1 **Dissolved greenhouse gases (nitrous oxide and methane) associated with the naturally iron-**

2 **fertilized Kerguelen region (KEOPS 2 cruise) in the Southern Ocean**

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ABSTRACT

The concentrations of greenhouse gases (GHGs) like nitrous oxide (N_2O) and methane (CH_4) were measured in the Kerguelen Plateau Region (KPR), an area with an annual microalgal bloom caused by natural Fe fertilization, which may stimulate microbes involved in GHG cycling. This study was carried out during the KEOPS 2 cruise during the austral spring of 2011. Oceanographic variables including N_2O and CH_4 (from surface to 500 m depth) were sampled in two transects along and across the KRP, the north-south (N-S) transect (46°-51°S, ~72°E) and the west-east (W-E) transect (66°-75°E, ~48.3°S); both associated with the presence of a plateau, polar fronts and other mesoscale features. The W-E transect had N_2O levels ranging from equilibrium (105%) to slight supersaturation (120%) with respect to the atmosphere. CH_4 levels fluctuated dramatically, with high supersaturations (120-970%) in areas close to the coastal waters of Kerguelen Island and in the polar front (PF). The N-S transect showed a more homogenous distribution for both gases, with N_2O and CH_4 levels from 88% to 171% and 45% to 666% saturation, respectively, but surface CH_4 peaked at southeastern stations of the KPR (A3 stations), where a phytoplankton bloom was observed. Both gases responded significantly, but in contrasting ways (CH_4 accumulation and N_2O depletion), to the patchy distribution of particulate matter as chlorophyll a. This seems to be strongly stimulated by Fe supply from different sources. Air-sea fluxes for N_2O (from -10.5 to 8.65, mean 1.71 µmol m^{-2} d^{-1}) and for CH_4 (from 0.32 to 38.1, mean 10.07 µmol m^{-2} d^{-1}) indicated that the KPR is both a sink and a source for N_2O, and a considerable and variable source for CH_4. These results are previously unreported for the Southern Ocean and it is suggested that it may be caused by an intense microbial CH_4 production.

1   1. **Introduction**

2   The increasing concentration of greenhouse gases (GHGs) in the troposphere, such as CO_2, N_2O and

3   CH_4, affect the Earth's radiative balance. Additionally, the increasing concentration of ozone-depleting

4   gases (such as chlorofluorocarbons and N_2O) in the stratosphere is weakening the ozone shield,

5   permitting higher levels of damaging ultraviolet radiation to reach the Earth's surface. The strength of

6   each GHG is determined by its respective residence time in the atmosphere (Cicerone and Orelamland,

7   1988) and the magnitude of emissions to the atmosphere, of which the oceans make an important

8   contribution (IPCC, 2007).

9   Although oceans are generally considered to be a net source of GHGs to the atmosphere, such as N_2O

10   and CH_4, the oceanic distribution of these GHGs and the amount of exchanged via the air-sea interface

11   is highly variable (Nevison et al., 1995; Holmes et al., 2000; Rhee et al., 2009). Thus, source and sink

12   behaviors of GHGs have been observed on different spatial and temporal scales. In general terms, these

13   behaviors depend on biological and physical processes that promote outgassing or sequestering

14   mechanisms. Physical and biological features of the Southern Ocean suggest the existence of a potential

15   for both the production and removal of CH_4 and N_2O (Rees et al., 1999; Tilbrook and Karl, 1994),

16   although very little information on dissolved N_2O and CH_4 distributions is currently available for the

17   region. The substantial spatial variation in regional gas exchange could be due to the increased gas

18   solubility in low-temperature Sub- and Antarctic waters, combined with either the downwelling

19   associated with intermediate and deep water formation over the convergence band (Antarctic Polar

20   Frontal Zone or "PFZ"), or the low-temperature Antarctic waters, along with the upwelling of deep and

21   intermediate waters in the southern part of the PFZ (Parker and Viver, 2012).

22   In different regions of the Southern Ocean, the surface layer is always supersaturated with CH_4 (Bates et

23   al. 1996; Tilbrook and Karl, 1994, Toshida et al., 2011), but this is not the case for N_2O that is observed

1	in an under- or super saturated condition (Law and Ling, 2001, Rees et al., 1997, Zhan and Chen,

2	2009). Aside from physical processes affecting GHG concentrations in the water column and their

3	concomitant air-sea fluxes, they additionally depend on organic matter (OM) availability and oxygen

4	levels, which determine whether aerobic or anaerobic OM respiration occurs (Codispoti et al., 2001;

5	Reeburgh, 2007). The availability of dissolved iron (dFe) should also be included as a variable affecting

6	GHG cycling; directly as several Fe-containing enzymes, which are involved in the electron transfer

7	chains in bacterial respiratory systems and Nitrogen cycling, are required for GHG cycling (Arrieta et al,

8	2004; Kirchman et al., 2003; Morel et al., 2003a) and, indirectly as dFe stimulates ocean productivity

9	which can enhance carbon and nitrogen export from the euphotic zone to the subsurface (Boyd and

10	Ellwood, 2010), resulting in a an increase of the microbial activities which may mediate GHG via

11	nitrification (Fuhrman and Capone , 1991),

12	N_2O is mainly produced during the first step of nitrification; the aerobic oxidation of NH_4^+ to NO_2^-, and

13	during partial denitrification, the anaerobic reduction of NO_3^-/NO_2^- to N_2O. N_2O can also be consumed

14	by complete denitrification via dessimilatory reduction to N_2 (Codispoti and Cristiensen, 1985) or

15	assimilatory N_2O reduction to NH_4^+ (Farias et al 2013). CH_4, on the other hand, is mainly formed by

16	methanogens during anaerobic OM degradation (Wuebble & Hayboe, 2001) or by methylotrophs during

17	CH_4 formation derived from transformations of methyl-compounds such as methylphosphonate (MPn)

18	(Karl et al., 2008), dimethyl-sulphoniopropionate (DMSP) (Damm et al., 2010) and dimethylsulphide

19	(DMS) (Florez-Leiva et al., 2013). In addition, CH_4 can be consumed (oxidized) via aerobic

20	methanothophy (Hanson and Hanson, 1996). Since Southern Ocean waters are well oxygenated, N_2O

21	formed by nitrification (Nevison et al., 2003) and CH_4 formed by either methanogenesis in suspended

22	particles (Scranton and Brewer 1977) or by methylotrophy, are thought to be the dominant mechanisms

23	of production in surface waters (Sun et al., 2011).

1   The main objective of the present study is to describe for first time the N_2O and CH_4 contents in the

2   Southern Ocean under the influence of natural fertilization events during the spring phytoplankton

3   bloom in the KPR. The determination of the role of the Southern Ocean in CH_4 and N_2O air–sea

4   exchange may be critical in understanding the factors/variables that influence GHG cycling. This

5   includes dFe which comes from different sources within the KPR, inducing mesotrophic conditions that

6   are associated with the coastal waters of Kerguelen Island, the area of quasi permanent phytoplanktonic

7   bloom in the Central Plateau area of the KPR(Blain et al., 2008; Chever et al., 2010), and with the

8   Antarctic Polar front and other mesoscale structures (Mongin et al., 2008, Lasbleiz et al., 2014).

9   2. **Methods**

10   **2.1. Study area**

11   Samples were collected within the Kerguelen Plateau Region or KPR (Fig. 1) during the KEOPS 2

12   cruise at stations along north to south (TNS,46°–51°S) and west to east (TWE, 66–75°E)transects. The

13   cruise was carried out from October 11th to December 11th, 2011, on board the research vessel (RV)

14   *Marion-Dufresne*. Some of the sample stations were located in the PFZ in the coastal shelf waters of

15   Kerguelen Island and within the southeastern KPR bloom (including station A3 from the previous

16   KEOPS 1 cruise), which are naturally Fe-enriched, however another station was sampled (St. R), which

17   is located beyond the KPR and considered to be representative of the HNLC area off the KPR (see Table

18   1). The hydrographic condition   of the sampling stations was selected according to a strategy based on

19   real-time ocean color and altimetry satellite images (d´Ovidio et al., 2012).

20   **2.2. Continuous and discrete sampling:** Continuous vertical profiles of temperature, salinity, dissolved

21   O_2, fluorescence and photosynthetically active radiation (PAR) were obtained using a conductivity

22   temperature and depth (CTD) sensor. Water was sampled with a CTD-Rosette sampler (SBE 32 24x10-

23   L Carousel Water Sampler with 10-L Niskin bottles). Water samples for gases (N_2O, CH_4), nutrients,

1 and pigments (sampled in this correlative order) were obtained from nine depths distributed between the

2 surface and a 500m depth. Water samples for CH_4 (triplicate) and N_2O (triplicate) analyses were taken in

3 20 mL glass vials and poisoned with $HgCl_2$ (0.1 ml of saturated $HgCl_2$ solution per vial). The vials were

4 then sealed with a butyl-rubber septum and aluminum cap, avoiding bubble formation, and stored at

5 room temperature in darkness until laboratory analysis. Syringes of 50 mL were directly connected to

6 the spigot of the Niskin bottles to take nutrient samples (NO_3^-, NO_2^-, PO_4^{3-} and $Si(OH)_4$) at each

7 sampled depth. Duplicate samples were collected and drawn through a 0.45 μm Uptidisc adapted to the

8 syringe, and then immediately analyzed using an autoanalyzer (more details in Blain et al, this volume).

9 Total chlorophyll-a (*TChl-a*) samples in triplicate were filtered into a 25 mm glass- fiber filter (GF/F),

10 and then immediately frozen (-20ºC). Samples were kept until later analysis by high performance liquid

11 chromatography (HPLC) (more details in Lasbleiz et al., 2014).

12 **2.3. Chemical analysis**: N_2O and CH_4 were analyzed by creating into the vial 5 mL of ultra-pure

13 Helium headspace throughout a gastight syringe, followed by an equilibration of gas and liquid phase in

14 the vial at 40°C , and then quantifying gases by a gas chromatograph determined by helium (He)

15 equilibration (5-mL helium headspace and 15-mL of seawater) at 40°C in the vial, followed by

16 quantification via chromatography. N_2O was analyzed in a Varian 3380 Gas Chromatograph using an

17 electron capture detector at 350°C and connected to an autosampler device. CH_4 was analyzed in a

18 Schimadzu 17A gas chromatograph using a flame ionization detector at 250°C through a capillary

19 column GS-Q at an oven temperature of 30º C. A calibration curve was made with four concentrations

20 for N_2O (0.1 ppm, 0.32, 0.5 ppm, and 1 ppm, by Matheson standards) and four concentrations for CH_4

21 (0.5, 1.78, 2 and 10 ppm, by Matheson standards). Both detectors linearly responded to these

22 concentration ranges. The analytical error for the N_2O and CH_4 analyses was less than 3% and 5%

23 respectively. The samples were taken in triplicate in 20 mL vials and carefully sealed to avoid air

1   bubbles. They were then preserved with 50 µL of saturated $HgCl_2$ and stored in darkness until analysis.

2   The ECD and FID detectors lineally responded to these concentration ranges and the analytical error

3   for the N_2O measurements for this study was about 3%. The uncertainty of the measurements was

4   calculated from the standard deviation of the triplicate measurements by depth. Samples with a variation

5   coefficient higher than 10 % were not taken into account for the gas database.

6   More details regarding the analysis of both gases can be found in Farias et al. (2009). Nutrients were

7   immediately analyzed onboard by standard automated colorimetric methods (Tréguer and LeCorre,

8   1975) using the continuous flow autoanalyser (Skalar). The precision and detection limit of the method

9   was, respectively, ±50 nM and 20 nM for NO3-, and ±30 nM and 110 nM for PO_4^- (more details in Blain

10   et al. this volume). NH4+ was measured by fluorometric analysis (Holmes et al., 2000) with a precision

11   of ±50 nM.

12   **2.4. Data analysis**: To interpret the vertical variation of N_2O and CH_4 and how biogeochemical

13   processes may affect their concentrations, the water column was divided into two layers according to

14   density gradient: (1) well-mixed and (2) subsurface from the base of the mixed layer (ML) to 500 m

15   (arbitrary depth used only for comparison proposes). Nutrient inventories for T*Chl-a*, N_2O and CH_4

16   were calculated by numerical integration of data at one meter (linear interpolation) increments based on

17   at least 4-6 sampled depths per layer. Saturation percentages of gases were calculated from the measured

18   CH_4 and N_2O concentrations and those estimated to be in equilibrium with the current gas concentrations

19   in the atmosphere (NOAA register (http://www.esrl.noaa.gov/gmd/hats/combined /N_2O.html), based on

20   *in situ* temperature and salinity according to the solubility parameterization CH_4 (Wiesenburg and

21   Guinasso, 1979) and N_2O (Weiss and Price, 1980). GHG flux through the air-sea interface was

22   determined using the following equation, modified by Wanninkhof (1992):

$$F = kw(T°, salinity) \cdot (C_w - C_a)$$

1   where kw is the transfer velocity from the ML to the atmosphere, as a function wind speed, temperature

2   and salinity in the ML according to parametrization, C_w is the mean gas concentration in the mixed

3   layer, while C_a is the gas concentration in the mixed layer expected to be in equilibrium with the

4   atmosphere. Since gas transfer velocity is related to wind speed, this was calculated according to the

5   well-known exchange models of Liss and Merlivat (1986) or LM86 and Wanninkhof (1992) or W92,

6   based on the dependence of the transfer velocity on wind speed. Wind speed and direction were obtained

7   from an onboard register using the ship's meteorological station as per international protocols. Wind

8   speed was estimated as a moving average of seven days before the sampling (stations) in order to

9   smooth out short-term fluctuations and highlight longer-term trends. The mixed layer depth was

10   calculated using a potential density-based criterion, defining the mixed layer depth (ML) as the

11   shallowest depth at which density increased by 0.02 kg m^{-3} from the sea surface value.

12   Pearson product-moment correlations (rs) were determined for GHG, and T*Chl-a* and nutrient

13   inventories were estimated in the ML and in the whole water column from surface to 500 m depth. The

14   threshold value for statistical significance was set as $p < 0.05$. A principal component analysis (PCA)

15   using the empirical orthogonal function (EOF; Emery and Thomson, 1997) was performed to find the

16   co-variability patterns of a number of stations located in spatial gradients in terms of nutrients, gases

17   (O_2, N_2O, and CH_4), T*Chl-a*, and dFe. This analysis excluded the stations from the NS transect as no

18   measurements were recorded (Quéroué et al, this volume). PCA were made with all biogeochemical

19   variables measured in the ML and with these variables obtained in the water column from the surface to

20   a depth of 500 m, in order to discern differences in the vertical structure.

21   **Results**

22   **3.1. Oceanographic conditions.**

1   Oceanographic characteristics of the sampled stations during the KEOPS 2 cruise are shown in Table 1.

2   Two transects, almost synoptically made across and along the KPR (survey region – Fig. 1) were

3   undertaken to establish the position of the main mesoscale structures as fronts (Figure 2). The Polar

4   Front (PF) crosses the KPR and demarcates certain physical structures (convergence process) visible

5   throughout temperature and salinity.

6   Regarding the W-E transect or TWE (66° to 75°E, along 47°S, Fig. 2 a,c,e), vertical cross sections of

7   temperature and salinity with a T-S diagram are illustrated in Fig 2 (a,c,e). Temperature and salinity

8   varied between 2.41° and 3.3°C, and between 33.60 and 34.67, respectively. A weak structure with

9   colder and fresher surface waters was registered in the FP, which crossed these transects twice, at ~71°E

10 (St. TWE03-04) and at ~73.5°E (StTWE07-08). Middle stations (Sts. TWE04, -05 and E) denoted an

11 area with a complex recirculatory system in a stationary meander of the PF (Park et al., 2014), hereafter

12 known as the Central Section. This section is superficial bathed by mixed Antarctic surface water

13 (AASW) and coincides with the area with the PF northward inflexion (Fig. 1). The presence of

14 Subantarctic mode water (SAMW) was observed east of 73.5° E (Sts. TWE07-08, Fig. 2f). In addition, a

15 marked variability in subsurface water was observed, ascribed to mixing water masses; this was

16 particularly strong in TWE within the PF, revealing a vertical mixing process produced by convergence,

17 particularly evident at St. TWEO7 (Fig. 2e). Regarding the N-S transect (46°-51°S, along ~72°E) or

18 TNS, Fig. 2 (b, d, f) shows vertical cross sections of temperature, salinity and a T-S diagram,

19 respectively. Temperature and salinity fluctuated from 1.67° to 4.17°C and from 33.67 to 34.68,

20 respectively, and a gradual decrease in temperature and an increase in salinity were observed in the

21 surface layer from north to south (Fig 2 b, d). There was a water parcelof a relatively colder water mass

22 spreading northward in subsurface waters. This was an expression of the PF, which marked the location

23 where the AASW moving northward descended rapidly and sank below a depth of 200 m depth (Fig. 2

1 b). These distributions coincided with the expected water mass distribution, this being the case for the

2 northern (Sts. TNS01-02) and southern (Sts. A3, TNS10) stations, mainly occupied from the surface to

3 250 m by the SAMW and the AASW, respectively (Fig 2f).

4 **3.2. Biogeochemical variables**

5 Figure 3 shows vertical cross sections along the TWE of biogeochemical variables including nutrients

6 (only NO_3^- and HPO_4^{2-}), T*Chl-a*, O_2 and GHGs. The surface layer continuously showed NO_3^-

7 concentrations, fluctuating from 22 to 27 µmol L^{-1} (typical condition of the AASW). However, a relative

8 depletion of NO_3^- was observed at the stations located north- and eastward of the PF (Fig 3a). PO_4^{3-}

9 presented the same pattern as NO_3^- and the N:P ratio of dissolved nutrients averaged around 14.5, with

10 the exception of some values of 13.2 from stations located closed to the PF (Fig. 3 b). *TChl-a* fluctuated

11 from 0.005 to 4.69 µg L^{-1} and peaked at Sts. TWE01-02 (both located in a coastal area 10 and 75 km

12 away from Hillsborough Bay coast) and Sts. TWE07-08 (to the north of PF). *TChl-a* showed a relative

13 decrease at stations located in the Central Section (Fig. 3c). The observed pattern (Lasbleiz et al., 2014)

14 significantly correlated with the dFe spatial distribution reported by Quéroué et al. (this volume). O_2

15 concentration varied form 320 µM (in surface water) to 185 µM (at 500 m deph), consistently

16 maintaining super saturation conditions (Fig 3d).

17 N_2O fluctuated from 14.0 to 25.4 nmol L^{-1} (equivalent to a range of 102-182.2% saturation, Fig 3e).

18 Superficially, the N_2O concentration was close to equilibrium with the atmosphere in surface waters in

19 the western and central section (70.5°- 73°E) and slightly undersaturated (around 90%) in surface waters

20 in sites   where the PF crosses the transect, i.e., Sts. TWE04 and TWE07 (Fig. 3e). N_2O levels

21 increased slightly attaining around 120% saturation towards subsurface water. CH_4 ranged from 1.4 to

22 31.35 nmol L^{-1}, equivalent to a range of saturation of 43-969%. In contrast to N_2O, surface waters were

23 always supersaturated in CH_4, showing the highest increase in gas levels (up to 970%) in coastal waters

1   close to Kerguelen Island, a relative decrease (<200% saturation) in the central section (between 71° and

2   73.5°S, or Sts TWE04, 05 and E2), and a strong increase (up to 778%) at St, TWE07. Remarkably, CH_4

3   concentrations in subsurface waters were low compared to the surface waters (Fig. 3f).

4   Vertical cross sections of biogeochemical variables along the TNS are shown in Figure 4. NO_3^- and

5   PO_3^{4-} gradually increased from north to south from 24 to 30 µmol L^{-1} and from 1.5 to 2 µmol L^{-1},

6   respectively (Fig 4 a, b). This spatial trend coincided with the expected transition of water mass

7   dominance and its mixing between the SAMW and the AASW (Fig 2 f). T*Chl-a* ranged from 0.005 to

8   2.391 µg L^{-1} and peaked in the southernmost stations (Sts. TNS08, -09 and A3-2; Fig. 4b) and coincided

9   with a slight increase in nutrients. These trends coincided with the presence of the central plateau area of

10   the KPR, where upwelling-like circulation was observed (Zhou, this volume), as indicated by

11   temperature and salinity distribution (Fig. 2 b, d). There a deep Fe-enriched and lithogenic silica

12   reservoir seems to be influencing the area (Lasbleiz et al., 2014; Quéroué et al., 2014). O_2 distribution

13   was similar to that observed in the WE transect.

14   N_2O concentrations ranged from 12.37 to 23.8 nmol L^{-1}, equivalent to 88.5% to 171% saturation. N_2O

15   levels close to equilibrium or undersaturation were often observed in surface waters, except at St.

16   TNS08 (Fig. 4e). CH_4 varied from 1.47 to 21.88 nM, or 45 to 666% saturation, and peaked in southern

17   stations (Fig 4f). Notably, *Chl-a* corresponded to the observed CH_4 in this transect. Southern stations,

18   such as St. A3, located in an area of relatively high bioavailable Fe and within a phytoplankton bloom,

19   had extremely low N_2O concentrations (less than 6.9 nM or 70% saturation).

20   PCA, including dFe and GHG data were obtained from the TWE as shown in Figure 5. The results did

21   not change when O_2 was removed from the analysis, indicating that this O_2 availability does not explain

22   the variability. Using environmental data come from the ML (Fig. 5a), stations located on the TWE were

23   grouped into three sets, clearly separating stations located on the eastern (north of the PF, St. TWE07),

1   the western or coastal area (TWE01-02), and Central section (Sts. TWE04, -05,E2). The variability

2   among stations can be predominantly explained by the first component, accounting for 75.7% of the

3   variance. Figure 5 demonstrates possible interpretations for relationships among the variables with their

4   respective weights assigned to each of them (illustrated with an eigenvector). The figure shows a close

5   relationship between N_2O, nutrients, CH_4, Fe and *Chl-a*. The PCA analysis using data from the entire

6   water column provided a similar grouping of the sample stations (Fig 5b).

7   **3.3. Vertical distribution of gases and other variables at selected stations**

8   Figure 6 shows typical profiles of oceanographic and biogeochemical variables (including gases).

9   Stations were separated *a priori* according to biogeochemical (PCA analysis for the case of the TWE;

10 Fig.5) and oceanographic criteria (T-S diagram, Fig. 2e, f). Selected stations included: Sts. A3, with a

11 quasi-permanent phytoplankton bloom (historical station sampled in KEOPS 1, Blain et al., 2007) and ,

12 low Fe levels (~ 0.18 nmol L^{-1}), but with the evidence n of an active uptake of dFe uptake; St. TWE07,

13 which had moderate dFe (~0.40 nmol L-1) and high TChl-a levels and also evidences of rapid dFe

14 uptake (Fourquez et. this volume). For comparative purpose, we include the most northern station of the

15 NST (St. TNS01), a well-known as a Fe-limited HNLC area (St. R), and a coastal station close to

16 Kerguelen Island, which had the highest dFe levels (up to 3.82 nmol L^{-1}. Vertical distribution of N_2O

17 and CH_4 differed markedly, while elevated CH_4 concentrations were mostly located superficially and in

18 the ML base and decreased as depth increased, N_2O concentrations gradually increased with depth. Gas

19 contents also differed between stations and were in similarly correlated with Chl-a and dFe levels.

20 Stations located in the extreme point of the WET (i.e., TWE01 and TWE07) had the highest CH_4 levels

21 (Fig 6), while N_2O levels were relatively low. On the other hand, Sts. TNS1 and A3, located in the

22 extreme north and south of the N-S transect presented relatively low levels of CH_4 compared to the WE

23 transect. Station R, which is located in one of the more oligotrophic conditions of the Southern Ocean

1   (special volume of KEOPS 1), had the lowest N_2O and CH_4 content, and both gases were

2   homogeneously distributed with depth (Fig. 6). This is consistent with the expected trophic condition

3   with T*Chl-a* levels of less than 0.5 µg L^{-1}.

4   **3.4. Nutrient, T*Chl-a*, dFe and GHG inventories and air-sea GHG exchanges**

5   Table 2 shows the inventories of NO_3, PO_4^{3-} and GHGs in the ML and the water column from the

6   surface to 500 m; mean GHG concentrations in the ML, wind speed and air-sea GHG fluxes are also

7   included. ML depths varied widely from 16 m (at the station near Kerguelen Island) to 181 m. The

8   T*Chl-a* pool, estimated on the basis of the photic layer, fluctuated from 8.77 to 75.45 mg m^{-2}. It was

9   notably greater at Sts. SPF and A3-2 (up to fivefold greater) than at more oligotrophic stations like St. R.

10   Surface NO_3^- and PO_4^{3-} inventories, which varied from 1.56 to 16.03 and 0.13 to 1.07 mol m^{-2},

11   respectively, did not show significant differences among stations. Minimal values were registered at

12   stations St. TWE07-08 and TNS01, both located north of the PF.

13   N_2O pools varied from 0.201 to 2.55 and from 1.12 to 10.05 mmol m^{-2} in the ML and whole water

14   column, respectively. Minimum values were registered in the ML at stations within or north of the PF.

15   These surface pools did not significantly correlate with TChl-a, but correlated strongly and negatively

16   with nutrients (rs: 0.91 p<0.001 for NO_3^- and rs: 0.92, p<0.001 for PO_4^{3-}). CH_4 inventories fluctuated

17   between 0.19 and 3.31 mmol m^{-2} for the ML and 1.06 and 7.44 mmol m^{-2} for the WC. Once again,

18   inventories in the ML were two and fivefold higher at Sts. TWE07 and A3-2, respectively, than at St. R.

19   CH_4 inventories were four and sevenfold higher in Sts. TWE07 and A3-2 than at St. R. The comparison

20   between the CH_4 inventories standardized by the thickness of the layer), obtained from the ML and from

21   the entire water column, indicate that the maximum values came from the ML´s base, remarkably in the

22   PF (Table 2). CH_4 pools correlated positively with T*Chl-a* pools (rs= 0.69; p<0.05), but did not show

1 any correlation with NO_3^- and PO_4^{3-}. Thus, minimum values for both nutrients were found when T*Chl-a*

2 was higher.

3   Average hourly wind velocity during the cruise was 10.53 ±5.52 m s^{-1}, occasionally falling below 0.31

4 m s^{-1} or rising above 29.1 m s^{-1}. The ML depth did not show any significant relationship to wind speed

5 (rs: 0.20 p=0.41) or the water mass structure (Table 1 and Fig. 2), but seems to be related to the complex

6 mesoscale circulation observed in the KPR (Park et al., 2014; Zhou et al. this volume). N_2O fluxes,

7 estimated by LM86, fluctuated between -9.69 and 10.02 (mean: 1.25±4.04 μmol m^{-2} d^{-1}), while those

8 estimated by W92 varied from -18.69 to 20.2 μmol m^{-2} d^{-1} (mean: 2.41±7.88). At high wind speeds,

9 such as those measured during the N-S transect (21-23 October 2011, mean value of 12.08 m s^{-1})

10 compared to those registered during the W-E transect (31 October – 02 November, mean value of 5.61

11 m s^{-1}), substantial differences were observed between the cubic (LM86) and the quadratic

12 parameterizations (W92). The latter increased in calculated fluxes by approximately a factor of two at

13 high wind speeds, while at low wind speeds the difference between LM86 and W92 was up to a factor of

14 ~1.6 (see Table 2). CH_4 fluxes varied from 0.21 to 38.1 (mean: 10.01±9.97) and from 0.32 to 70.24

15 (mean: 21.27±21.07) μmol m^{-2} d^{-1}, when LM86 and W92 were used, respectively. The study area at

16 times acts as a source of very high CH_4 effluxes into the atmosphere, particularly at stations St. TNS09

17 and St. A3-3, where emissions were around three times as high as those calculated for St. R. There are

18 important differences between the two parameterizations, although the same trend was obtained among

19 stations (Table 2).

20 **4. Discussion**

21 **4.1. Physical and geochemical characteristics**

1   The Antarctic Polar Front (PF) marks an important climate boundary in terms of oceanic heat and salt

2   budgets and a biogeochemical frontier with respect to GHG content and air-sea GHG fluxes (such as

3   N_2O and CH_4). The PF path exhibits considerable variability, meandering and forming eddies and rings.

4   The location of the PF is mainly determined by the movements of deep waters and is probably strongly

5   influenced by topography and bathymetric features such as the Drake Passage and the Kerguelen Plateau

6   (Sandwell and Zhang, 1989; Patterson, 2005). These mesoscale structures in the study area are always

7   associated with strong vertical and lateral mixing and advection (Park and Viver, 2012, Park et al., 2014;

8   Zhou et al, this volume) that could create fertilization mechanisms (by both Fe and nutrient like silicate),

9   therefore provoking *TChl-a* production which in turn is being stimulated by the addition dFe from

10   different sources (Quéroué et al. this volume).

11   In some regions, the main Fe input is from atmospheric deposition (Jickells et al., 2005). However, this

12   was not the case in the KPR. The main sources of iron that were evidenced in the KPR, that could also

13   potentially fertilize the northern section of the plateau, were direct runoff from the Kerguelen Island,

14   glacial melting and sedimentary inputs (Quéroué et al., 2014). Actually, the water masses found at

15   stations north of the PF (e.g. TEW07) interacted more with the plateau and the shallow coastal waters of

16   Kerguelen Island, than with the water masses from the recirculation area. This theory is consistent with

17   the circulation data discussed by Park et al. (2014) who demonstrated that water masses are carried

18   northwards between the island and the recirculation area and finally looped back east of the recirculation

19   area.

20   The origin of the bloom in the central part of the plateau possibly comes from a deep Fe-enriched

21   reservoir which was observed also above the Kerguelen Plateau during the KEOPS1 cruise (Blain et al.,

22   2008; Chever et al., 2010). Non reductive dissolution of resuspended sediments is a potentially

23   important source of dFe; at station A3, high lithogenic silice (LSi) concentrations (1.34 ± 0.07 µmol L^{-1};

1 Lasbleiz et al., 2014) were observed just above the seafloor in the benthic boundary layer (BBL), also

2 suggesting sedimentary inputs. In fact, using Ra isotopes to trace Fe, Sanial et al. (2014) indicated that

3 Fe could be supplied from sedimentary sources, as well as laterally advected from the southern region of

4 Heard Island and exchanged through the Polar Front. Similar results were found during KEOPS 1 by

5 Mongin et al. (2008), Zhang et al. (2008), and Maraldi et al. (2009).

6 Iron fertilization in the KPR has in influence on phytoplankton growth and primary production (PP), and

7 other microbial activities (Cavagna et al., 2014; Christaki et al., 2014), as well as relative CH_4

8 accumulation (Fig. 3,f and Fig. 4f) and some N_2O depletion (Fig 3e) were also observed. The gas

9 distribution pattern clearly matched with TChl-a and PCA grouped stations as was made by Queroue et

10 al (this volume) using dFe. The separation of stations comprises coastal area (Sts. TWE01, -02), PF (St.

11 STWE07) and central plateau region (Sts. A-3).   In the case of KEOPS 2, phytoplanktonic blooms

12 were mainly represented by a microplanktonic community (Lasbeiz et al, this volume) as those

13 observed in the north Polar Front (St. TWE07) and the central part of the KPR (A3) stations displayed

14 high rates of iron uptake (Quéroué et al, 2014). The mentioned areas, resented variable but high

15 particulate Fe of biogenic origin (van der Merwe et al., 2014), confirming an increased biological

16 uptake, which in turn determines a rapid dFe turnover. The observed gas distribution patterns raise

17 questions as to how the complex circulation and some mesoscale structures support relatively high

18 T*Chl-a* accumulation and microbial activities in comparison to surrounding waters, and particularly

19 whether there are some fertilization mechanisms (including the addition Fe and nutrients) promoting

20 GHG cycling and the concomitant microbial activities.

21 **4.2. N_2O cycling**

22 Fuhrman and Capone (1991) pointed out that stimulating ocean productivity by Fe addition, which

23 enhances nitrogen export from the euphotic zone to the subsurface layer, can result in enhanced N_2O

1 formation via stimulated nitrification. This stimulation could occur through the activation of

2 metalloproteins that are involved in various steps of ammonium and nitrite oxidation, as ammonia

3 oxidizing nitrifiers use iron-containing ammonia monooxygenase (AMO) and hydroxylamine

4 oxidoreductase (HAO) to oxidize NH_4^+ and NH_2OH, respectively, to NO_2^- (Morel et al, 2003b). Since

5 N_2O is a powerful greenhouse gas, 300 times more radiative than CO_2 per molecule, Fe addition could

6 counteract the climatic benefits of atmospheric CO_2 drawdown (Jain et al., 2000). The link between Fe

7 fertilization and enhanced N_2O formation via nitrification was supported by Law and Ling (2001), who

8 found a small but significant N_2O accumulation in the pycnocline during the Southern Ocean Iron

9 Enrichment Experiment (SOIREE) at 61°S, 140°E. Jin and Gruber (2003) subsequently predicted the

10 long-term effect of Fe fertilization on global oceanic N_2O emissions using a coupled physical-

11 biogeochemical model. Based on the model outputs, they concluded that Fe fertilization induced N_2O

12 emissions that could offset the radiative benefits of the CO_2 drawdown. However, during other Southern

13 Ocean Iron Enrichment Experiments (EIFEX), Walter et al. (2005) found no N_2O enrichment after

14 artificial Fe fertilization.

15 Our findings revealed that natural Fe fertilization did not seem to stimulate N_2O accumulation

16 superficially (within the bML). The N_2O inventory estimates from areas of higher accumulation of

17 biomass were not significantly different with respect to those estimated for St. R, which was used as a

18 reference station (Table 2). Contrary to what was expected, no increase in N_2O content was observed at

19 stations close to Kerguelen Island (St TWE01, TWE02), which are highly enriched by dFe from fresh

20 water and sediments (Quéroué et al., this volume). This trend suggests that nitrifiers in surface water are

21 not being significantly stimulated by Fe supply from the sediments. At subsurface water (below ML to

22 500 m depth) N_2O accumulation may be associated to nitrification   In fact,   dual nitrate isotopic

23 composition ($\delta\ ^{15}N-NO_3^-$ and $\delta\ ^{18}O-NO_3^-$) revealed an increasing of values for both isotope values as water

1 depth increase in subsurface waters (100–400 m) as being the result of partial consumption of available

2 nitrate in surface waters, export of low δ ^{15}N in Particulate Nitrogen (NP) and remineralisation–

3 nitrification there (Dehairs et al., 2014) Although, values of δ ^{15}N-NO$_3^-$ and δ ^{18}O- NO$_3^-$ in surface water

4 also suggested that nitrification is also occurring in surface water, but with a considerable variation

5 Remarkably, the St. TW07-08 and A2-3 were in equilibrium and slightly depleted in N$_2$O (Fig. 3e; Table

6 2). The only plausible explanation is that mixing process produced at the PF (St. TWE07) (which have

7 moderate Fe levels, high T*Chl-a* and evidence of active Fe uptake) may stimulate the N fixers, as

8 demonstrated by Mills et al. (2004), Berman-Frank et al. (2007), and Moore et al. (2009). N-fixing

9 microorganisms may have an effect on the N$_2$O inventory as they could be used as an alternate substrate

10 for fixers, as suggested by Farias et al. (2013). Thus, biological N$_2$O fixation could be using and

11 assimilating N$_2$O, producing N$_2$O depletion and a concomitant undersaturation. N-fixation has been

12 observed in the cold waters of the Arctic and Antarctic (Blais et al., 2012; Diez et al., 2012, Diez

13 unpublished data), as well as in cold upwelled water (Fernandez et al., 2011), suggesting that N$_2$O

14 fixation may also be action and it is a well-spreading process than originally expected. Coincidently, St.

15 SPF also had the highest surface N-fixation (Gonzalez et al. this volume), suggesting that N$_2$O is used as

16 a substrate by diazotrophs (Farias et al., 2013) and that this process is stimulated by enhanced Fe supply.

17 N$_2$O undersaturation or equilibrium with the atmosphere was observed in the N-S transect (Fig, 4e),

18 particularly at stations north of the PF bathed by SAMW. This suggests that some process is removing

19 or consuming this gas in the upper water column. A notable level of undersaturation was also observed

20 at St. A3-2, which is located in the recurring phytoplankton bloom and in a regime of relatively high dFe

21 concentración due to the presence of the Plateau (Blain et al., 2007).

22 N$_2$O undersaturation has been reported, although rarely, in Polar and Sub-polar Ocean regions (Butler et

23 al., 1989; Law and Ling, 2001; Foster et al., 2009). Physical processes related with gas solubility and

1 deviations of from atmospheric equilibrium gas concentration could not explain the observed

2 undersaturation. If these physical variables change in less time than that required for equilibrium of the

3 gases with the atmosphere, there may be a gas deficit. Thus, deviation from the equilibrium condition

4 could be caused by rapid heating or cooling, refreshing, and/or a mixing of water masses (Sarmiento and

5 Gruber, 2006). An analysis of these potential changes was made for the AASW and the SAMW. A

6 cooling (decreasing T°C> 3) or freshening processes (decreasing S from 34 to 10) are required to

7 produce the observed undersaturation, neither of which was observed during the sampling (Table 1), or

8 expected during this season (Park and Viver, 2012). Additionally, if the two water masses were mixed

9 proportionally, as they are, the resulting process cannot produce undersaturation regarding the original

10 N_2O levels and their temperature and salinity signature. Recently, Chen et al. (2014) reported that

11 surface water of the Southern Ocean of Indian sector were understaturated in N_2O, reflecting also a N_2O

12 influx. This phenomenon in the surface water may result from ice melt water intrusion and

13 northeastward transport of the AASW. However, in the KPR, N_2O undersaturation seems to be located

14 in area of high particle concentration under the influence if in the SAMW (northern the PF),

15 Thus, a preliminary analysis indicates that biological processes are responsible for the N_2O

16 undersaturation and the concomitant influx from the atmosphere. In contrast, subsurface waters have

17 higher N_2O concentrations (saturations from 120% to 180%) than surface waters, which indicate a net

18 accumulation. In this case the plausible process responsible for N_2O accumulation is aerobic ammonium

19 oxidation (Codispoti et al., 2001), but no significant difference was noted at the stations with the highest

20 T*Chl-a* levels, indicating that N_2O production by nitrification was not substantially stimulated at those

21 stations

22 **4.3. CH$_4$ cycling**

1   There have been few studies on CH_4 distribution and production in the Southern Ocean (Lamontag et al.,

2   1973; Tilbrook and Karl, 1994; Heeschen et al., 2004). There, surface water has been reported to be

3   undesaturated or lightly saturated with respect to atmospheric CH_4, as the result from the entrainment of

4   CH_4 depleted deep water into surface water and from the seasonal ice cover acting as a barrier for gas

5   exchange (Toshida et al., 2011). Regarding the effect of iron addition on CH_4 cycling Wingenter et al.

6   (2004) found low levels of CH_4 production (less than 1%) during artificial Southern Ocean Fe

7   enrichment experiments (SOFex). Simulated large-scale Southern Ocean Fe fertilization (OIF) also

8   resulted in anoxic conditions which may favor anaerobic methanogenesis (Oschlies et al. 2010).

9   However, our results show that surface and subsurface water are supersaturated in CH_4 with a fourfold

10   enrichment in CH_4 with respect to the control area (Fig. 3e), this was associated to areas with elevated

11   T*Chl-a* levels and iron uptake by microbial communities (Fourquez et al., 2014).). Results showed

12   marked spatial differences in CH_4 content measured in the W-E and N-S transect (t-student: 3.21

13    $p<0.001$) (Fig. 3f and 4f), and that surface CH_4 accumulation generally coincided with areas of relatively

14   higher dFe levels, which in turn favors primary production (PP). Likewise, the CH_4 accumulation at

15   pycnoclines (Fig. 6) indicates that most CH_4 came from accumulated particles sinking from the surface

16   water, as commonly observed by Holmes et al. (2000) in different marine systems. The PCA analysis,

17   which included the measurement of dFe revealed a close relationship between CH_4 accumulation and Fe

18   availability and clearly grouped in areas with different biogeochemical characteristics. The fact that the

19   western and eastern sections showed high Fe levels (Quéroué, this volume) relative to the Central

20   Section of the W-E transect, and that these sections had high CH_4 levels, suggests that Fe in some way

21   stimulates CH_4 production. A similar situation occurs in Sts.A3 with high T*Chl-a* levels and PP rates, as

22   shown by Cavagna et al. (2014). For example, station A3-2 and TWE07 (maximum T*Chl-a*) had the

23   highest integrated primary production rates (up to 3380 mg m^{-2} d^{-1}) and the lowest C export level of

1   around 2-3% (Cavagna et al., 2014), this suggests an intense level of PP supported by regenerated N

2   sources. These contrast with condition found at St. R with the lowest rate of regenerated production

3   (with a PP rate of around 135 mg m^{-3} d^{-1} and an exported C rate of around 25% of PP).

4   Two hypotheses exist about CH$_4$ production in surface waters. One is that it should only occur in

5   association with anoxic particles (Karl and Tilbrook, 1994) most of them being produced by grazing

6   zooplankton, as methanogenic bacteria were considered to be present in an anaerobic microenvironment

7   in organic particles (pellets) or in the guts of zooplankton (Alldredge and Cohen, 1987; Karl and

8   Tilbrook, 1994)The other hypothesis was formulated more recently, that that phytoplankton blooms

9   should favor zooplankton grazing process and/or stimulate bacterioplankton activity as CH$_4$ is generated

10   via the degradation of organic methyl compounds by bacteria (Karl et al 2008).

11   Increased grazing of microbes by microzooplankton, as observed by Christaki et al. (2014) and may

12   contribute to particle recycling (rich in organic carbon and DMSP), and increase the potential for

13   methanogenesis (Weller et al., 2013). Yoshida et al. (2011) found that high CH$_4$ production in the

14   Southern Ocean probably resulted from the grazing processes of Antarctic krill and/or zooplankton fed

15   on phytoplankton, and the subsequent microbial methanogenesis. This was in line with the findings of

16   iron and biomass enriched sites exhibited the highest carbon fluxes at 100 m depth, mainly dominated

17   by large fecal pellets, rather than phytodetrital aggregates (Laurenceau et al., 2014).

18   On the other hand, aerobic CH$_4$ production in the water column could be associated with heterotrophic

19   activities. Christaki et al. (2014) showed that the highest bacterial production rates (up to 110 mg C m^{-2}

20   d^{-1}), and the greatest abundance of heterotrophic bacteria were associated with stations where the

21   phytoplankton bloom was developed (TWE07 and A3-2). Recent evidences indicate that methylotrophs

22   are candidates for mediated CH$_4$ generation using methylated compounds as DMSP and DMS (Florez-

23   Leiva et al., 2013; Weller et al., 2013). Among these heterotrophic microorganisms DMS degradation

1   can be ascribed to methylotrophic bacteria (Vissher et al., 1994) that derive energy from the conversion

2   of methyl into other products, as well as using S as a source for methionine biosynthesis (Kiene et al.,

3   1999). Current studies of natural and cultivated SAR11 alphaproteobacteria (strain Ca. P. ubique

4   HTCC1062; Sun et al., 2011) indicate that these microorganisms, among the most abundant

5   heterotrophic bacteria in surface waters, possess genes that encode for oxidation pathways of a variety of

6   one-carbon compounds, and have the capacity for demethylation and C1 oxidation, but do not

7   incorporate C1 compounds as biomass. These facts suggest a close relationship between phytoplankton,

8   the only producers of DMSP (Yoch, 2002), and microbial communities which may be recycling DMS.

9   Phyto-bacterioplankton relationships control DMS turnover, which could result in several mechanisms

10   of DMSP/DMS degradation (Simó et al., 2002; Vila-Costa et al., 2006) and produce CH_4 (Damm et al.,

11   2010; Florez-Leiva et al., 2013; Weller et al., 2013). These authors showed that phytoplankton species

12   composition and biomass in different bloom phases, as well as eddy dynamics, were important

13   determinants of CH_4 saturation and emission.

14   Regarding vertical distribution of this gas, profiles indicate that most CH_4 is being formed at the surface

15   and at pycnoclines (at the base of the ML), and consumed at subsurface and intermediary depths (Figure

16   6). Thus, CH_4 distribution appears to be controlled largely by biological mechanisms rather than by

17   mixing, contrary to what has been reported by Heeschen et al., (2004). In general, surface waters of the

18   Southern Ocean were undesaturated with respect to atmospheric CH_4 as the result of the entrainment of

19   CH_4 depleted deep water to the surface and from seasonal ice cover acting as a barrier for gas exchange.

20   We observed CH_4 undersaturation, fluctuating between 40% and 90%, at most sampled stations at

21   depths of > 200. It is unlikely that undersaturation results from the entrainment of CH_4-depleted waters

22   that have high levels of gas solubility, but also by a biological consumption. It is more likely that a

23   biological mechanism is involved. The only known process able to consume CH_4 is methanotrophy, and

1   the fact that subsurface waters were depleted of CH_4 suggests that CH_4 consumption is higher than

2   production, or that no production occurs in subsurface waters. Interestingly, although CH_4 microbial

3   oxidation occurs throughout the water column and is recognized as an important process that reduces

4   CH_4 emissions (Reeburgh et al., 2007; Rehder et al., 1999), microbial communities mediating aerobic

5   CH_4 oxidation have scarcely been investigated. There have been few measurements of aerobic CH_4

6   oxidation in marine environments, and measurements taken from open systems under oligotrophic

7   regimes (Tilbrook and Karl, 1994, Holmes et al., 2000) have found lower levels of oxidation than in the

8   oxic/anoxic interface (Sansone and Martens, 1978 Reeburgh et al., 1991).

9   **4.4. CH_4 and N_2O emission in the southern Ocean**

10   Highly dynamic gas exchanges were registered in the KPR, with source and sink scenarios for N_2O and

11   just a source scenario for CH_4. Since the mean wind speed did not exceed 14 m s^{-1}, LM86 and W92

12   parameterizations represent the more conservative overestimation estimates of gas exchange in the area

13   (Frost and Upstill-Goddard, 2003). The gas inventories in the ML reflect the effect of gas transport

14   mainly via turbulent mixing and advection, which can be accelerated by the action of wind but also by

15   the microbial activity in surface waters. The ML depth did not correlate to wind speed (rs: 0.31, p<

16   0.05). This fact would explain how much of the content of the gases in the ML may come from in situ

17   production or consumption. CH_4 fluxes were higher at stations located at the PF and A3, where

18   phytoplaktonic blooms were observed (see Table 2), but the tendency was the reverse for N_2O, with an

19   influx into the aforementioned stations. CH_4 emission rates during this study were higher than previous

20   measurements (Table 2), with a range of 0.1 to 3.0 µmol m^{-2} d^{-1} for the Pacific Ocean (Bates et al.,

21   1996; Holmes et al., 2000; Sansone et al., 2001) and 0.5 to 9.7 µmol m^{-2} d^{-1} for the Atlantic Ocean

22   (Oudot et al., 2002; Forster et al., 2009). In the South Pacific ocean (10°-64°S, 140°E), crossing the PF,

23   Yoshida et al. (2011) reported CH_4 fluxes ranging from 2.4 to 4.9 µmol m^{-2} d^{-1}.

In the case of N_2O, the estimates in this study were in the expected range for the oligotrophic open ocean (Nevinson et al., 1995). N_2O undersaturation and a concomitant influx were estimated, although this situation has not yet been well described for the Southern Ocean. N_2O sinks can occasionally be observed (Butler et al., 1989; Law and Ling, 2001), the most plausible explanation for which is N_2O assimilation by N-fixing microorganisms. This process may be responsible for the estimated N_2O influx.

5. Implications

The dynamics of the both gases differ substantially both spatially and vertically (surface to 500m depth), indicating that different mechanisms are being activated producing an active gas during recycling. Our findings also show that in areas of active fertilization and biogenic particle accumulation, CH_4 accumulates while N_2O becomes depleted. This study suggests that the Antarctic Polar Zone plays a significant role in surface CH_4 production and subsequent air-sea gas exchange. These results did not agree with some previous studies of artificial fertilization experiments in the Southern Ocean, even though only a few previous studies exist, indicating that the turnover and evolution of microbial communities in mesoescale structure are fundamental for the development of substrates and conditions for CH_4 regeneration. Surface N_2O does not spatially respond to natural stimulation, at least in terms of N_2O production via nitrification or that N_2O consuming are faster than N_2O producing process, but in subsurface water N_2O accumulation seems to take place via nitrification).

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1
2 **Figure caption**
3
4 Figure 1. Map showing the location of biogeochemical stations sampled during the KEOPS 2 cruise.
5 Bathymetric topography is shown in the main oceanographic region. The orange line delimits the
6 position of the polar front. The sampled transects are indicated.
7
8 Figure 2. Left column: a)Temperature (T°C), c)Salinity and e) T-S diagram for W-E transect. Station
9 located under the influence of PFZ (purple) is shown, showing enhanced water mass mixing. Arrows
10 indicate position of PF crossing this transect. Right column:b)Temperature(T°C), d) Salinity and f) T-S
11 diagram for W-E transect.
12
13 Figure 3. Vertical cross section of a) nitrate (μmol L^{-1}); b) phosphate (μmol L^{-1}); c) chlorophyll-a (μg
14 L^{-1}); d) dissolved oxygen (μmol L^{-1}), e) nitrous oxide (nmol L^{-1}) and f) methane (nmol L^{-1}) for for
15 zonal transect between 69-75°E. Arrows indicate position of PF crossing this transect
16
17 Figure 4. Vertical cross section of a) nitrate (μmol L^{-1}); b) phosphate (μmol L^{-1}); c) chlorophyll-a (μg
18 L^{-1}); d) dissolved oxygen (μmol L^{-1}), e) nitrous oxide (nmol L^{-1}); f) methane (nmol L^{-1}) for the
19 meridional transect between 45°-51°S.
20
21 Figure 5. PCA analysis with environmental data including dissolved iron obtained in zonal transect
22 (TWE). PCA comprises a) data from the surface to the ML´s base and b) environmental data from the
23 surface to 500 m depth. Each station along with the eigenvectors are included.
24
25 Figure 6. Vertical distribution of biogeochemical variables from selected stations with particular
26 oceanographic and biogeochemical characteristics. Different biogeochemical regimes are defined as
27 HNLC area (St. R), northern and southern area of Polar front (St. NS01 and A3) and within the Polar
28 front (Sts. TWE03 and TWE07)
29
30

Table 1. General oceanographic features of the sampled stations during the KEOPS 2 cruise

Biogeochemical Provinces	Stations	Latitude	Longitude	Date	Bottom Depth	MLD	Temperature	Salinity	Oxygen
		°E	°S	mm-dd-yy	(m)	(m)	(ºC)		(µmol/Kg)
	OISO-6	-44.59	52.06	10-15-11	3260	110	3.68 (3.66-3.68)	33.80 (33.80-33.81)	317.4 (314-318)
	OISO-7	-47-4	58.00	10-16-11	4300	127	4.75 (4.73-4.76)	33.79 (33.8-33.81)	308.4 (305-309)
N-S transect									
	A3-1	-50,38	72.05	10-19-11	535	181	1.68 (1.68-1.73)	33.89 (33.85-33.91)	325.9 (321-327)
	A3-2	-50.38	72.05	10-16-11	527	165	2.16 (2.10-2.18)	33.91 (33.911-33.913)	333.2 (329-335)
	TNS10	-50.12	72.07	10-21-11	565	163	1.67 (1.59-1.68)	33.90 (33.80-33.93)	325.9 (314-327)
Eddy	TNS09	-49.47	72.12	10-21-11	615	137	1.75(1.66-1.89)	33.91(33.80-33.84)	321.1 (265-331)
Eddy	TNS08	-49.27	72.14	10-21-11	1030	139	2.11 (2.06-2.12)	33.869 (33.86-33.87)	329.4 (324-328)
	TNS07	-49.08	72.17	10-22-11	1890	62	2.10 (1.95-2.16)	33.86 (33.86-33.87)	327.7 (327-331)
	TNS06	-48.48	71.18	10-22-11	1885	67	2.32 (2.23-2.42)	33.846 (33.84-33.85)	327.6 (315-316)
	TNSO5	-48.28	72.12	10-22-11	2060	114	2.22 (2.09-2.26)	33.85 (33.85-33.86)	326.7(323-328)
	TNS03	-47.05	71.55	10-23-11	540	111	2.17 (2.06-2.26)	33.89(33.88-33.89)	307.6(304-310)
	TNS02	-47.19	71.42	10-23-11	520	65	3.60 (3.38-3.67)	33.69 (33.68-33.69)	318.6 (317-319)
	TNS01	-46,.49	71.30	10-23-11	2280	45	4.02(3.96 -4.13)	33.71(33.71-33.72)	316.1 (315-318)
HNLC	RK2-2	-50.21	66.43	10-23-11	2300	111	2.11 (2.06-2.14)	33.78 (33.77-33.78)	326.7 (326-327)
E-W transect									
(Shelf)	TEW1	-49,08	69.50	10-31-11	86	16	3.27 (3.17-3.36)	33.61(33.61-33.62)	344.16 (340-345)
(Shelf)	TEW2	-48,53	70.39	10-31-11	84	40	2.55 (2.49-2.68)	33.75 (33.75-33.76)	332,0 (327-337)
(Shelf)	TEW3	-48,47	71.01	10-31-11	565	62	2.17 (2.12-2.31)	33.86 (33.86-33.87)	329.69 (328-331)
(NPF)	TEW4	-48,37	71.28	11-01-11	1585	95	2.54 (2.41-2.60)	33.85 (33.85-33.86)	334.60 (331-337)
	TEW5	-48,28	72.47	11-01-11	2275	60	2.51 (2.39-2.60)	33.84 (33.84-33.85)	331.42 (327-336)
(SPF)	TEW7	-48,27	73.59	11-02-11	2510	17	4.02 (3.91-4.10)	33.78 (33.784-33.79)	315.95 (346-349)
	TEW8	-48,28	75.19	11-02-11	2786	22	4.15 (4.08-4.18)	33.76 (33.76-33.77)	338.75(347-350)
Time Series Stations									
	E1-1	-48.27	72.11	10-28-11	2056	84	2.48 (2.36-2.54)	33.85(33.84-33.85)	331.54(328-333)
	E1-2	-48.31	72.04	11-01-11	2003	42	2.42 (2.28-2.56)	33.85 (33.85-33.86)	331.68 (329-333)
	E1-3	-48.41	71.58	11-03-11	1915	41	2.74 (2.60-2.81)	33.84 (33.84-33.85)	332.08 (331-332)
	E1-4W	-48.45	71.25	11-11-11	1384	67	2.36 (2.07-2.51)	33.90 (33.90-33.91)	329.95 (326-332)
	E1-4E	-48.42	72.33	11-12-11	2210	77	3.15 (2.78-3.19)	33.84 (33.83-33.85)	329.89 (326-331)
	E1-5	-48.24	71.50	11-18-11	1920	36	2.53 (2.50-2.62)	33.85 (33.85-33.85)	326.97(330-333)

Table 2. Inventories of gases and nutrients estimated in the mixed layer (ML) and the entire water column, along with GHG concentrations, wind velocities and concomitant estimated gas exchange across the air-sea interface

Station	Inventory in the MLD					Inventory in the Water Column				GHGs		Wind	Flux LM86		Flux W92	
	*Chl-a	CH$_4$ mmol m^{-2}	N$_2$O	NO$_3^-$	PO$_4^{3-}$	N$_2$O	CH$_4$	NO$_3$-	PO$_4^{3-}$	N$_2$O	CH$_4$		N$_2$O	CH$_4$	N$_2$O	CH$_4$
	mg m^{-2}	m^{-2}	mmol m^{-2}	mol m^{-2}	mol m^{-2}	mmol m^{-2}	mmol m^{-2}	mol m^{-2}	mol m^{-2}	nM	nM	m s^{-1}	µmol m^{-2} d^{-1}		µmol m^{-2} d^{-1}	
N-S Transect																
A3-1	12.60	3.00	2.43	5.41	0.293	5.72	4.12	7.342	0.940	13.73	6.56	6.58	-1.54	18,75	-2.96	35.93
A3-2	35.48	3.31	1.81	4.38	0.300	5.273	3.31	15.04	1.024	11.64	8,,37	11.39	-10.5	14.24	-22.9	29.70
TNS10	14.09	1.39	2.56	4.79	0.319	9.29	2.17	16.03	1.077	15.49	7.79	12.66	3.57	14.90	6.56	27.48
TNS09	35.58	1.33	2.23	3.91	0.254	7.51	1.87	12.53	0.864	15.89	14.54	14.38	5.08	38.10	9.36	70.26
TNS08	23.23	0.68	2.16	3.98	0.260	9.27	1.58	15.75	1.038	15.46	5.65	11.89	4.29	7.80	7.92	14.38
TNS07	25.45	0.25	1.02	1.69	0.111	9.99	1.80	15.74	1.072	16.92	4.01	11.89	8.65	2.03	15.55	3.66
TNS06	16.33	0.57	0.92	1.83	0.123	8.65	2.54	15.93	1.070	13.81	8.74	11.89	-0.78	17.59	-1.20	31.64
TNSO5	17.19	0.74	1.68	3.07	0.212	9.27	2.46	15.39	1.070	14.67	6.41	11.40	1.81	9.91	3.26	17.82
TNS03	17.28	0.88	1.75	3.06	0.214	7.75	3.14	12.46	0.875	11.05	7.23	11.40	4.13	9.93	6.85	16.44
TNS02	11.25	0.26	0.91	1.73	0.123	8.27	1.57	15.08	1.046	13.92	4.38	9.73	1.48	3.03	2.45	5.00
TNS1	11.21	0.39	0.63	1.07	0.076	8.89	3.16	14.17	0.976	13.95	8.48	9.73	2.26	14.40	3.74	23.84
RK2-2	14.89	0.64	1.63	2.79	0.197	2.83	1.06	4.900	0.347	14.83	6.29	6.86	0.89	4.09	1.34	6.15
W-E Transect																
TEW1	9.78	0.19	0.26	3.40	0.412	1.18	1.30	1.560	0.111	15.29	9.50	4.60	0.87	3.15	1.69	6.15
TEW2	9.87	0.43	0.62	0.84	1.073	1.12	1.74	1.873	0.133	15.03	9.88	4.60	0.54	3.24	1.06	6.33
TEW3	8.77	0.73	0.91	0.51	1.566	7.41	2.40	14.97	1.072	15.56	14.09	4.60	0.67	5.25	1.32	10.24
E1-2	15.33	0.52	0.20	0.82	1.167	9.78	2.80	15.24	1.051	14.95	11.42	6.92	1.34	11.67	2.01	17.57
TEW4	35.53	0.40	1.63	0.30	2.468	10.3	1.81	15.74	1.106	16.62	3.50	6.92	3.76	0.21	5.67	0.32
TEW5	23.11	0.38	0.99	0.52	1.619	10.21	2.61	15.62	1.099	16.31	6.35	6.92	3.28	4.34	4.94	6.54
TEW7	75.45	0.19	0.23	2.39	0.353	9.26	7.44	15.23	1.087	12.90	10.87	8.04	-0.96	15.42	-1.52	23.78
TEW8	59.52	0.10	0.37	1.52	0.472	10.05	1.59	15.27	1.058	15.77	4.95	8.04	5.25	3.52	8.10	5.42

*Inventories estimated from the photic zone