particulate matter
20 concentrations observed at TEW-4 compared to the other stations of the TEW transect at the
21 beginning of the cruise.

22 As compared to the easternmost part of the study area in the PF, the stations south of the PF
23 exhibited moderate biomasses. Inside the meander of the PF, two stages in the development of
24 the siliceous phytoplankton community were observed in the course of the cruise. At the
25 beginning, particulate matter concentrations were moderate and slightly decreasing from the
26 first (E-1) to the third visit (E-3). The microplanktonic size fraction ($> 20 \mu\text{m}$) contribution to
27 siliceous biomass was also decreasing while the nanoplanktonic size fraction contribution
28 increased from 34.5 % at the first visit (E-1) to 47.5 % of the siliceous biomass at the third
29 visit (E-3) (Fig. 12). By contrast, the two last visits (E-4E and E-5) showed an increase in
30 phytoplankton biomass dominated by large diatoms and concentrated over a shallower depth.
31 Closset et al. (this volume) also reported these two contrasted periods through the $\int\text{D}:\text{P}$ ratio
32 defined as the ratio of Si dissolution rates (D) to Si production rates (P) integrated over the

1 euphotic zone. From E-1 to E-3, increasing \int D:P ratio evidenced an increased BSi loss due to
2 enhanced BSi dissolution in surface waters, while decreasing \int D:P ratio between E-4E and E-
3 5 resulted from enhanced BSi production rates and revealed bloom conditions. Together,
4 these results would suggest that the start of the bloom period (E-4E and E-5) was preceded
5 by a non-lasting phytoplankton development before the first sampling (E-1). This short bloom
6 event could have been aborted by adverse hydrodynamic conditions before the beginning of
7 the cruise. This was consistent with the increase in the proportion of empty diatoms frustules
8 from E-1 to E-3 (from 5.1 % to 25.7 %; Lasbleiz et al., in prep.) and the increase of
9 phytodetrital and fecal aggregates observed at depth by Laurenceau et al. (this volume). The
10 important role of mesoscale structures and turbulence in the control of primary production
11 and light availability have already been reported by previous studies (e.g. Lancelot et al.,
12 2000; Lévy et al., 2001; Read et al., 2007). We hypothesize that the instability of the mixed
13 layer depth before the beginning of the cruise could have generated deepening events
14 providing unfavourable light conditions for phytoplankton growth. Our hypothesis is
15 supported by the σ_θ profiles which indicate the existence of a secondary pycnocline around
16 130 m at E-1 and a continuous gradient with no clear mixed layer from the surface down to
17 200 m depth E-3 (data not shown). Furthermore, the slight increase in zooplankton abundance
18 from E-1 to E-3 (Carlotti et al., this volume) suggests that phytoplankton growth was not
19 mainly impacted by grazing pressure. Another feature of the area south of the PF was the
20 presence of a minimum of biomass in the central core of the complex recirculation meander
21 (corresponding to station TEW-5). This central core stands out from the rest of the study area
22 by the presence of a deep silica maximum (between 300 and 400 m; Fig. 10a) mainly
23 associated to microplanktonic size particles ($> 20 \mu\text{m}$). There could be several explanations
24 for this peculiar feature. (1) Given the low Si biomass at the surface, the presence of large and
25 non-living diatoms at depth could reflect the sedimentation of an early bloom that could have
26 been quickly driven to an end due to adverse hydrodynamic conditions, as discussed above. A
27 vertical net haul down to 100 m depth at TEW-5 revealed the dominance of the heavily
28 silicified diatoms *Fragilariopsis kerguelensis* as well as *Corethron pennatum* (Armand L.,
29 pers. comm., 2013). However no sediment sample was collected at this station to evidence
30 their eventual influence on vertical export. (2) Mesoscale activity could also have favored the
31 transfer and the accumulation of biogenic silica at depth in the central meander area which is
32 characterized as a region of general downwelling (Zhou et al., this volume). (3) Finally, the

1 northward circulation from the KP could have advected large and non-living diatoms already
2 sedimenting at depth coming from productive southern waters.

3 **4.2 Impact of natural iron enrichment on Chl *a* and phytoplankton** 4 **communities**

5 4.2.1 The off-plateau HNLC stations

6 During the KEOPS2 cruise, the off-plateau station R2 showed the lowest chlorophyll biomass
7 (39.0 mg m^{-2} ; Fig. 2a) despite high macronutrient concentrations of the surrounding waters
8 (Blain et al., this volume). In this HNLC area, one limiting factor was likely iron availability
9 as suggested by the low iron concentrations in surface waters ($\sim 0.1 \text{ nmol L}^{-1}$; Quéroué et al.,
10 this volume) and the Fe-Cu incubation experiments (Bowie et al., this volume; Sarthou et al.,
11 this volume). Light could also have been (co-)limiting as the mixed layer extended down to
12 $\sim 120 \text{ m}$ almost exactly coinciding with the 0.01 % surface light level. Chl *a* concentrations
13 were in the same order of magnitude as that measured in typical HNLC waters of the
14 Southern Ocean (Bathmann et al., 1997; Gall et al., 2001; Froneman et al., 2004) and more
15 specifically, of the Kerguelen region (Cailliau et al., 1997; Uitz et al., 2009). Integrated
16 chlorophyll biomass was however higher than the lowest values corresponding to the poorest
17 areas of the Southern Ocean (range: $10 \text{ to } 20 \text{ mg m}^{-2}$) suggesting the slight phytoplankton
18 development that may have occurred shortly before the site visit. In contrast to the other
19 stations of the study area, the off-plateau station R2 showed a lower microphytoplankton
20 contribution (47 % of total Chl *a* biomass; Fig. 2b) due to a higher proportion of
21 nanophytoplankton (39 % of total Chl *a* biomass; Fig. 2c). This result was expected from
22 previous artificial and natural iron-fertilization experiments (Gall et al., 2001; Hoffmann et
23 al., 2006; Moore et al., 2007; Lance et al., 2007). Increased contributions of nano-sized
24 communities (small diatoms or flagellates) were reported under iron limited conditions
25 (Sunda and Huntsman, 1997; Timmermans et al., 2001; Armand et al., 2008; Uitz et al.,
26 2009). Cell counts confirmed the dominance of nanoflagellates at station R2 in terms of C
27 biomass (Lasbleiz et al., in prep.). Several species of dinoflagellates and the silicoflagellate
28 *Dyctiocha speculum* were also important contributors to C biomass compared to diatoms. At
29 station R2, the Chl *a* : Fuco ratio (3.7) and Chl *a* : 19'BF ratio (11.0) were respectively higher
30 and lower than those measured for diatoms (Wright and Jeffrey, 1987; Ediger et al., 2001).

1 Such Chl *a* : Fuco and Chl *a* : 19'BF ratios have been reported for dinoflagellates in previous
2 studies (Johnsen and Sakshaug, 1993; Ediger et al., 2001).

3 Like the station R2, the off-plateau station TNS-1 was distinguished from the study area by its
4 low chlorophyll biomass (52.1 mg m⁻²; Fig. 2a) and higher proportion of nano- (41 %) and
5 pico- (20 %) phytoplankton (Fig. 2c et 2d). Even if there are no available data to confirm it, a
6 limitation by iron seems almost likely given the tenuity of the surface mixed layer (from 20 to
7 35 m), the high abundance of macronutrients (Blain et al., this volume) and the low grazing
8 pressure (Carlotti et al., this volume). At station R2 and TNS-1, the picophytoplankton
9 contribution to chlorophyll biomass was higher (up to 20 %) than in the rest of the study area
10 but relatively low by comparison to previous studies in HNLC waters (Kopczyńska et al.,
11 1998; Gall et al., 2001). Similar results were reported for the HNLC station of the first cruise
12 KEOPS1 (Uitz et al., 2009).

13 4.2.2 The iron-fertilized stations

14 By contrast, larger developments of phytoplankton were observed in the iron-fertilized
15 Kerguelen region, confirming the classical stimulation of phytoplankton growth under iron-
16 replete conditions (Martin, 1990). Integrated chlorophyll biomass (152.5 ± 77.4 mg m⁻²;
17 Fig. 2a and 7) fell in the range typically reported for different regions of the Southern Ocean
18 (Peeken, 1997; Wright and van den Enden, 2000; Uitz et al., 2009). Some very high
19 productive stations (A3-2, E-4W2 and the area from TEW-7 to TEW-8) were comparable to
20 the highly productive regions like the Ross sea (Goffart et al., 2000), reflecting the high
21 productivity of the early bloom. The large development of diatoms was notably evidenced at
22 station A3 where Chl *a* biomass increased 3.5-fold from October to November.

23 All over the iron-fertilized area, chlorophyll biomass was largely dominated by large diatoms
24 (> 20 μm; Fig. 2b and 7), as suggested by the higher concentrations in fucoxanthin over the
25 other pigments. Previous artificial iron-fertilization experiments reported the shift from nano-
26 and/or picophytoplanktonic communities to large diatoms (> 20 μm) after Fe-addition (Gall et
27 al., 2001; Hoffmann et al., 2006; Lance et al., 2007). The dominance of large diatoms was
28 also observed in other natural Fe-fertilized regions of the Southern Ocean (Bathmann et al.,
29 1997; Moore et al., 2007; Uitz et al., 2009).

30 Interestingly, relatively high Chl *a* biomasses were found below the mixed layer all over the
31 iron-fertilized area. This feature was also observed during KEOPS1 at the Plateau reference

1 station A3 and resulted in the progressive formation of a deep chlorophyll maximum (DCM)
2 associated to a deep biogenic silica maximum at 125 m (Mosseri et al., 2008; Uitz et al.,
3 2009). Uitz et al. (2009) explained this DCM by the accumulation of inactive but living algal
4 cells at the deep temperature-driven pycnocline. During KEOPS2, a second density gradient
5 (identified from the σ_θ profiles) deeper than the MLD was observed for most of the stations
6 over the iron-fertilized area. Furthermore, Si-production by diatoms was lower but still
7 observed below the mixed layer although irradiance levels were $< 1\%$ PAR
8 (Photosynthetically Active Radiation; Closset et al., this issue; Lasbleiz et al., in prep.). The
9 acclimation of phytoplankton to low light levels has already been reported by Cullen (1982)
10 and more recently by Banse (2004) and Marra et al. (2014). In addition, cell counts revealed
11 that the community composition was rather the same within and beneath the mixed layer, with
12 the difference that the proportion of empty cells was higher beneath the mixed layer. These
13 observations would suggest that Chl *a* biomass below the mixed layer would result from the
14 sedimentation of living diatoms from the upper layer rather than *in situ* growth of a specific
15 deep-dwelling community. Characterized by low light levels and high nutrient
16 concentrations, the layer between the surface mixed layer and the second pycnocline would
17 also allow a slight growth of phytoplankton. Thereafter, this accumulation of sinking cells
18 could be enhanced by the shift of phytoplankton communities towards more heavily silicified
19 diatoms, observed later in the season by Armand et al. (2008). Together all these observations
20 could explain the occurrence of the DCM observed at the Plateau reference station A3 during
21 the demise of the bloom (Uitz et al., 2009).

22 **4.3 Element composition and stoichiometry**

23 **4.3.1 Si, C, N, P stocks**

24 Above 200 m, the iron-fertilized stations were characterized by the progressive development
25 of micro-sized diatoms ($> 20\ \mu\text{m}$) resulting in high biogenic silica and particulate organic
26 matter concentrations at some productive stations (A3-2, E-4W2, and the area from TEW-7 to
27 TEW-8; Fig. 8 and 12). These high concentrations fell in the range of those measured in the
28 PFZ in spring (Quéguiner et al., 1997; Brzezinski et al., 2001; Quéguiner and Brzezinski,
29 2002). At the HNLC reference station, BSi stocks were clearly lower due to a higher
30 proportion of nanoflagellates (39 %).

1 Below 200 m, the biogenic silica (especially at A3, E-4W, TEW-7 and TEW-8) was
2 dominated by the smaller (0.8 to 20 μm) size fraction despite the development of large
3 diatoms in surface waters (Fig. 11 and 12). This could either reflect the sedimentation of
4 small diatoms coming from a short bloom event before sampling or/and an active degradation
5 of diatoms at the top of the mesopelagic zone inducing the fragmentation of siliceous
6 planktonic particles by grazers. Given that organic matter is preferentially degraded relative to
7 biogenic silica, the hypothesis of an enhanced degradation from 200 m and beyond could
8 explain the low POC export reported by Planchon et al. (this volume) who also report
9 elevated ^{234}Th : ^{238}U ratios slightly > 1 in between 250 and 700 m at E-3 and in between 200 to
10 600 m at E-5. Similarly, Jacquet et al. (this volume) report a Ba_{xs} maximum centered around
11 400 m at E-3 and E-5 which indicates an increased remineralisation of organic matter. From
12 various sediment trap deployments at 200 m depth, Laurenceau et al. (this volume) evidenced
13 a negative correlation between primary productivity and export efficiency, suggesting that the
14 highest productive stations were the least efficient to carbon export.

15 4.3.2 Elemental stoichiometry Si:C, Si:N and Si:P in particulate matter

16 Both artificial and natural iron-fertilization experiments have documented the influence of
17 iron on the elemental ratios of phytoplankton communities (Hutchins and Bruland, 1998;
18 Takeda, 1998; Franck et al., 2000; Hare et al., 2007; Moore et al., 2007). They usually
19 mention higher (2 to 3 times) Si:C, Si:N and Si:P ratios under Fe-stress as compared to values
20 under Fe-replete conditions (Si:C = 0.13, Si:N = 1.1; Brzezinski, 1985). This is supposed to
21 indicate the development of more heavily silicified diatoms under iron-stress (Hutchins and
22 Bruland, 1998; Takeda, 1998). Surprisingly, we report here an opposite trend (Fig. 13): the
23 iron-fertilized stations mentioned above evidenced 2-fold higher Si:C and Si:N ratios than
24 those of the HNLC station R2 (close to Brzezinski's ratios). The high Si:C and Si:N ratios
25 observed at the iron-fertilized stations could be explained by a differential recycling of
26 organic matter and biogenic silica, increased Si requirements by the dominant species and/or
27 the presence of empty cells. Bacterial activity and grazing pressure by zooplankton could
28 explain the preferential degradation of soft organic matter over BSi dissolution in surface
29 waters. However, in the early productive period, their impact on particulate matter
30 stoichiometry is probably not yet significant: Christaki et al. (this volume) indicates that a few
31 percent of primary production (gross community production; Cavagna et al., this volume) at

1 A3 are channeled through the microbial loop and the mesozooplankton. Furthermore,
2 countings revealed that the numbers of empty cells were very low compared to living cells at
3 the iron-fertilized stations (Lasbleiz et al., in prep.), which could not explain such high
4 Si:C/N/P ratios.

5 The high Si:C, Si:N and Si:P ratios of the productive stations would then rather indicate the
6 presence of phytoplankton communities dominated by heavily silicified diatoms. Our
7 interpretation agrees with the high Si uptake rates, compared to C and N uptake rates,
8 measured at A3, E-4W and F-L (located between TEW-7 and TEW-8) by Closset et al. (this
9 volume). These results are consistent with Si:C production ratios reported for the PFZ during
10 austral spring and reaching values as high as 0.45 in the Pacific sector (Brzezinski et al.,
11 2001) and 0.32 to 1.19 in the Atlantic sector (Quéguiner and Brzezinski, 2002). However,
12 while these authors attribute the strong silicification to limitation by iron, it seems, in our
13 instance, that the ratios we observe during the early blooms are rather related to the taxonomic
14 composition of diatom assemblages. It is interesting to notice that the highest Si:C ratio of
15 1.19, reported by Quéguiner and Brzezinski (2002), was observed during the early stage of a
16 bloom development dominated by *Corethron criophilum* and *Fragilariopsis kerguelensis*, and
17 that the Si:C ratio then decreased to the lower value of 0.32 later in the season. Our
18 observations would thus suggest that biogenic particulate matter at the onset of the blooms of
19 naturally iron-fertilized environments could be typically Si enriched compared to C, N and P,
20 due to the presence of specific diatom communities. Our finding is a major difference
21 between the experiments of natural fertilization and artificial fertilization in the Southern
22 Ocean. In the latter, diatoms that grow are often referred to as opportunistic species such as
23 *Pseudo-Nitzschia* spp. and *Chaetoceros* spp. and these taxa are also those involved in the
24 pioneer works of Hutchins and Bruland (1998) and Takeda (1998). Apart from this general
25 trend, the European Iron Fertilisation Experiment (EIFEX) did not evidence the classical
26 decrease of Si:C and Si:N ratios observed in artificial iron-experiments (Hoffmann et al.,
27 2006; Smetacek et al., 2012). Initial Si:C, Si:N and Si:P elemental ratios (respectively 0.24,
28 1.5 and 18.0) increased from 1.8 to 2.6 times in 37 days after the first fertilization. This
29 feature was attributed to a shift, more pronounced compared to the other artificial fertilization
30 studies, towards more heavily silicified diatom species. Furthermore, the laboratory cultures
31 of two Southern Ocean diatom species (*Fragilariopsis kerguelensis* and *Chaetoceros*
32 *dichaeta*) highlighted the species-specific response to iron availability in the elemental

1 composition (Hoffmann et al., 2007). Under natural conditions, the control of stoichiometric
2 ratios is thus more complex and depends largely on the diatom community structure, itself
3 depending on the dominant species adapted to their specific set of environmental conditions.

4 Although surprising at first sight, the low Si:C and Si:N ratios observed at R2 (Fig. 13) are
5 explained by the dominance of non-siliceous organisms (mostly nanoflagellates) decreasing
6 Si proportion compared to C and N in the bulk particulate matter. Diatoms contribution to C
7 biomass was however significant (representing 34 % of the particulate organic carbon at the
8 surface; Lasbleiz et al., in prep.) which could reflect a short development of a diatom
9 assemblage just prior our sampling. This is consistent with the high dissolution rates of BSi
10 observed in surface waters (Closset et al., this volume) and the high mineralization activity
11 evidenced in the mesopelagic zone (Jacquet et al., this volume). It is likely that particular
12 biogeochemical conditions characterizing the start of the productive period would have
13 induced a progressive shift in the community composition. At the end of winter, the reference
14 station R2 would be characterized by high-nutrient waters, and unfavorable light conditions
15 for diatom growth. By early spring, iron concentrations were relatively low but likely
16 sufficient to trigger a short phytoplankton growth as soon as light conditions became
17 favorable. Given the low iron winter stock available, the bloom quickly stops well before the
18 diatoms have had time to use the stock of macronutrients. This would induce optimal
19 conditions to the development of heterotrophic communities, able to grow on the decaying
20 bloom of diatoms.

21 4.3.3 Elemental stoichiometry C:N, C:P and N:P in organic particulate matter

22 During KEOPS2, we observed a consistently lower N:P ratio compared to the canonical
23 Redfield ratio of 16 (Fig. 13). Moreover, among the different stations, the cluster of
24 productive stations located north of the PF had a significantly lower average N:P ratio
25 (10.5 ± 3.3) than all other clusters (> 11). Indeed the N:P ratio is highly variable in
26 phytoplankton (Geider and La Roche, 2002) and tends to be lower than 16 in nutrient-replete
27 cultures of phytoplankton. Klausmeier et al. (2004) showed that the optimal phytoplankton
28 stoichiometry varied, with $N:P < 16$ associated with phytoplankton growing exponentially and
29 $N:P > 16$ at competitive equilibrium. For diatoms, Sarthou et al. (2008) have reported an
30 average ratio of 10 ± 4 , based on the review of available literature. In the field, N:P ratios vary
31 also widely (Martiny et al., 2013) and low values have been reported in association to the

1 dominance of diatoms (Arrigo et al., 2002). Our observations of low N:P ratios are consistent
2 with the dominance of diatoms in the KEOPS2 region. The lowest N:P ratio in the most
3 productive region is also confirmed by the temporal evolution of nitrate and phosphate
4 distributions which show a preferential drawdown of phosphate in this region (Blain et al.,
5 this volume).

6 Ecophysiological studies of the effect of iron limitation on phytoplankton elemental ratio has
7 led to different and somewhat contradictory results. The results of Price (2005) with
8 *Thalassiosira weissflogii* suggested that iron limitation leads to a decreased N:P ratio.
9 However Hoffman et al. (2007) working with *Fragilariopsis kerguelensis* and *Chaetoceros*
10 *dichaeta* did not observe any change in C/N/P ratios in relation to iron limitation. During
11 EIFEX, the initial N:P ratios and their evolution as the bloom developed were very different
12 for two different size classes (Hoffmann et al., 2006). For the microphytoplankton (> 20 µm),
13 N:P was < 16 before fertilization and increased as the iron fertilized bloom developed. For
14 nanoplankton (2 µm to 20 µm) the opposite trend was observed: the initial N:P ratio was close
15 to 16 and decreased in the course of the bloom. In the case of the natural iron fertilization
16 around Kerguelen, we also observed a large variability between stations. But large changes
17 have also been documented at the seasonal scale. N:P of 17 ± 2 was measured in March
18 (Copin-Montegut and Copin-Montegut, 1978) at stations east of the Kerguelen Islands that
19 were close to the cluster of stations E. All these results suggest that the variability of N:P
20 ratios occurring in response to iron fertilization is ecologically driven. How these changes
21 translated in the N and P elemental composition of sinking particulate matter would certainly
22 deserve further studies.

23 The C:N ratio was close to the Redfield ratio only at the HNLC station (Fig. 13). For all other
24 stations, the C:N ratio was significantly lower but without any difference between the
25 different clusters of stations. This confirms that the C:N ratio is generally not largely affected
26 by iron limitation (Price, 2005; Hoffmann et al., 2007). Low values were previously reported
27 in the Southern Ocean including the Kerguelen region (Copin-Montegut and Copin-Montegut,
28 1978; Tréguer et al., 1988). This was considered as a general feature of the iron limited
29 Southern Ocean and interpreted as an excess of P accumulation during Fe-limited growth of
30 phytoplankton (Price, 2005). Hoffmann et al. (2006) also observed low C:P ratios in HNLC
31 waters of the Atlantic sector of the Southern Ocean, with only a modest increase in response
32 to iron fertilization. Our results from KEOPS2 also report low C:P ratios in response to iron

1 fertilization (Fig. 13). However similarly to what was discussed above for N:P, C:P increased
2 to values close to the Redfield ratio at the end of the season (Copin-Montegut and Copin-
3 Montegut, 1978).

4 In the Southern Ocean, iron limitation and iron fertilization may favor P accumulation in
5 phytoplankton for different physiological or ecological reasons, leading to N:P and C:P lower
6 than Redfield ratios. However this conclusion based on average values may hide differences
7 especially on temporal scales that are not resolved by the resolution of this data set. Overall,
8 our results also confirm a tendency of a decrease of C:N:P ratios in nutrient-rich high latitude
9 waters highlighted by Martiny et al. (2013) by comparison with warmer oligotrophic or
10 upwelling areas.

11 4.3.4 Seasonal evolution of Si, C and N cycles at the southeast plateau bloom

12 The KEOPS program provides information on the biogeochemical functioning of the
13 southeastern KP at two different periods of the seasonal cycle: the early spring (October-
14 November, 2011 - KEOPS2) and the late summer (January-February, 2005 - KEOPS1).
15 Combining the two data sets at station A3 gives us the first opportunity to describe the
16 seasonal evolution of Si, C and N cycles under natural iron fertilization in relation to
17 community composition.

18 During the KEOPS2 cruise, the first visit at A3 (October 20, A3-1) was characteristic of early
19 bloom conditions. Low biogenic and particulate organic matter concentrations were observed
20 despite high nutrients (Blain et al., this volume) and iron concentrations (Bowie et al., this
21 volume) as well as a low mesozooplankton grazing pressure (Carlotti et al., this volume).
22 Phytoplankton growth was most likely limited by low irradiance levels as expected in winter
23 and early spring (Boyd, 2002). Integrated elemental ratios (over 200 m) were close to the
24 canonical ratios of Redfield et al. (1963) and Brzezinski et al. (1985), reaching values of 0.13
25 for Si:C, 1.2 for Si:N, 16.9 for Si:P, 9.0 for C:N, 128.7 for C:P and 14.3 for N:P.

26 At the second visit (November, 16), a large development of diatoms was observed above the
27 KP due to more favorable light conditions. Biogenic silica and particulate organic matter
28 concentrations were at least 2 fold higher than in October (713.3 mmol Si m⁻² for BSi,
29 2,267 mmol C m⁻² for POC, 435.9 mmol N m⁻² for PON, and 29.3 mmol P m⁻² for POP) and
30 Si production fluxes were among the highest reported so far in the Southern Ocean (47.9
31 mmol Si m⁻² d⁻¹; Closset et al., this issue). Si:C and Si:N ratios (respectively 0.31 and 1.6)

1 were higher than Brzezinski's ratios (1985). This could directly result from the high Si:C and
2 Si:N uptake ratios (respectively 0.30 and 1.5) reported by Closset et al. (this volume) which
3 were remarkably close to our stock ratios, meaning that it is a characteristic of the species
4 growing in our study area. At this period, the organic carbon produced would be transferred to
5 small zooplankton populations which in turn would feed the large zooplankton population
6 (Henjes et al., 2007). The C budget of Christaki et al. (this volume) however, indicates that an
7 overall small fraction of primary production is transferred to higher trophic levels. Added to
8 the low vertical export of C reported by Planchon et al. (this volume), both observations are
9 strong arguments of biogenic matter retention in the surface mixed layer at the beginning of
10 the KP bloom.

11 During the KEOPS1 cruise, the period from 19th January to 12th February corresponded to the
12 last active stage of the productive period. At the start of the cruise, an unusually high level of
13 BSi had already accumulated ($2,105 \text{ mmol Si m}^{-2}$) in the mixed layer which progressively
14 declined until February (Mosseri et al., 2008). The C:N ratios of particulate matter were
15 higher than in November, and increased with depth, ranging from 6.7 at the surface to 8.7 at
16 129 m (Trull et al., 2008). This was attributed to the increase of POC concentrations with
17 depth, likely induced by settling of the increasingly senescent diatom bloom over the plateau
18 (Mosseri et al., 2008; Trull et al., 2008). Si:C and Si:N uptake ratios were close to 0.13 and 1.
19 However, the high NO_3^- concentrations in surface waters compared to H_4SiO_4 depletion at the
20 end of the bloom suggested a strong decoupling between the seasonal consumption of these
21 two nutrients. This could be due to differential remineralisation rates between Si and N, as
22 evidenced by elevated concentration of ammonium, and by the ability of diatoms to grow on
23 ammonium as nitrogen source (Mosseri et al., 2008). The system would thus behave as a
24 strong silicon pump favoring Si export to deep waters compared to N. A decoupling between
25 C and N cycles was also hypothesized: high amounts of exported C were reported evidencing
26 a strong biological pump of C (Mosseri et al., 2008; Trull et al., 2008). So, the end of the
27 productive period would be associated to the main event of massive export of biogenic silica
28 and organic matter as proposed by Quéguiner (2013). This feature seems coherent when
29 comparing the most abundant diatom species found in surface waters at the end of the
30 productive period and those found in sediment thanatocoenoses. Indeed, *Eucampia antarctica*
31 and *Chaetoceros* resting spores were the dominant species both in surface waters and in the

1 sediments (Armand et al., 2008; Wilks, 2013) suggesting enhanced export of particulate
2 matter at the end of the productive period.

3 **4.4 LSi as tracer of lithogenic matter transport?**

4 All over the study area (Fig. 14 and 15), LSi concentrations fell in the same range of values
5 previously measured in the Southern Ocean, both in the PFZ (Quéguiner et al., 1997;
6 Quéguiner, 2001; Leblanc et al., 2002) and the POOZ (Quéguiner et al., 1997; Bucciarelli et
7 al., 2001). TNS-1 and R2 stations showed low LSi concentrations typically observed for
8 regions far from continental influence ($< 0.04 \mu\text{mol L}^{-1}$; Leblanc et al., 2002). Surprisingly, a
9 local maximum was reported at 500 m at station R2, reflecting particulate lithogenic inputs at
10 depth. A similar pattern was found for particulate and dissolved trace metals (Bowie et al.,
11 this volume; Quéroué et al., this volume; van der Merwe et al., this volume). In these studies,
12 lateral transport of lithogenic matter from the Leclaire Rise, a large seamount located west of
13 station R2, was hypothesized to explain this local maximum.

14 In contrast to R2 and TNS-1, two regions were characterized by very high LSi concentrations
15 typically reported for regions subjected to continental influence (Bucciarelli et al., 2001): the
16 coastal waters over the entire water column (TEW-1 to TEW-3) and the reference plateau
17 station A3 near the bottom. For the coastal waters (TEW-1 to TEW-3), LSi could come from
18 multiple lithogenic sources such as soil erosion, riverine discharges or aeolian inputs
19 (Bucciarelli et al., 2001). At A3, the maximum concentration near the bottom would rather
20 reflect sediment resuspension in the water column. Another striking feature at A3 was the
21 relatively high concentrations from the surface down to 300 m. Two potential sources of
22 lithogenic material could explain these higher concentrations: LSi could come from below
23 due to an elevated vertical mixing or from the extensive shoal around the Heard/Mc Donald
24 Islands by horizontal advection (Blain et al., 2007; Park et al., 2008a). Interestingly,
25 maximum concentrations were found at 400 m for E-4W2 and between 600 and 700 m at the
26 different visits of the complex system of recirculation (stations E). This could evidence lateral
27 transport of LSi-rich waters coming from the plateau and more likely from the Heard/Mc
28 Donald Islands in the case of E-4W. Our results were consistent with the study of Bowie et al.
29 (this volume) which reported lithogenic particulate iron coming from the plateau between 400
30 and 600 m at E-1, E-3 and E-5.

1 In the PF area (from TEW-7 to TEW-8), relatively higher concentrations compared to
2 surrounding waters ($> 0.11 \mu\text{mol L}^{-1}$) were observed over the water column. Such a pattern
3 was already reported by previous studies in different sectors of the Southern Ocean
4 (Quéguiner et al., 1997; Bucciarelli et al., 2001). At the southern border of the PFZ in the
5 Atlantic sector, high LSi concentrations were associated to local inputs from atmospheric
6 deposition. By using the NOAA HYSPLIT 1-day and 5-day backward trajectory atmospheric
7 model, no atmospheric inputs were evidenced as suggested by the absence of air masses
8 flowing over the eastern area north of the PF (Quéroué et al., this volume). However,
9 considering that no direct measurements of dust deposition were performed during KEOPS2,
10 the hypothesis of aeolian inputs cannot be completely rejected. In addition, a recent study
11 performed in the Kerguelen region demonstrated that atmospheric deposition fluxes have
12 been underestimated until now (Heimbürger et al., 2012). Both aeolian inputs and lateral
13 advection of LSi-rich waters could thus explain the relatively higher concentrations between
14 TEW-7 and TEW-8. LSi-rich waters would probably result from the northwest transport of
15 deep waters from the KP (Zhou et al., this volume) or from the mixture of the advected
16 coastal waters with the subantarctic water (Bucciarelli et al., 2001). The station TNS-2,
17 located north of the PF, would also suggest aeolian dust deposition coupled with lateral
18 advection of LSi-rich waters by evidencing local LSi maximums at the surface and
19 subsurface.

20 By comparing particulate iron and other trace metal distribution (Bowie et al., this volume),
21 similar patterns were observed at R2, A3 and E stations over the water column. This suggests
22 that LSi would be a good tracer to track lithogenic material inputs (and indirectly iron) from
23 aeolian transport, terrestrial erosion as well as sediment resuspension to the water column. All
24 the more so that the Kerguelen Islands are mainly composed of flood basalt, a Si-rich rock
25 (Gautier, 1987). In this study, several potential sources were mentioned to explain the
26 distribution of lithogenic matter all over the study area. The northward transport of lithogenic
27 matter and vertical transport from deep waters enriched in lithogenic materials were expected
28 from the KEOPS1 study (Blain et al., 2007; van Beek et al., 2008; Park et al., 2008a).
29 Furthermore, even if the contribution of atmospheric inputs is still matter of debate (Cassar et
30 al., 2007; Heimbürger et al., 2012), dust deposition could play a significant role in supplying
31 lithogenic matter in the Kerguelen region.

1 **5 Conclusions**

2 The distribution of particulate matter and phytoplankton community structure above the
3 natural iron-fertilized Kerguelen region was strongly impacted by the complex mesoscale
4 structure of water masses, generated by the interaction between the KP topography and the
5 Polar Front pathway. In early spring, the eastern side of the KP was characterized by a mosaic
6 of biogeochemical situations that could be divided into five contrasted environments. A
7 productive coastal area was first isolated by a shelf break front from a second area less
8 productive corresponding to a cold water tongue circulating northward and likely limited by
9 light availability. The situation was different in the meander of the PF, where the complex
10 mesoscale activity induced a phytoplankton development delayed by comparison to the KP
11 itself. Two high productive areas were located at the easternmost study area north in the PF
12 and over the southeastern KP where light conditions and nutrients (including iron) availability
13 were favorable to phytoplankton growth. Biogeochemical properties of the eastern flank of
14 the KI supports the idea that the extensive bloom of the southeastern KP was, at least partly,
15 advected northwards.

16 The comparison between the iron-fertilized productive sites and the iron-limited HNLC area
17 showed that iron stimulated the accumulation of large ($> 20\mu\text{m}$) siliceous particulate matter at
18 the onset of the bloom. Under iron stress, the low Si biomass was mainly associated to mixed,
19 nanoflagellate-dominated, phytoplankton population but Si:C:N:P ratios were unexpectedly
20 close to the typical values for nutrient-replete diatoms, which was likely due to the presence
21 of siliceous detritus from an earlier bloom. In the iron-fertilized areas, we showed a patchy
22 response of particulate matter distribution and stoichiometric ratios but with overall elevated
23 Si:C:N:P. This suggests the presence of heavily silicified diatoms contrary to the classical
24 paradigm of Hutchins & Bruland (1998) and Takeda (1998). The variable and patchy nature
25 of responses in the natural surroundings of the KI calls for cautious consideration in
26 extrapolating the results from artificial iron fertilization experiments.

27 The seasonal evolution of the bloom over the southeastern KP (A3 station) is characterized by
28 a progressive evolution of the Si:C:N ratios and the phytoplankton community composition
29 probably resulting in different export regimes at the beginning (retention in the ML) and the
30 end of the productive season (massive vertical export). At the onset of the bloom, the weak
31 vertical export, mainly driven by nanoplanktonic size fraction of biogenic silica, could be the

1 result of the fragmentation of particles originating from aborted late winter blooms. Given the
2 high Si:C:N ratios in the surface waters and the expected preferential degradation of organic
3 matter by small zooplankton community in the course of the productive period, the system
4 behaves as a moderate silicon pump in spring. At the end of the bloom, the increasing
5 influence of silicic acid depletion and changes in the phytoplankton community structure
6 result in decreased Si:C and Si:N ratios. Additionally, increased grazing pressure from
7 mesozooplankton leads to a massive export of biogenic silica and carbon organic matter at
8 depth which occurs later in the season (Rembauville et al., in prep.). In the natural iron
9 fertilized Kerguelen region, understanding the patchy development of distinct blooms with
10 varying Si:C:N:P composition and the ultimate fate of produced biogenic silica and organic
11 carbon (as in the “silica-sinkers” vs “carbon-sinkers” hypothesis; Assmy et al., 2013) calls for
12 a finer characterization of diatoms interspecific contribution to both Si production and C
13 biomass, which can only be addressed by taxonomic studies and cellular labelling (Lasbleiz et
14 al., in prep.). As emphasized by Boyd (2013), the concept of functional group tends to fall
15 short when probing its responses to environmental forcings and diatom floristic shifts impact
16 on global biogeochemical cycles needs to be further understood.

17

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27

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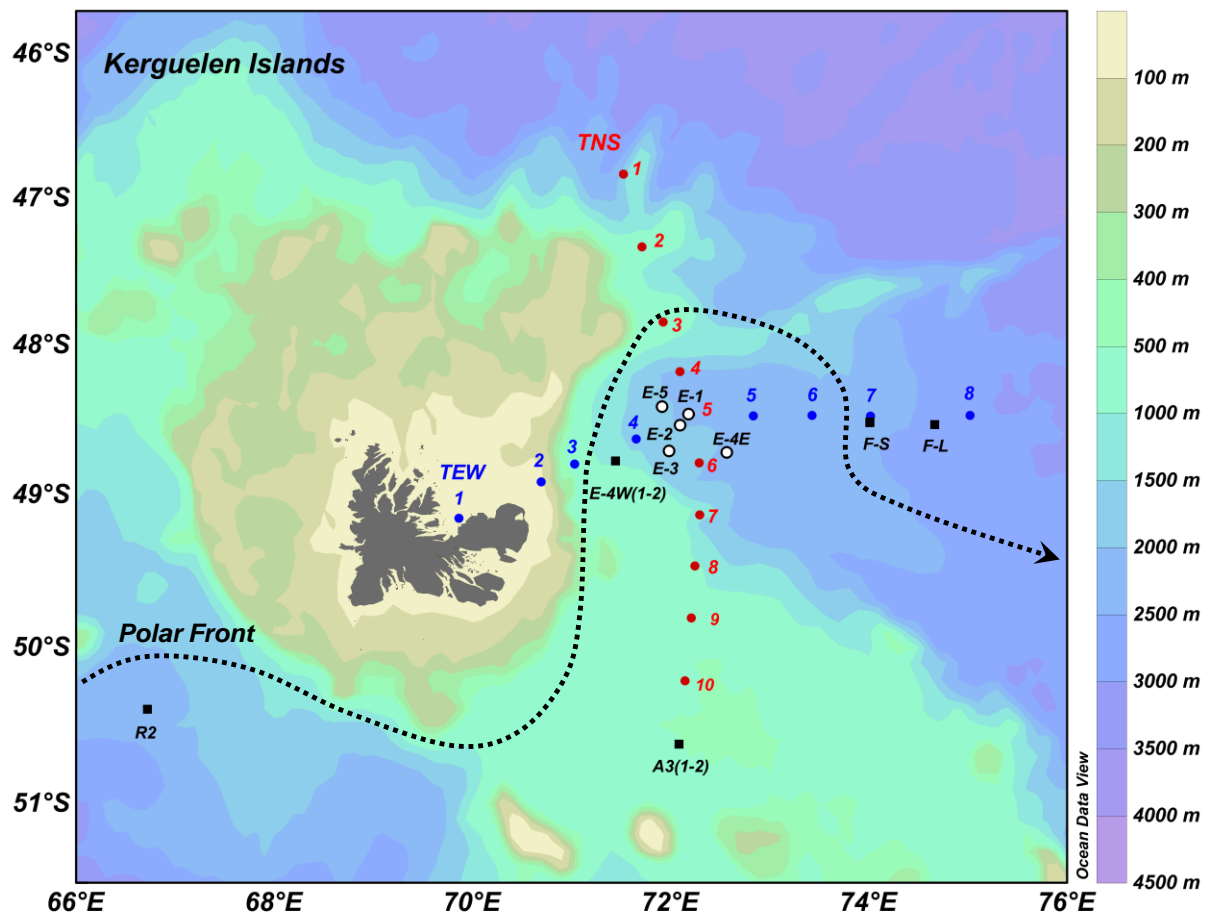
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16 Table 1. Integrated concentrations in BSi, POC, PON and POP (in mmol m^{-2}) over 200 m
17 depth (except for the coastal station TEW-2, integrated over 70 m) North and South of
18 the Polar Front.

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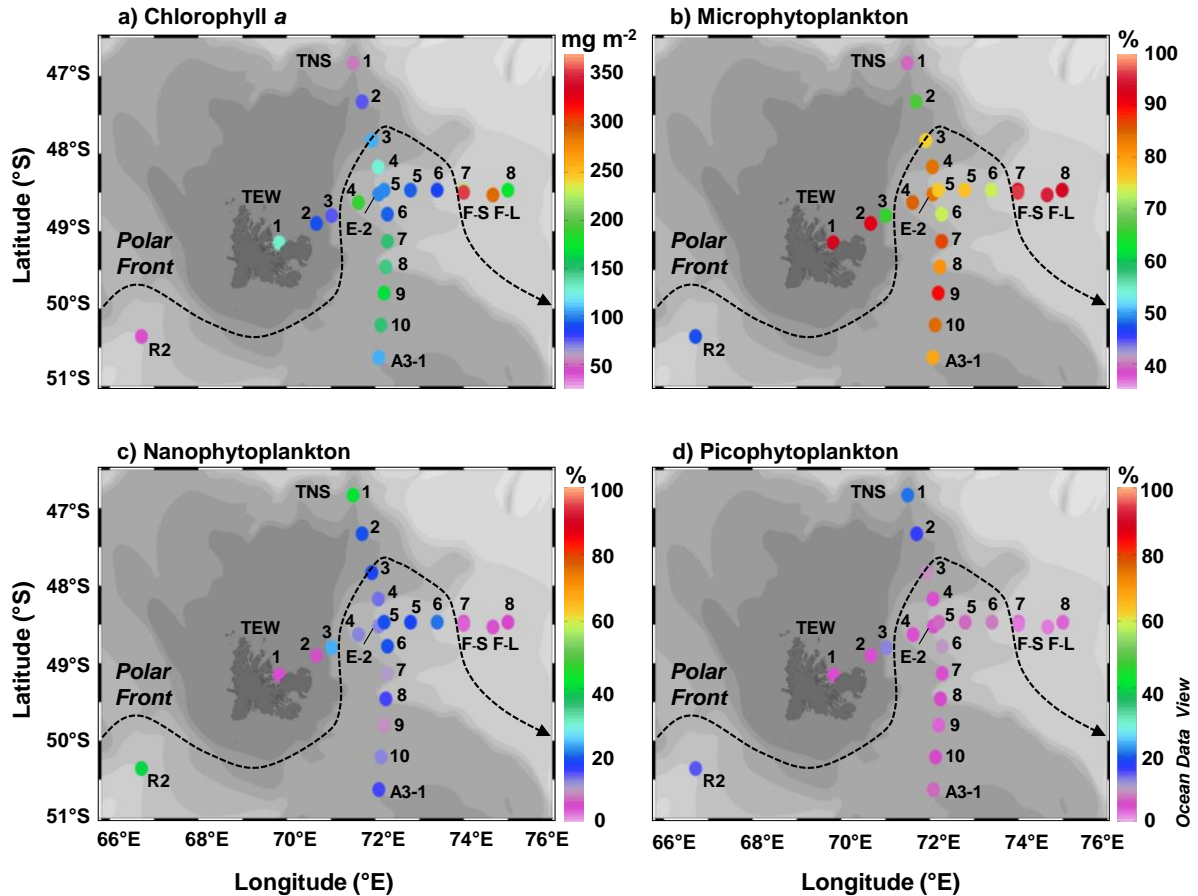
| | Integrated concentrations (mmol m^{-2}) | |
|--------------|--|---|
| | North of the PF (Stations TEW-2, TEW-3, TNS-1, TNS-2) | South of the PF (Stations TEW-4 to TEW-6, TNS-3 to TNS-10, A3-1) |
| Σ BSi | 33.5 - 141.0 | 240.0 - 460.3 |
| Σ POC | 456.9 - 629.6 | 562.9 - 1,164.2 |
| Σ PON | 83.1 - 144.9 | 143.5 - 250.3 |
| Σ POP | 5.7 - 10.1 | 8.7 - 18.9 |

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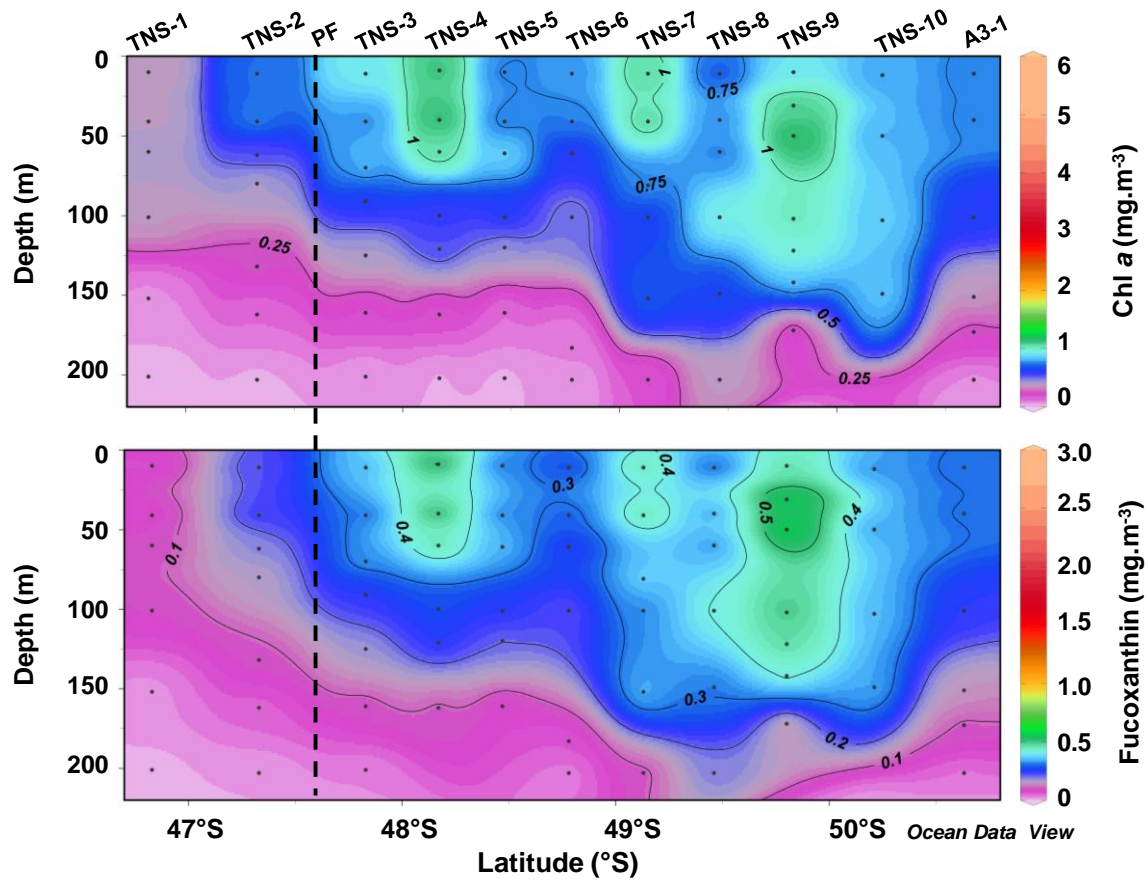


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 2 Figure 1. Location of the sampling stations. Transects from North to South (TNS) and from
 3 West to the East (TEW) are indicated in red and blue respectively. The blank filled circles
 4 correspond to a time-series of a recirculation system (E-1, E-2, E-3, E-4E and E-5). The
 5 stations F-L and F-S are located in the eastern bloom in the Polar Front Zone. A3 and E-4W
 6 are respectively the reference southeastern Kerguelen Plateau bloom and the reference eastern
 7 flank of the Kerguelen Plateau. Both were visited twice (1-2). R2 is the HNLC reference
 8 station. The dotted line represents the approximate location of the southern branch of the
 9 Polar Front.

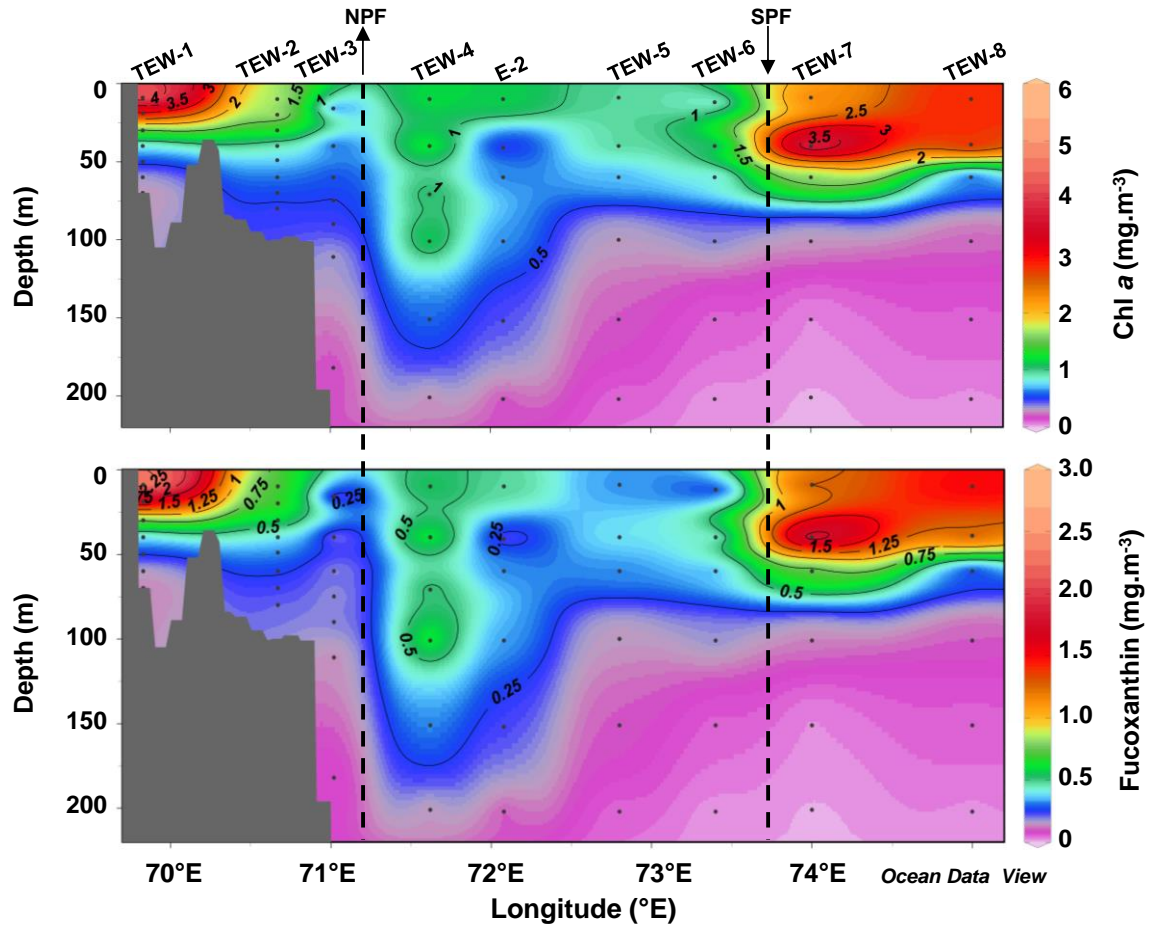
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 2 Figure 2. Distribution of depth-integrated total chlorophyll *a* (a) and contribution of micro-
 3 (b), nano- (c), picophytoplankton (d) communities to total biomass. Vertical integrations were
 4 made from the surface to 200 m except for the coastal stations TEW-1 and TEW-2 where data
 5 were integrated down to 70 m. The TNS transect (comprising A3-1) was sampled from the
 6 20th to the 23rd October, while the TEW transect (comprising E-2) was sampled between the
 7 31th October and 2nd November. Station R2 was sampled between the two transects on the 25th
 8 October, while stations F were sampled after the two transects, on the 6th November (F-L),
 9 and the 8th November (F-S). The dashed line represents the Polar Front trajectory.
 10



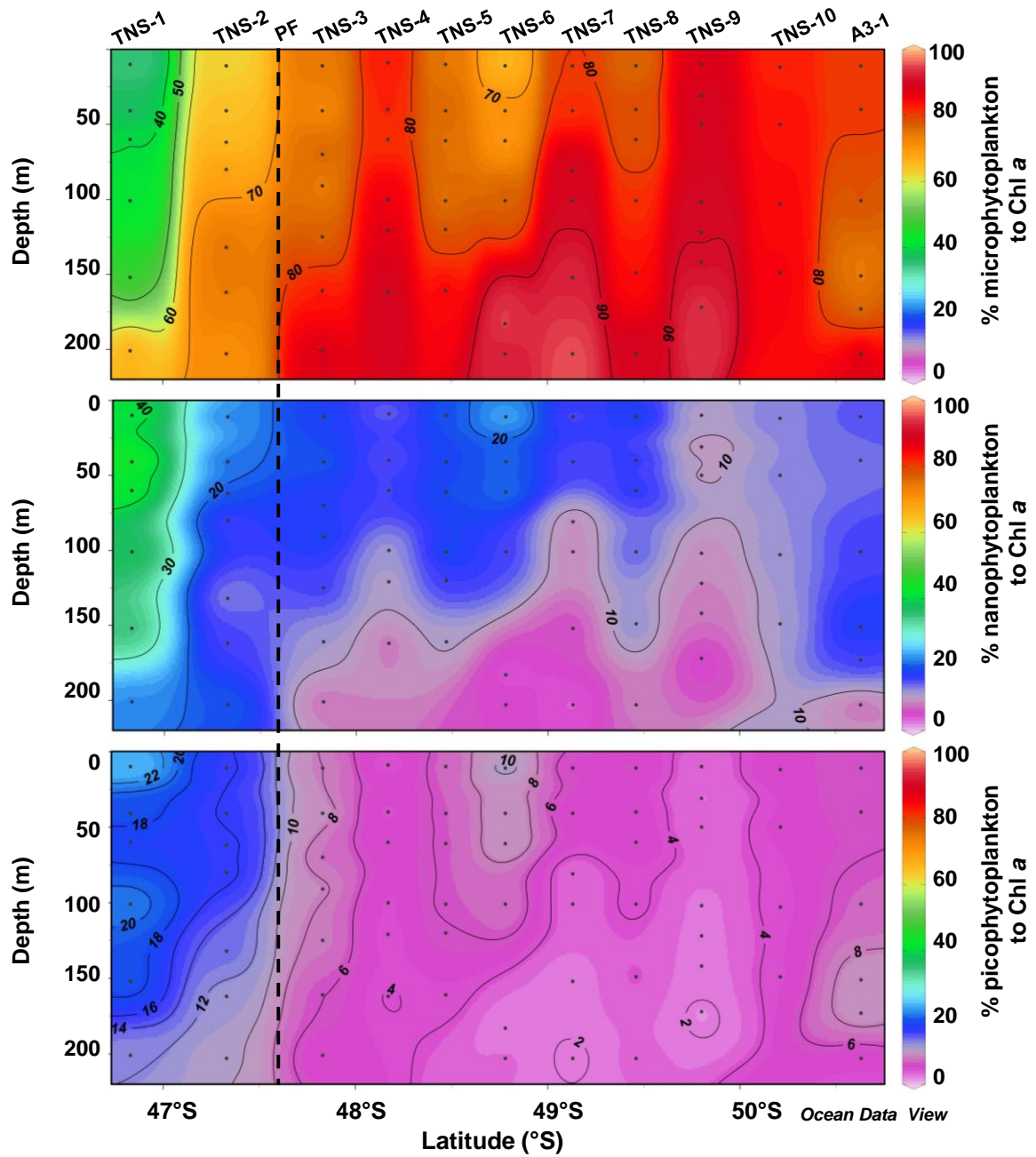
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 2 Figure 3. Vertical distribution of total chlorophyll *a* (Chl *a*) and fucoxanthin concentrations
 3 along the TNS transect. The dashed line represents the approximate location of the southern
 4 branch of the Polar Front (PF).
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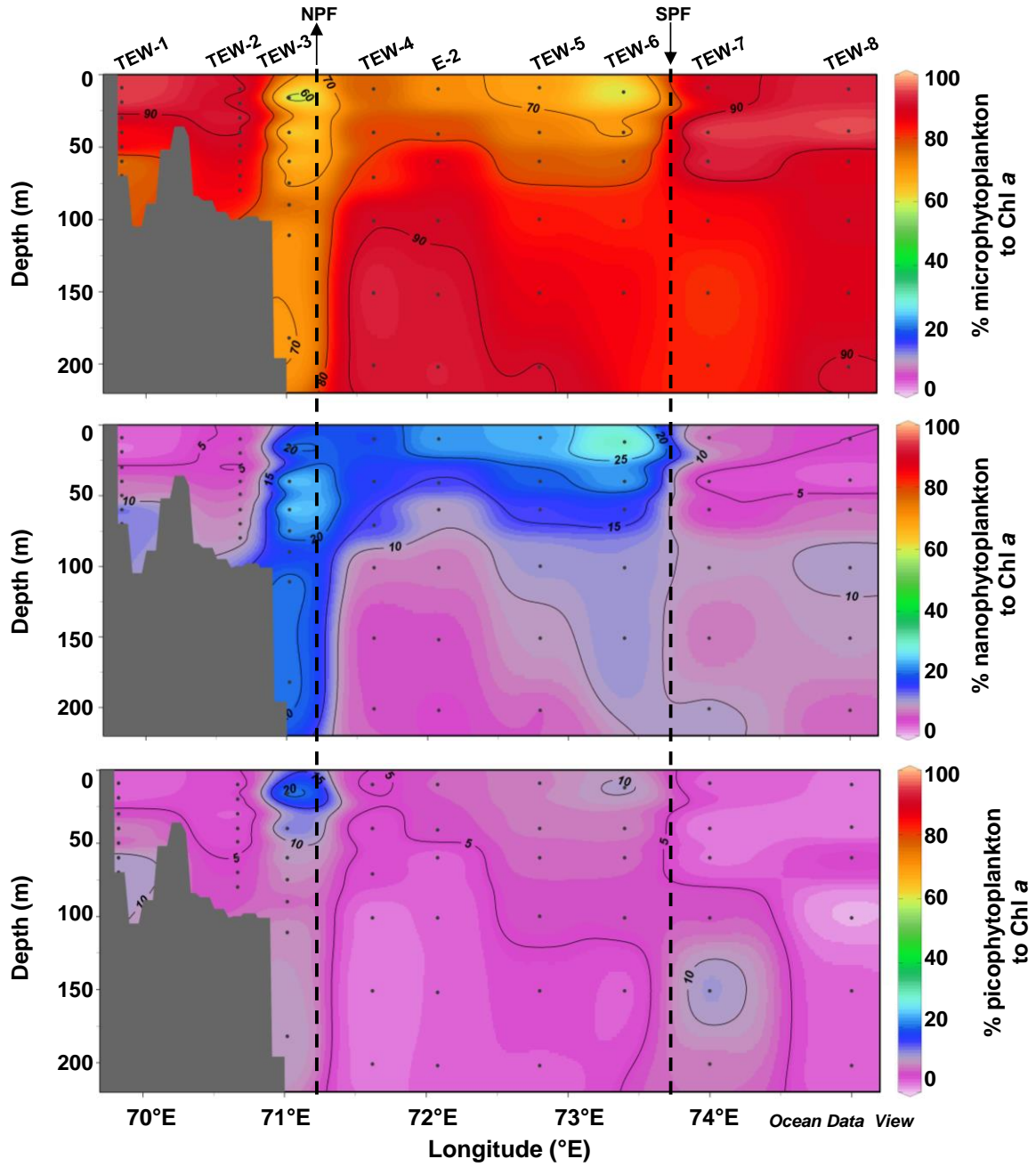
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2 Figure 4. Vertical distribution of total chlorophyll *a* (Chl *a*) and fucoxanthin concentrations
 3 along the TEW transect. The dashed lines represent the approximate location of the southern
 4 branch of the Polar Front going to the north (NPF) and to the south (SPF).

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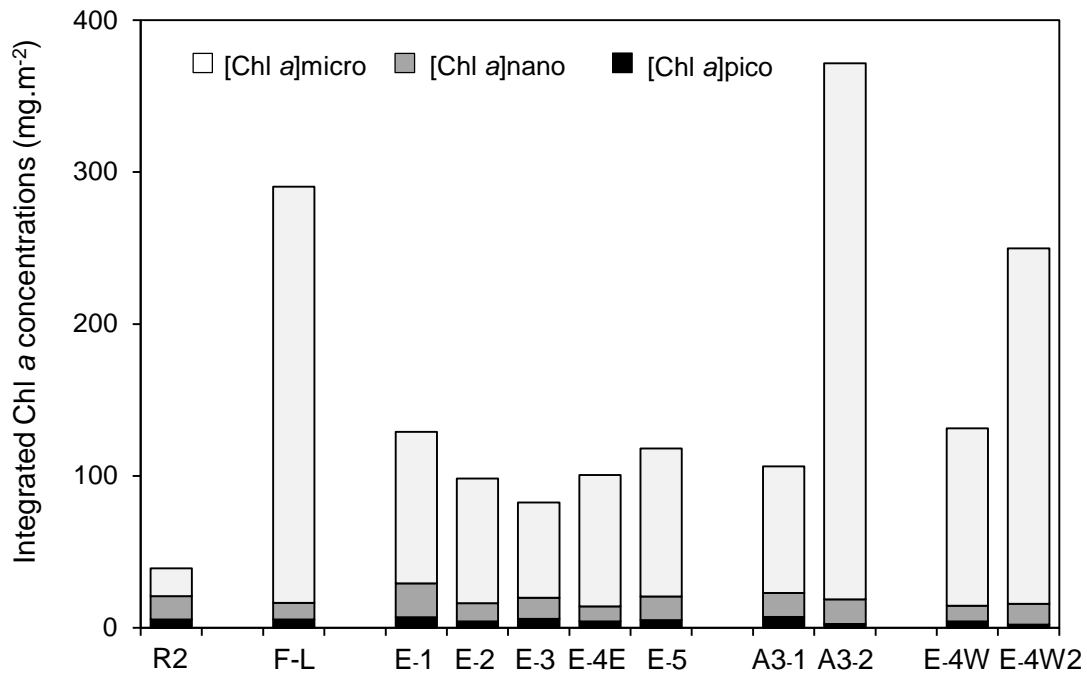
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 2 Figure 5. Vertical distribution of micro-, nano- and picophytoplankton community
 3 contributions to total biomass along the TNS transect. The dashed line represents the
 4 approximate location of the southern branch of the Polar Front (PF).
 5



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2 Figure 6. Vertical distribution of micro-, nano- and picophytoplankton community
 3 contributions to total biomass along the TEW transect. The dashed lines represent the
 4 approximate location of the southern branch of the Polar Front going to the North (NPF) and
 5 to the South (SPF).

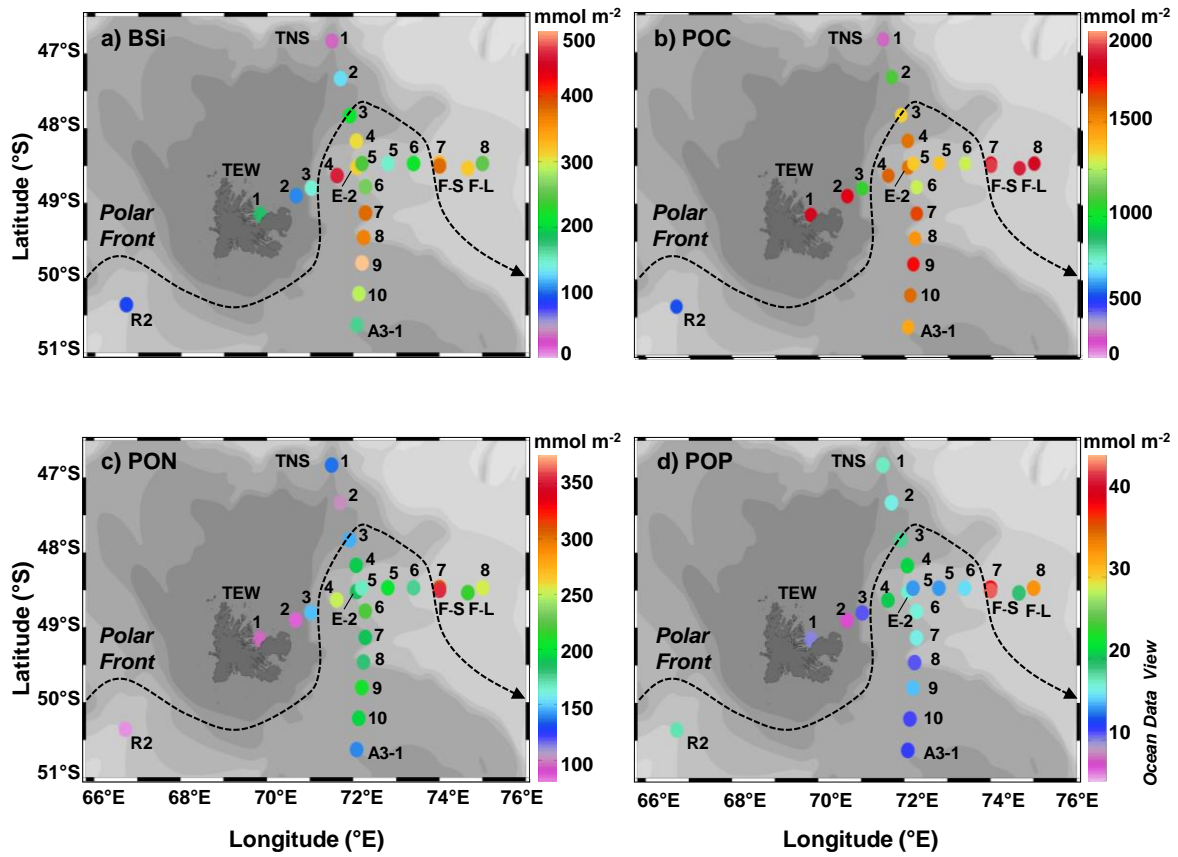
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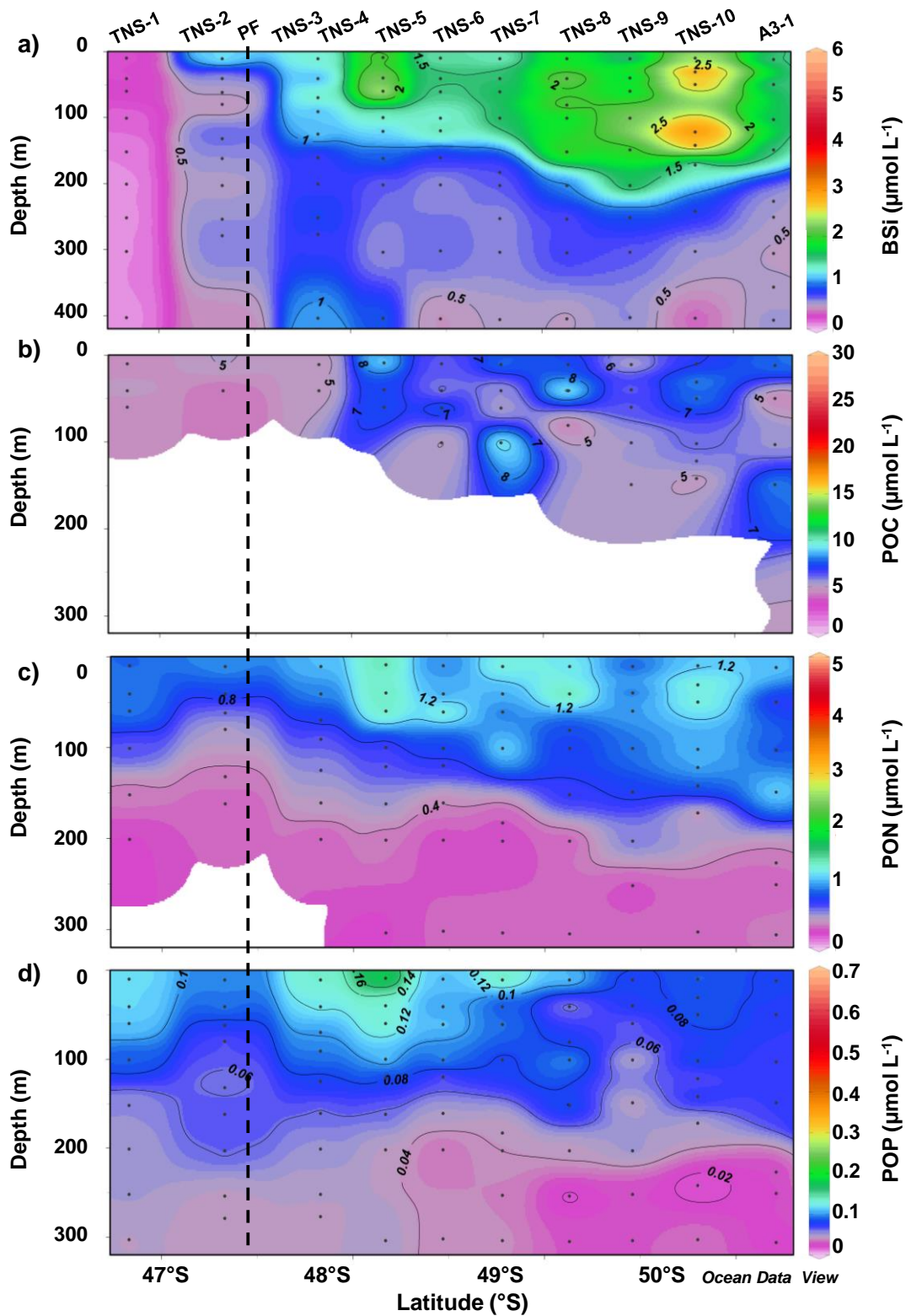
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2 Figure 7. Temporal evolution of Chl *a* concentrations associated with micro- ([Chl *a*]micro),
 3 nano- ([Chl *a*]nano) and picophytoplankton ([Chl *a*]pico) within 200 m at the complex system
 4 of recirculation (five visits chronologically numerated : E-1 (10/29) , E-2 (11/01), E-3
 5 (11/03), E-4E (11/13), E-5 (11/19)), at the plateau reference station A3 (two visits: A3-1
 6 (10/20) and A3-2 (11/16)) and at station E-4W (two visits : E-4W (11/12) and E-4W2
 7 (11/18)). The station F-L (integrated within 150 m) and the HNLC reference station R2 are
 8 presented for comparison.

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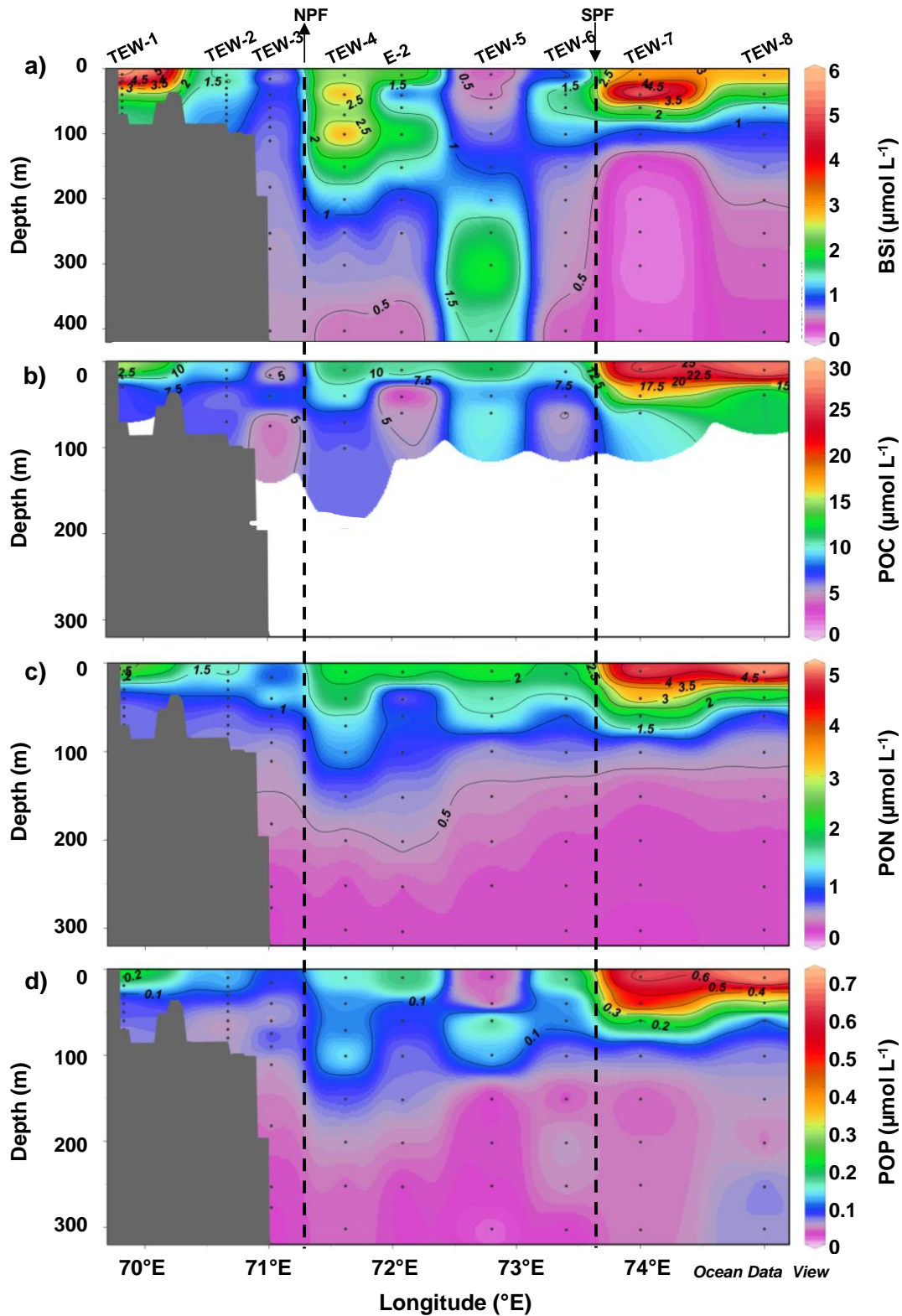


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 2 Figure 8. Distribution of biogenic silica (a), particulate organic carbon (b), nitrogen (c) and
 3 phosphorus (d) (same vertical integrations and legends as Fig. 2).

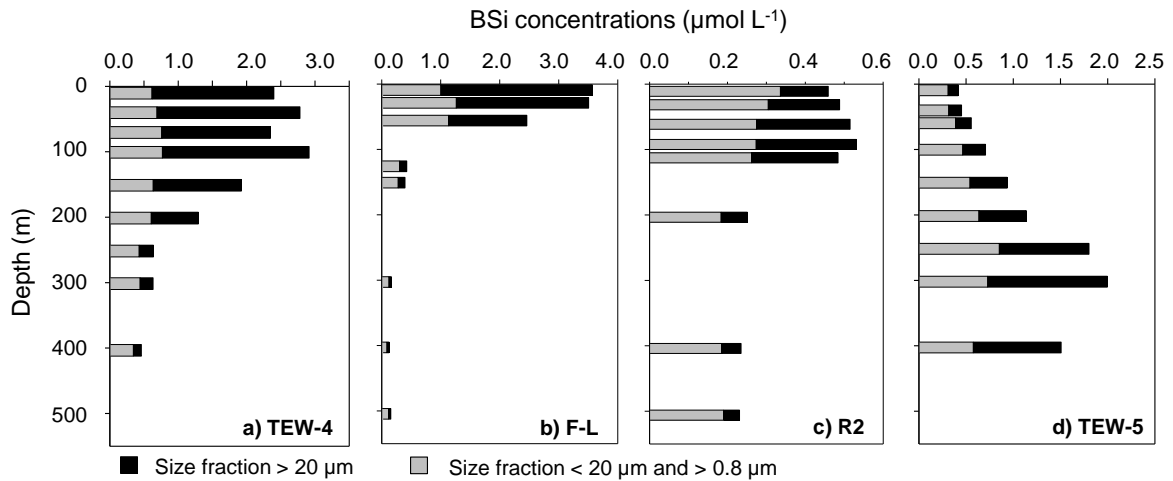


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2 Figure 9. Vertical distributions of BSi (a), POC (b), PON (c), POP (d) concentrations along
 3 the TNS transect. The dashed line represents the approximate location of the southern branch
 4 of the Polar Front (PF).



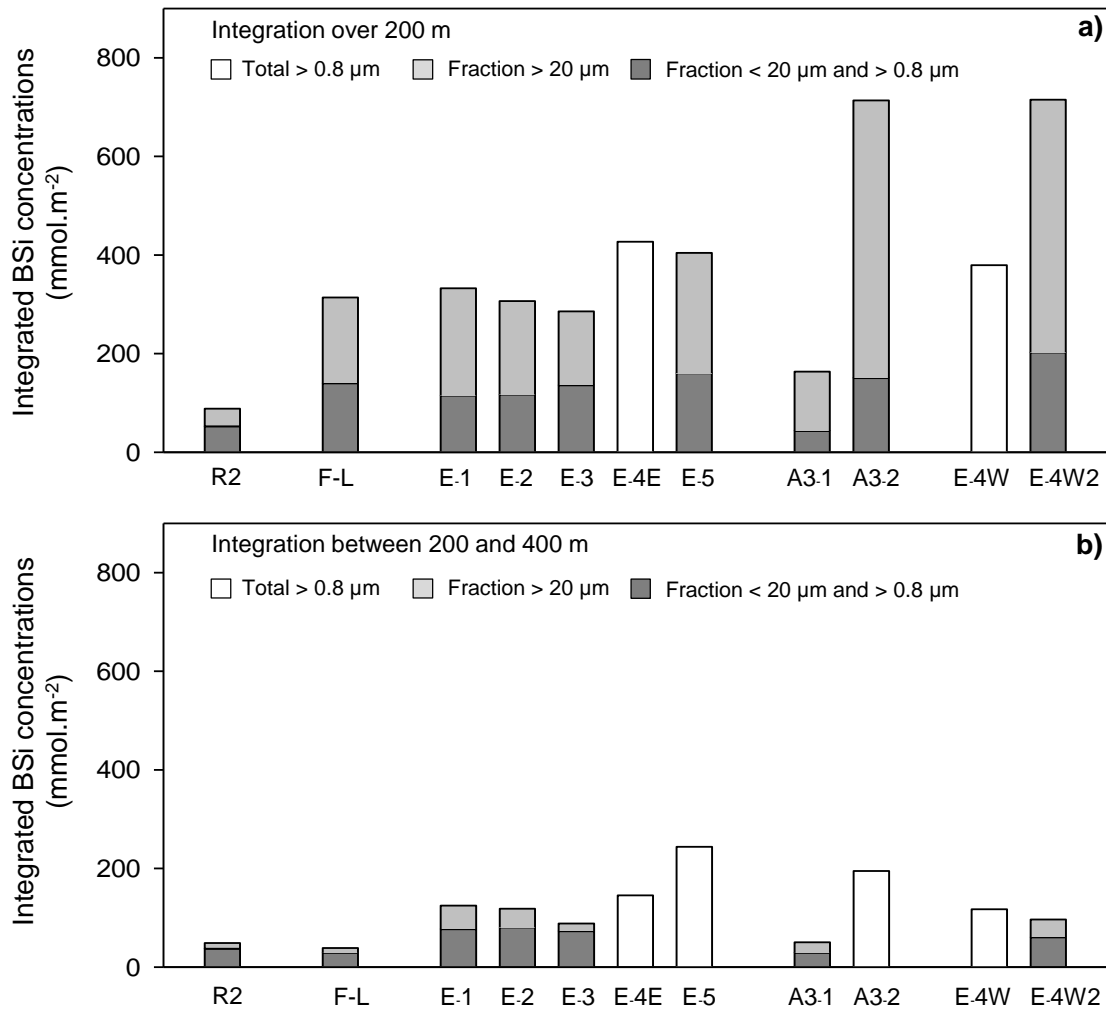
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 2 Figure 10. Vertical distributions of BSi (a), POC (b), PON (c), POP (d) concentrations along
 3 the TEW transect. The dashed lines represent the approximate location of the southern branch
 4 of the Polar Front going to the North (NPF) and to the South (SPF).



1

2 Figure 11. Vertical profiles of BSi concentrations for two size fractions (> 20 µm in black and
 3 between 0.8 and 20 µm in grey) at TEW-4 (a), F-L (b), R2 (c) and TEW-5 (d). These four
 4 stations were chosen to illustrate the four typical vertical profiles observed over the study
 5 area: TEW-4 represents typical profile of the stations A3-2 and E (from E-1 to E-5), F-L
 6 represents typical profile of stations E-4W and those located in the PFZ, R2 represents typical
 7 profile of the low productive stations (R2, TNS-1, TNS-2, TEW-2, TEW-3, TEW-5 and
 8 TEW-6) and TEW-5 is the only station showing such a vertical profile.

9

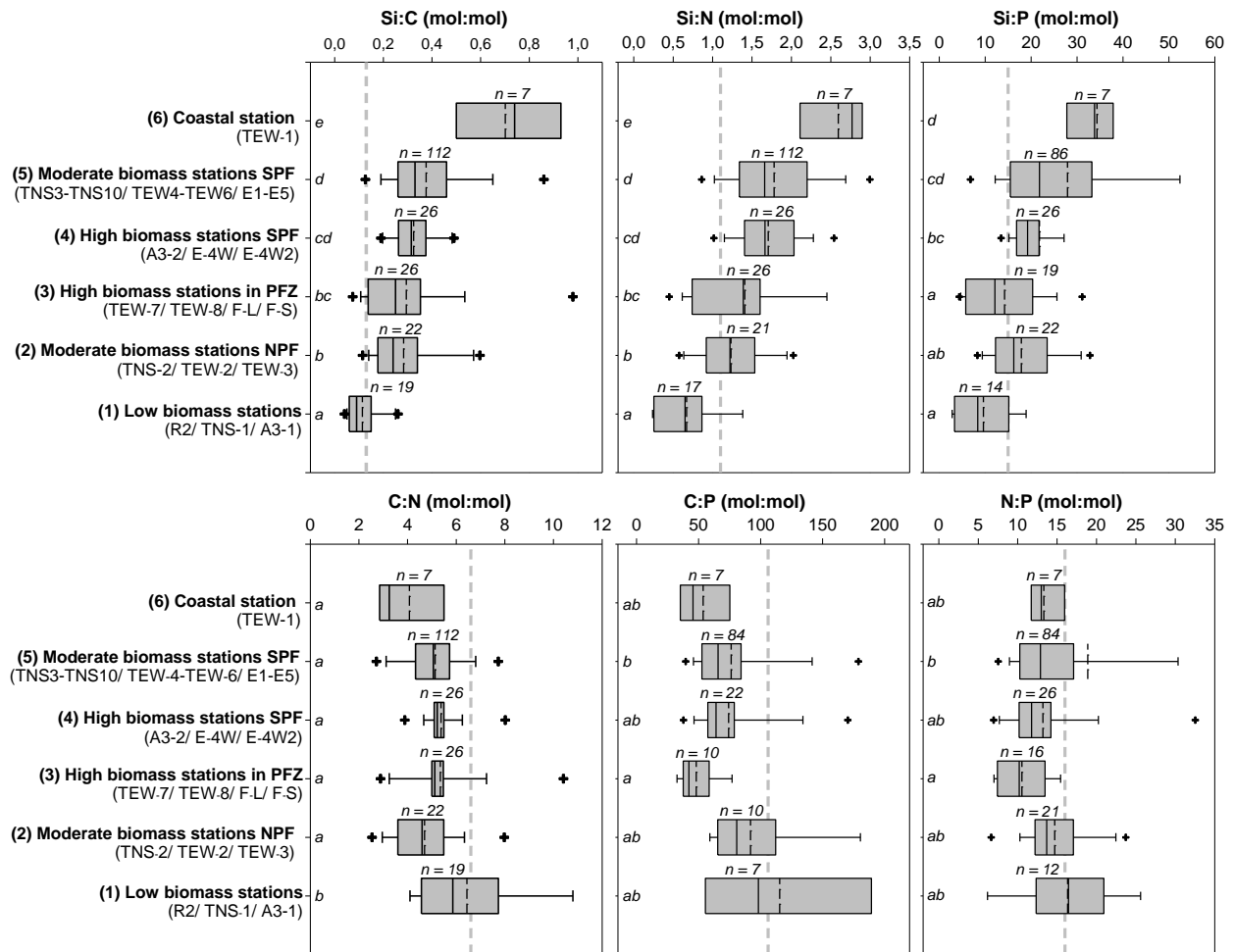


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2 Figure 12. Temporal evolution of BSi concentrations within 200 m (a) (except for A3-2 where
 3 data were integrated down to 160 m) and between 200 and 400 (b) for three size fractions
 4 ($> 0.8 \mu\text{m}$, between 0.8 and $20 \mu\text{m}$ and $> 20 \mu\text{m}$) at the complex system of recirculation, at
 5 the plateau reference station A3, at station E-4W (stations legend as in Fig. 7). The station F-
 6 L and the HNLC reference station R2 are presented for comparison. At some stations, size-
 7 fractionation was not performed because of logistical problems on-board.

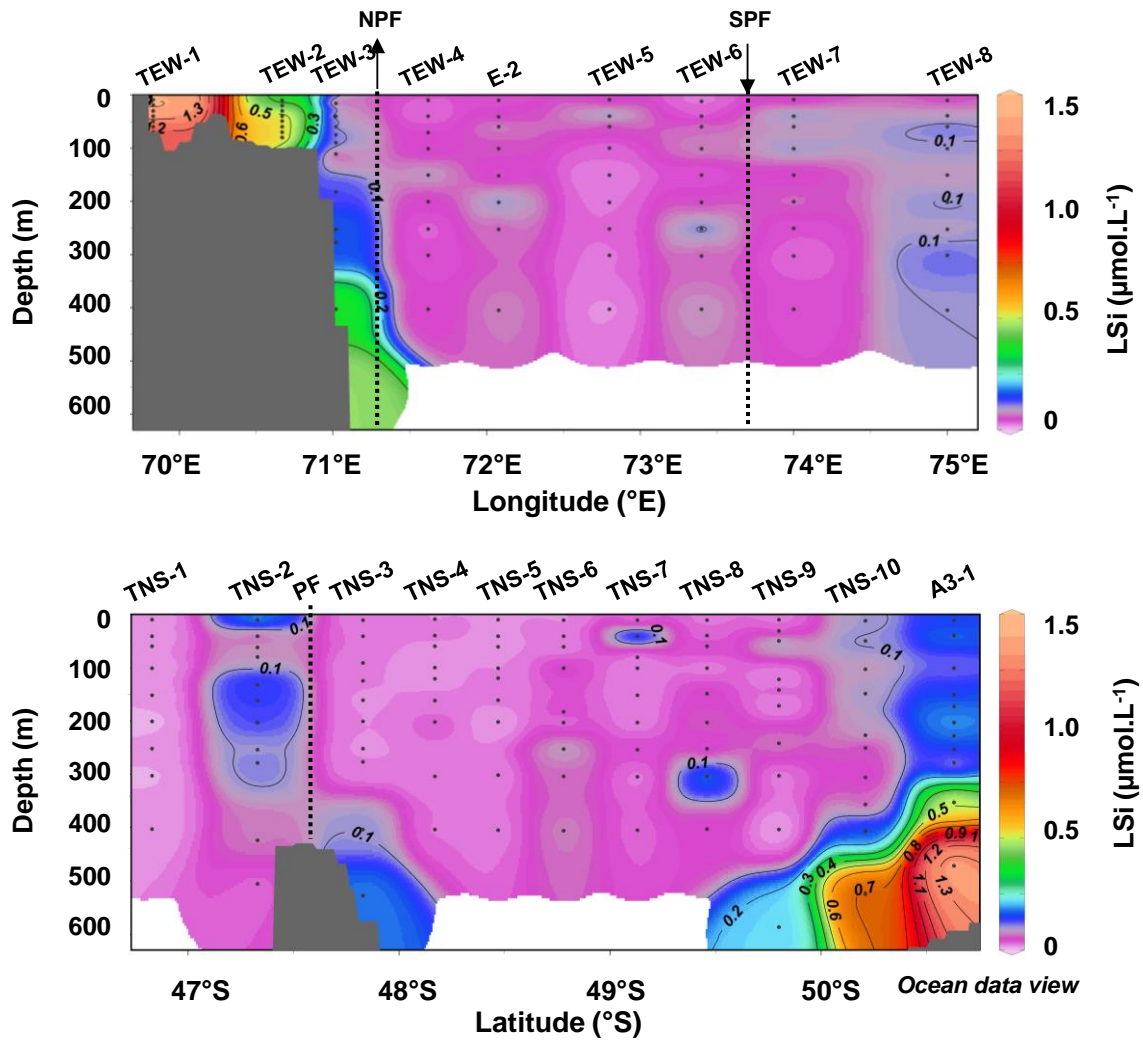
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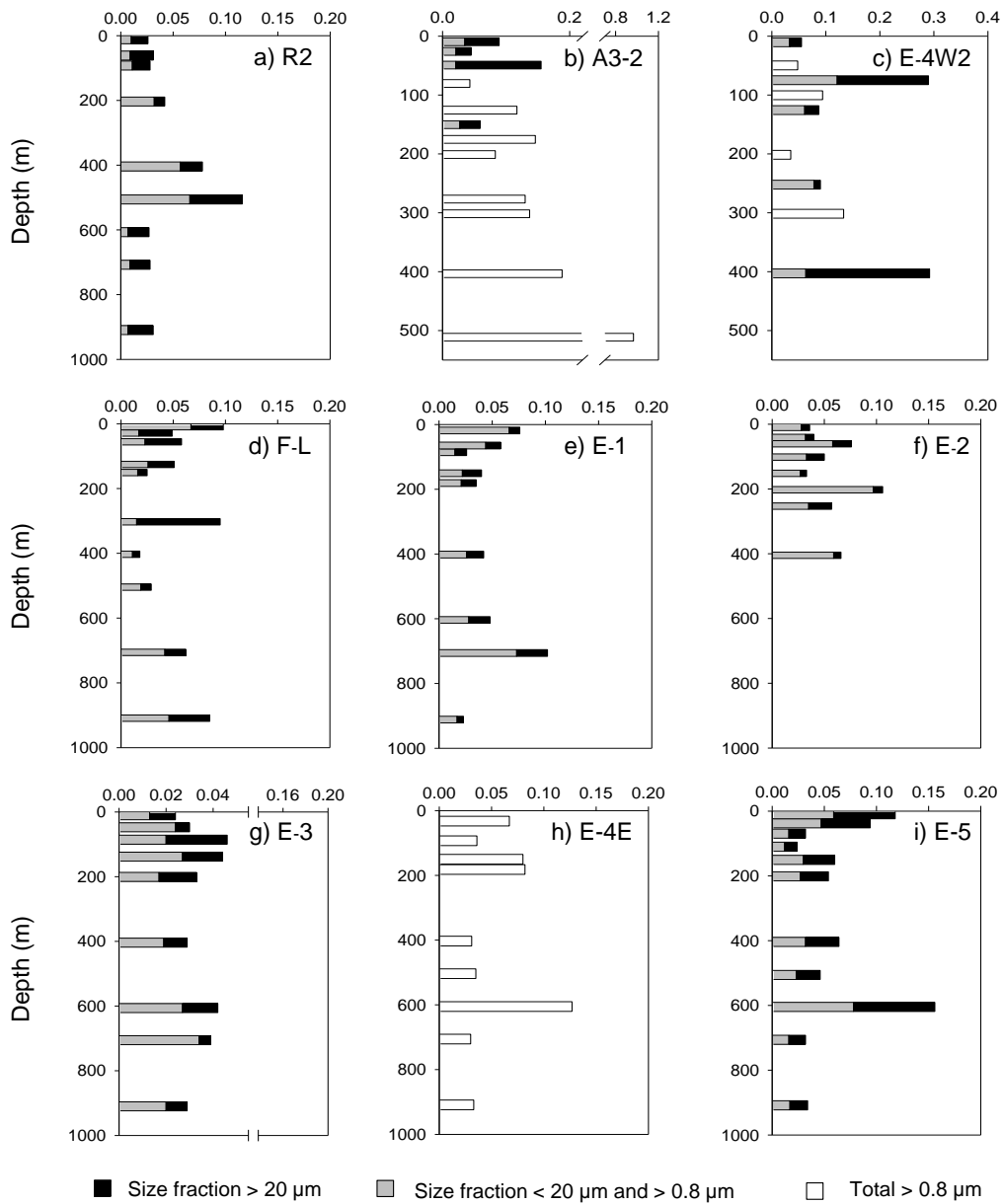
2 Figure 13. Box plots of the Si:C, Si:N, Si:P, C:N, C:P and N:P molar ratios within 200 m
 3 (except for TEW-1 and TEW-2 where data were restricted within 70 m) for 6 clusters of
 4 stations located in the Polar Front Zone (PFZ), north (NPF) and south of the Polar Front
 5 (SPF). The length of the box corresponds to the distance between the 5th and the 95th
 6 percentiles. The plain line and the dashed line inside the box represent the median and the
 7 mean respectively. The vertical lines extend to the minimum and maximum values of the
 8 cluster. The cross symbols correspond to outliers and “n” is the number of values in each
 9 cluster. The grey dashed lines represent the typical values of Si:C (0.13), Si:N (1.1) and
 10 Si:P (15) for nutrient-replete diatoms reported by Brzezinski (1985) and the typical values of
 11 C:N (6.6), C:P (106) and N:P (16) reported by Redfield et al. (1963). The clusters of which
 12 medians are not statistically different are indicated by the same letter (Mann-Whitney U-test,
 13 $p > 0.05$).



1

2 Figure 14. Vertical distribution of lithogenic silica (LSi) concentrations along the TEW and
 3 TNS transects. The dotted lines represent the approximate location of the southern branch of
 4 the Polar Front going to the North (NPF) and to the South (SPF).

5



1

2 Figure 15. Vertical profiles of lithogenic silica (LSi) concentrations for three size fractions
 3 (> 0.8 μm , between 0.8 and 20 μm and > 20 μm) at stations R2 (a), A3-2 (b), E-4W2 (c), F-L
 4 (d) and at stations E: E-1 (e), E-2 (f), E-3 (g), E-4E (h), E-5 (i).