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Interannual variability of vertical particle fluxes in the Ross Sea (Antarctica)

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Abstract

This study presents new data on biogenic and terrigenous particle fluxes collected by an oceanographic mooring (Mooring A) deployed in the south-western Ross Sea (Antarctica) in the frame of the Italian Long-Term Ecological Research network (LTER-Italy). Results from the years 2005 and 2008 document high mass fluxes during the summer and early autumn seasons, not coincident with the algal bloom. Downward particle fluxes exhibit a high inter-annual variability of both particulate fluxes and composition that seem related to the different factors as the phytoplankton increases, occurring between the beginning of February and the end of March, to the variations in the sea ice extent and to the resuspension and/or lateral advection processes. The flux variability may have been influenced by Iceberg B-15 that resided in the investigated area between 2000 and 2005. The decoupling of biogenic silica and organic carbon cycles is documented by differences in the rates of their respective key processes: biogenic silica dissolution and organic carbon degradation.

Keywords

Particle flux, sediment trap, mooring, Antarctica, Ross Sea, LTER

Introduction

The Ross Sea is the region with the highest values of primary production and carbon sequestration through the biological pump in the Southern Ocean (Arrigo et al. 2008a; Hoppe et al. 2017). It represents a key area for investigating changes in primary productivity and their relationship with sea ice cover, physical and chemical parameters of the water column and the availability of nutrients as the iron supply. All these parameters affect the phytoplankton blooms, the zooplankton grazing and, consequently, both retention and export of carbon within the water column and at the seafloor (Frignani et al. 2000). The export of carbon from the surface to the deep ocean via the sinking of particulate organic matter is a major process of the ocean carbon cycle and a key factor in the regulation of the atmospheric CO_2 level (Siegenthaler et al. 2005).

The study of particles collected by automated sediment traps provides an important tool for establishing how and when environmental and biological factors modulate export of the organic matter produced at the surface. The export fluxes change within and between ocean regions as a function of primary productivity and temperature (Laws et al. 2000) and vary inter-annually (Ducklow et al. 2008; Church et al. 2013). However, the processes governing the export from the surface to the deep sea and its efficiency are still poorly known, especially in the Southern Ocean (Takahashi et al. 2009). Previous sediment trap data from Antarctic and Arctic seas suggested a close temporal coupling between the spring-summer phytoplankton blooms and high particle flux (Collier et al. 2000; Anadon and Estrada 2002; Fischer et al. 2002; Arrigo et al. 2008b; Ducklow et al. 2008, 2015; Honjo et al. 2010; Forest et al. 2011; Sampei et al. 2012; Weston et al. 2013).

The aim of this research was to increase the current knowledge of the seasonal and inter-annual variability of vertical particle fluxes in the Ross Sea and to understand the factors influencing the quantity and the quality of the trapped material. For this purpose, we analysed the sediment trap samples collected at two different depths (360 and 770 m) from the Mooring site A during 2005 and 2008. This site is part of the Italian Long-Term Ecological Research network (LTER-Italy) and provides a suite of data essential for investigating the biogeochemical cycles in the south-western Ross Sea.

The present study also allowed us to record the Ross Sea particle flux variability during and after the residence of Iceberg B-15, which occurred near the investigated area between 2000 and 2005.

This large (230 × 80 km^2) iceberg with a draft of 300 m calved from the Ross Ice Shelf near Ross Island on 21 March 2000 and broke into two parts (B-15A and B-15B) on 10 May 2000. B-15B exited the Ross Sea in 2000, while B-15A was transported by currents and was pinned between Ross and Franklin Islands for a period of five years (Arrigo and van Dijken 2004). Icebergs may disturb regional ocean processes for several years with important impacts on physical oceanography (Robinson and Williams 2012) and the local ecosystem (Arrigo et al. 2002; Seibel and Dierssen 2003). Recording and understanding the spatial and temporal variability of downward particle fluxes in relation to the iceberg presence is of great interest, particularly when considering the present climate warming scenarios.

Study area

The Ross Sea is located in the Pacific sector of the Southern Ocean, between Cape Colbeck at 158°W and Cape Adare at 170°E. On the southern side, it is bounded by the Ross Ice Shelf, at around 78.5°S, which extends over nearly half the continental shelf and is about 250 m thick on its northernmost side (Budillon et al. 2002). The Ross Sea is characterised by a wide and deep continental shelf with a mean depth of 500 m. The circulation on the Ross Sea shelf is rather complex and variations in physical properties along the seawater column determine a vertical structure from the surface to the bottom.

Mooring A is located in a quite flat area characterised by high biogenic fluxes through the water column (Langone et al. 2003) and by weak currents at the bottom flowing from Terra Nova Bay (TNB) polynya (Mangoni et al. 2017). In this region, the long-lasting seasonal ice cover inhibits fine sediment and organic matter accumulation on the sea-floor (Langone et al. 1998). Here currents are quite weak, allowing large particles to sink in close proximity (< 20 km) to the production area (Jaeger et al. 1996; Frignani et al. 2000). As a consequence, high primary productivity typically leads to high accumulation of biogenic silica in nearby sediments (Jaeger et al. 1996).

Diatom blooms occur abundantly in the Ross Sea (Smith and Nelson 1985; Leventer and Dunbar 1996) and, when ice melts, these blooms border the marginal ice zone for most of the austral summer (Ravaioli et al. 1999). Investigations performed in this area report that diatoms are the dominant primary producers and their fluxes are characterised by both seasonal and interannual variability (Leventer and Dunbar 1996) principally linked to changes in the water current regime (Frignani et al. 2000).

The area has been affected by the presence of Iceberg B-15 between 2000 and 2005 and reopened in the year 2005 when the Iceberg moved (Manzoni 2006).

Materials and methods

Data collection

Mooring A (https://deims.org/86b6465c-b604-4efa-9145-0805f62216f4) was deployed in 1991 in the south-western region of the Ross Sea polynya, between Franklin Island and Ross Island (Fig. 1), at 76°41'S latitude and 169°02'E longitude at 832 m water depth, to monitor the oceanographic regime and the accumulation rate in this region. It was active until year 2010 and was managed through collaboration between Italian and American scientific institutions.

Mooring A was equipped with two time-series McLane Labs PARFLUX sediment traps, coupled with an Aanderaa RCM9 single point current meter and an SBE 16 SeaCat conductivity and temperature recorder at about 360 and 770 m water depths, respectively. The upper level trap allowed the measurement of the export from the pro-

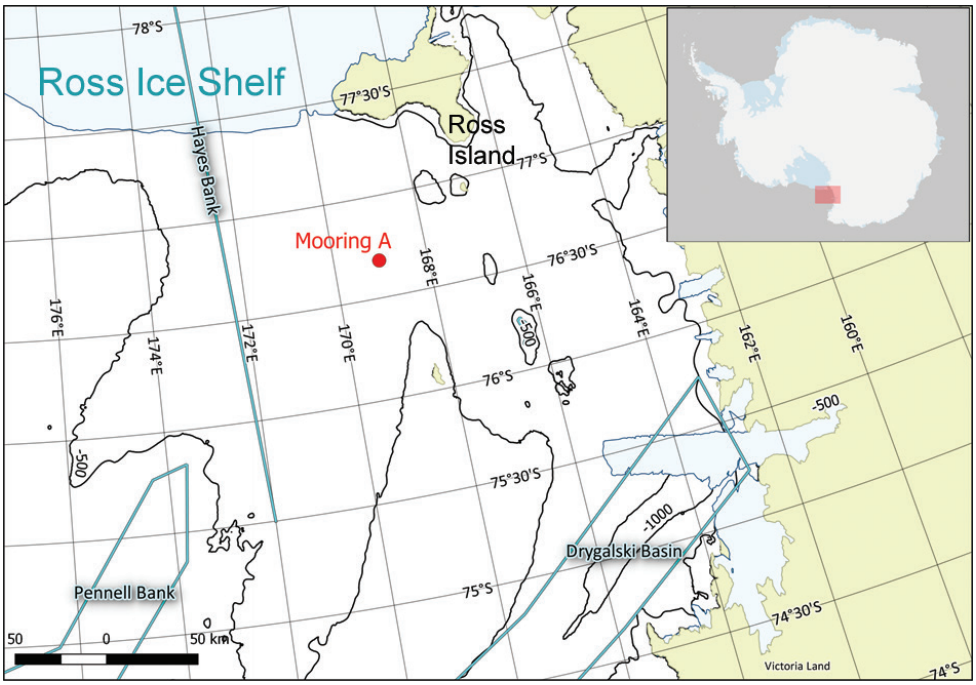

Figure 1. Position of Mooring A in the south-western Ross Sea. The bathymetric contour levels were produced using the dataset provided by the International Bathymetric Chart of the Southern Ocean, IBCSO (Arndt et al. 2013) and the QGIS 2.14 software package.

ductive layer of the water column while the near-sea bottom trap provided data about the water-sediment interface fluxes. The depth of the top trap was selected in order to avoid possible damages caused by the passage of Iceberg B-15 (2000–2005), which caused the loss of an instrument array during previous studies.

In 2005, both sediment traps were equipped with 21 collection cups, while in 2008, each trap contained 13 cups. The sediment traps were cone-shaped with a collecting area of 0.5 m^2 and they collected material between 8 February 2005 and 16 January 2006, and between 1 February 2008 and 1 February 2009. To prevent organic degradation during deployment, trap sample cups were filled with filtered seawater containing a pH-buffered (1 g l^{-1} of sodium borate) solution of 5% formalin.

Unfortunately, the 2005 dataset was not complete as some bottles broke during transport to the laboratory and the little amount of material collected in some trap cups (< 20 mg) precluded geochemical analysis. However, 11 samples from the top trap and 12 from the bottom trap were analysed and 8 of them, both from the top and bottom traps, were related to the same sampling period. A total of 22 and 26 samples were analysed from the 2005 and the 2008 deployments, respectively. Trap samples were kept constantly refrigerated and later stored in a cold room at 4 °C at the CNR-ISMAR laboratory in Bologna.

Sample treatment and analytical methods

Samples collected during 2005 were treated and analysed at the CNR-ISMAR of Bologna following a modified Heussner's method proposed by Chiarini and co-workers (Heussner et al. 1990; Chiarini et al. 2013), while the samples collected during 2008 were split and analysed at the Stanford University following the Dunbar and Mucciarone (2003) method. These two methods differ in the sample preparation, as in the modified Heussner's method the splitting procedure is carried out with a peristaltic pump, whereas in the Dunbar and Mucciarone (2003) protocol, it is done with a Folsom Plankton Splitter. As a consequence, the protocol of Dunbar and Mucciarone (2003) is faster than the modified Heussner's method. Despite the differences, the results obtained with the two adopted methods were comparable (Chiarini et al. 2013).

First, the supernatant was removed and part of it was preserved for further analyses, then the sample was sieved through a 580 μm filter mesh to separate the coarse sediment from the finest sediment. The larger-sized swimmers that might block the peristaltic pump were removed before the sample was split to obtain three different fractions of material depending on its initial abundance. Of these material fractions, one was kept as an archive, one was kept wet and the last one was freeze-dried. An accurate picking was carried out under a stereomicroscope in order to remove organisms which entered the trap actively (active flux) and to obtain only the passive flux for biogenic silica, carbon and nitrogen analyses.

Biogenic silica (BioSi, considered as opal $SiO_2 \cdot 1.5H_2O$, with about 10% of water) content was obtained using the DeMaster (1981) dissolution method. Total nitrogen and organic carbon contents were determined using a Carlo-Erba CHN analyser (Stanford: Carlo-Erba NA 1500). The composition of the particulate matter was calculated as:

$$\%CaCO_3 = (\%C_{tot} - \%C_{org}) \cdot 8.33$$
$$\%\text{lithogenic} = 100 - (\%C_{org} \cdot 2) - \%CaCO_3 - \%\text{BioSi} - \%N_{tot}.$$

The flux estimations were subject to uncertainties (about 6%) related to the efficiency of material collection and to chemical (material solubilisation), physical (hydrodynamic) and biological (swimmers/active migration) factors (Sanchez-Vidal et al. 2015). BioSi, organic carbon, $CaCO_3$ and total mass flux determinations present errors of about 4.1%, 2%, 1–5% and 4.5%, respectively (Collier et al. 2000; Sanchez-Vidal et al. 2015). Chemical analyses were conducted on grounded freeze-dried samples both at CNR-ISMAR and Stanford University.

Sea ice concentrations were derived from daily data from the National Snow and Ice Data Center, obtained with the DMSP-F11, F13 and F17 Special Sensor Microwave Imager/Sounder (SSMIS), using the NASA Team algorithm for calculation of the sea ice concentration (Cavalieri et al. 1996). The sensor resolution is 25 × 25 km^2 and the sea ice concentration data represented the daily values averaged on the grid

cell containing the location of Mooring A. Sea ice concentration data were processed starting from November 2004 to December 2005 and from November 2007 to December 2008. Chlorophyll-*a* (chl-*a*) concentrations (available from 1997) were derived from the Moderate Resolution Imaging Spectroradiometer (MODIS) sensor on the Aqua satellite (4 km resolution). The data can be considered cloud free, since they are averaged over 8 days in order to reduce the bias due to cloud cover. The accuracy for chl-*a* data from MODIS is ± 35%. Data were processed using the Giovanni online data system, developed and maintained by the NASA GES DISC (http://disc.sci.gsfc.nasa.gov/giovanni/overview/index.html). Chl-*a* concentration data were processed from 1 October 2004 to 6 March 2005 and from 1 October 2007 to 6 March 2008, averaged over an area of about 45 km of radius centred on the Mooring A site. The chl-*a* concentrations were averaged over the region 76.60S–76.89S latitude and 167.87E–169.10E longitude for comparison with the sea ice data and water column particle fluxes.

Mass balance of particle fluxes

The mass balance is based on the assumptions that lithogenic fluxes are conservative and that the material laterally advected has the same composition of vertical flux (Frignani et al. 2000). Consequently, the values obtained are considered rough estimates.

As the lithogenic material is the only material that does not undergo degradation when sinking to the seafloor, it is used to determine the magnitude of resuspension and lateral advection. The amount collected by the top trap was considered as 100% and the difference between the top and the bottom trap was then determined by the amount of material removed or resuspended. The fraction of material that did not result from vertical sinking was thus determined.

Assuming the material that arrives into the bottom trap due to external inputs has the same composition as the material related to the vertical flux, the amount of BioSi and organic carbon (OC) gathered or removed can then be determined. To do this, we considered the BioSi and the OC removed or added with the same percentage of lithogenic material with respect to the top level. The relationship between the BioSi and the OC amount collected in the bottom trap and the expected amount indicated the percentage of dissolution or degradation of the various elements along the water column.

Results

Particle fluxes and composition

Annual integrated mass fluxes during 2005 were 42.2 g m^{-2} yr^{-1} at the top trap and 102.7 g m^{-2} yr^{-1} at the bottom trap, while during 2008, the values were 47.8 g m^{-2} yr^{-1} and 36.1 g m^{-2} yr^{-1}, respectively (Table 1).

During 2005 year, total mass fluxes were lower in the top trap (from 1.9 mg m^{-2} d^{-1} to 557.3 mg m^{-2} d^{-1}) than in the bottom trap (from 32.8 mg m^{-2} d^{-1} to 712.5 mg m^{-2} d^{-1}). In contrast, during 2008, mass fluxes were higher in the top trap (from 5.0 mg m^{-2} d^{-1} to 409.6 mg m^{-2} d^{-1}) and lower in the bottom trap (from 6.0 mg m^{-2} d^{-1} to 226.1 mg m^{-2} d^{-1}) (Table 2 and Fig. 2).

In the top trap, the highest mass fluxes were observed in February and in March 2005, while in the bottom trap, they increased in the second part of January and in April 2005. In general, BioSi fluxes were about one order of magnitude higher than

Table 1. Annual integrated fluxes of total mass, biogenic silica (BioSi), organic carbon (OC), nitrogen (N), calcium carbonate and lithogenic (g m^{-2} yr^{-1}), and SiO_2/OC molar ratio during 2005 and 2008 at Mooring A. The sampling days represent the integrated period of the fluxes at the two levels (top trap and bottom trap). In brackets, the estimated values of annual mass fluxes in 2005 (see text for details).

Years	Level	Sampling days	Mass	BioSi	OC	N_{tot}	$CaCO_3$	Lithogenic	molar SiO_2/OC	Molar C/N
2005	top	257	42.2 (54.9)	15.0	2.3	0.4	7.6	15.6	1.0	7.0
	bottom	229	102.7 (113.2)	33.1	3.9	0.7	6.8	54.3	1.8	7.2
2008	top	365	47.8	10.8	3.8	0.6	20.1	11.8	0.4	7.5
	bottom	365	36.1	9.1	2.5	0.4	12.1	9.7	0.8	7.6
1994*	top	355	59.3	26.3	10.6	–	–	–	0.5	9.2
	bottom	355	86.9	52.4	4.1	–	–	–	2.5	9.6

*Data from Langone et al. (2003)

Table 2. Temporal series of total mass, relative content (%) of biogenic silica, organic carbon, nitrogen and $CaCO_3$ and absolute values of organic carbon (OC) and biogenic silica (BioSi) fluxes at Mooring A in 2005. Days indicate the sampling time. Anomalous values are marked with an asterisk (*).

Bottle	Start	Stop	Days	Total flux (mg m^{-2} d^{-1})	%OC	%BioSi	%N	%$CaCO_3$	OC (mg m^{-2} d^{-1})	BioSi (mg m^{-2} d^{-1})
Top 1	08/02/2005	15/02/2005	7	395.1	6.3	39.5	1.2	14.6	25.0	156.1
Top 2	15/02/2005	25/02/2005	10	557.3	6.4	44.8	1.2	13.1	35.9	249.6
Top 5	15/03/2005	31/03/2005	16	514.2	4.6	49.5	0.8	10.1	23.7	254.5
Top 7	15/04/2005	30/04/2005	15	342.8	2.3	22.5	0.9	42.7	19.4	77.0
Top 9	31/05/2005	15/06/2005	15	30.2	4.7	0.3*	0.8	85.3	1.4	0.1
Top 10	15/06/2005	30/09/2005	107	39.6	2.0	18.7	0.9	17.3	2.2	7.4
Top 11	30/09/2005	01/11/2005	32	1.9	2.4	23.8	0.4	1.1	0.1	0.5
Top 13	15/11/2005	01/12/2005	16	25.7	4.1	25.5	0.7	0.6	1.0	6.6
Top 14	01/12/2005	16/12/2005	15	40.3	5.8	27.7	0.9	3.4	2.4	11.2
Top 15	16/12/2005	01/01/2006	16	107.0	5.2	22.6	0.8	1.3	5.5	24.2
Top 17	08/01/2006	16/01/2006	8	65.7	1.0	46.5*	1.6	3.8	6.3	30.5
Bot 1	08/02/2005	15/02/2005	7	397.7	6.5	44.7	1.2	4.2	25.6	177.8
Bot 2	15/02/2005	25/02/2005	10	466.9	5.7	46.6*	1.1	11.5	26.4	217.6
Bot 4	15/03/2005	31/03/2005	15	569.7	3.7	50.9*	0.7	10.6	20.8	290.2
Bot 7	15/04/2005	30/04/2005	15	550.9	5.4	39.4	1.0	16.0	29.9	217.1
Bot 9	31/05/2005	15/06/2005	15	32.8	13.5	9.2	2.2	42.0	4.4	3.0
Bot 10	15/06/2005	30/09/2005	107	216.7	3.0	17.6	0.5	4.5	6.6	38.1
Bot 12	30/09/2005	01/11/2005	14	230.2	1.3	27.0	0.2	1.1	3.0	62.2
Bot 14	15/11/2005	01/12/2005	15	83.1	1.6	26.4	0.3	0.4	1.3	21.9
Bot 15	01/12/2005	16/12/2005	16	233.5	1.9	28.5	0.3	0.6	4.4	66.5
Bot 16	16/12/2005	01/01/2006	7	372.9	3.0	43.0	0.5	0.1	11.2	160.2
Bot 17	08/01/2006	16/01/2006	8	712.5	5.0	39.7	0.8	0.8	35.6	282.5

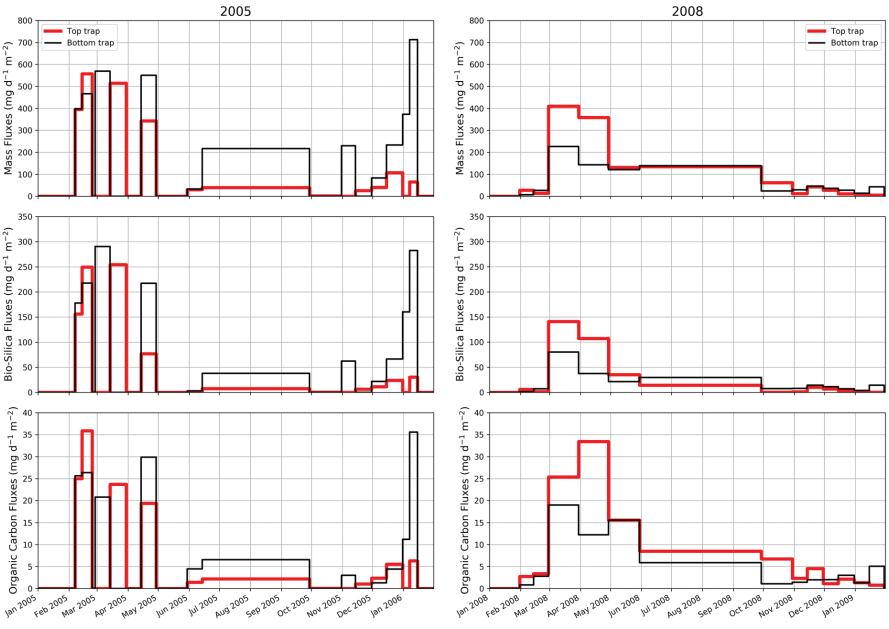

Figure 2. Mass, biogenic silica and organic carbon fluxes at the top and bottom traps measured in 2005 (left) and in 2008 (right) at Mooring A.

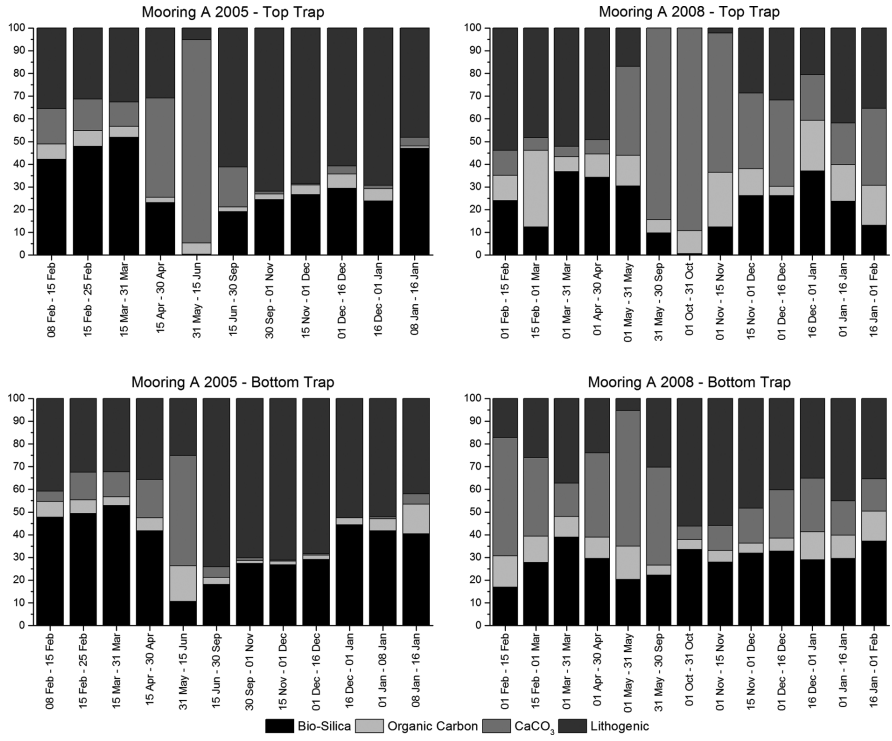

Figure 3. Percentage sample composition at the two levels of Mooring A during 2005 and 2008.

organic carbon fluxes and reached their maximum values during March 2005 and March 2008 at both levels (Fig. 2). The percentages of the major components of the total mass flux are listed in Table 2 (2005) and Table 3 (2008) while their temporal variations are shown in Figure 3. The amount of biogenic material, i.e., OC and BioSi, reached about 50% of the total flux during the austral summer of both years. In 2005, we observed higher concentrations of lithogenic material in both traps, with values of about 70% from September to January (Fig. 3). During 2008, the particle composition in the top trap samples showed high seasonal variability. In the first part of the year, lithogenic material comprised about 50% of each sample. From May to November, samples were predominantly composed of $CaCO_3$, with concentrations ranging from 70% to 90%.

In order to compare our results with previous ones obtained from Mooring A in 1994 by Langone et al. (2003), we tentatively estimated the missing data from 2005 using the fluxes from the periods immediately before and after the data gaps as well as the typical mass flux pattern related to these periods (Table 1). Estimated mass fluxes were around 500 mg m^{-2} d^{-1} during the first 15 days of March and about 350 mg m^{-2} d^{-1} during the first 15 days of April and we obtained an integrated mass flux of

Table 3. Temporal series of total mass, relative content (%) of biogenic silica, organic carbon, nitrogen and $CaCO_3$ and absolute values of organic carbon (OC) and biogenic silica (Bio-Si) fluxes at Mooring A in 2008. Days indicate the sampling time.

Bottle	Start	Stop	Days	Total flux (mg m^{-2} d^{-1})	%OC	%BioSi	%N	%$CaCO_3$	OC (mg m^{-2} d^{-1})	BioSi (g m^{-2} d^{-1})
Top 1	01/02/2008	15/02/2008	15	27.4	10.0	21.5	1.3	9.9	2.8	5.9
Top 2	15/02/2008	01/03/2008	14	14.5	25.2	9.3	4.5	4.2	3.4	1.3
Top 3	01/03/2008	31/03/2008	30	409.6	6.2	34.5	1.0	4.2	25.4	141.2
Top 4	31/03/2008	30/04/2008	31	346.8	9.3	31.0	1.5	5.7	33.4	107.4
Top 5	30/04/2008	31/05/2008	31	131.4	11.9	26.8	2.5	34.5	15.6	35.2
Top 6	31/05/2008	30/09/2008	122	135.1	6.3	10.6	0.8	82.4	8.5	14.3
Top 7	30/09/2008	01/11/2008	32	60.2	10.8	0.7	3.1	85.4	6.7	0.4
Top 8	01/11/2008	15/11/2008	14	11.8	19.4	10.0	4.4	49.5	2.3	1.2
Top 9	15/11/2008	01/12/2008	16	42.7	10.6	23.4	1.9	29.8	4.5	10.0
Top 10	01/12/2008	16/12/2008	15	27.7	4.0	25.1	0.7	36.5	1.1	7.0
Top 11	16/12/2008	01/01/2009	16	11.7	18.3	30.2	3.1	16.4	2.1	3.5
Top 12	01/01/2009	16/01/2009	15	9.6	13.9	20.4	2.3	15.7	1.3	2.0
Top 13	16/01/2009	01/02/2009	16	5.0	15.0	11.1	2.1	28.8	0.8	0.6
Bot 1	01/02/2008	15/02/2008	15	6.8	12.1	14.9	1.9	45.85	0.8	1.0
Bot 2	15/02/2008	01/03/2008	14	28.6	10.4	24.9	1.6	31.03	2.8	7.1
Bot 3	01/03/2008	31/03/2008	30	226.1	8.4	35.6	1.5	13.45	19.0	80.4
Bot 4	31/03/2008	30/04/2008	31	138.3	8.5	27.0	1.9	34.04	12.2	37.4
Bot 5	30/04/2008	31/05/2008	31	121.3	12.8	17.7	2.5	52.00	15.6	21.5
Bot 6	31/05/2008	30/09/2008	122	139.3	4.2	21.2	0.5	41.43	5.9	29.5
Bot 7	30/09/2008	01/11/2008	32	23.8	4.3	32.1	0.8	5.51	1.1	7.6
Bot 8	01/11/2008	15/11/2008	14	29.3	4.8	26.6	0.8	10.45	1.4	7.8
Bot 9	15/11/2008	01/12/2008	16	46.3	4.2	30.5	0.8	14.79	2.0	14.2
Bot 10	01/12/2008	16/12/2008	15	36.6	5.5	30.9	1.0	20.04	2.0	11.3
Bot 11	16/12/2008	01/01/2009	16	27.3	11.0	25.8	1.9	20.98	3.0	7.1
Bot 12	01/01/2009	16/01/2009	15	13.9	9.3	26.8	1.5	13.76	1.3	3.7
Bot 13	16/01/2009	01/02/2009	16	43.3	11.7	32.8	1.8	12.63	5.1	14.2

54.9 g m^{-2} yr^{-1}. The fluxes for the periods 15 February – 25 February and 15 March – 31 March were 557.30 and 514.16 mg m^{-2} d^{-1}, respectively, so we estimated a flux of 500 mg m^{-2} d^{-1} for the period in-between. Following this procedure, the annual flux at the bottom was 113.2 g m^{-2} yr^{-1}.

Sea ice

The sea ice coverage in mooring area, analysed from November 2004 to December 2005 and from November 2007 to December 2008, exhibited the highest values from April to November and the lowest values in January and February, in both years. In the timeframe of the present study, the sea ice concentration decreased from November to January with a minimum value at the end of February in both 2005 and 2008. From the end of February, the sea ice concentrations increased, reaching values greater than 90% by the end of March. The increase in the ice cover was quite fast, occurring in less than 5 weeks, in some cases. From April to November, sea ice concentrations oscillated around an average of 90.5%, sometimes reaching 100% (Fig. 4).

Physical properties of sea water

In 2005, the temperature recorded at the top trap (360 m) showed little variability from January to June (mean -1.89 °C, max -1.84 °C, min -1.91 °C). The salinity ranged from 34.61 to 34.70, with constant values of about 34.64 until June, increasing to 34.74 and exhibiting more variability through January 2006 (Fig. 5a). Temperatures at the bottom trap (770 m) showed quite constant values near -1.89 °C. Salinity values were quite variable from January to June 2005, averaging around 34.74, then they began to decrease until August. From August through the end of the year, salinity values were constant with a mean value of 34.72 (Fig. 5b). During 2008, at the top level (360 m), the temperatures showed nearly constant values (-1.90 °C) from mid-June through to December 2008. The highest salinity (34.69) was recorded in early February, then it decreased from March to June (34.60). From June, salinity increased until November and then decreased again (Fig. 5c).

Swimmers

In the year 2005, the top sediment trap collected very few intact organisms that could be considered active swimmers and they were mainly represented by crustaceans and polychaetes. They were removed before calculating the vertical fluxes. Abundant empty or broken shells of the pteropod *Limacina helicina*, faecal pellets of different shapes and sizes, and degraded organisms (considered as part of the passive flux) were found in late summer and early autumn samples. Mucilaginous material was abundant from February to mid-March. It is worth mentioning that half of the top trap bottles con-

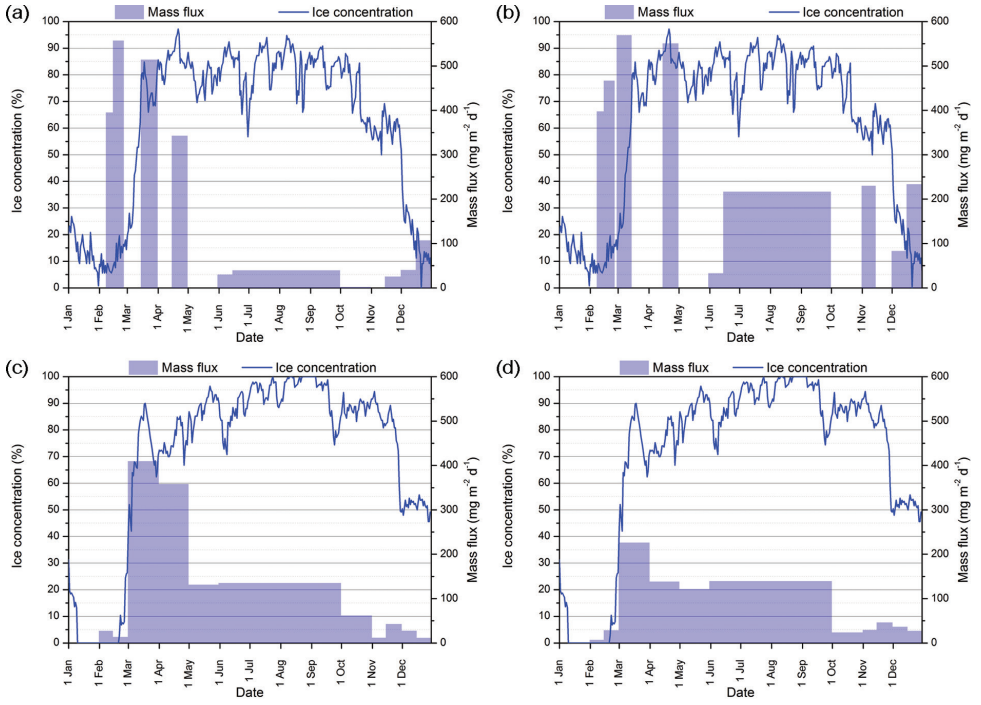

Figure 4. Sea ice concentration and mass fluxes during 2005 and 2008 **a, c** at the top and **b, d** at the bottom sediment traps, respectively.

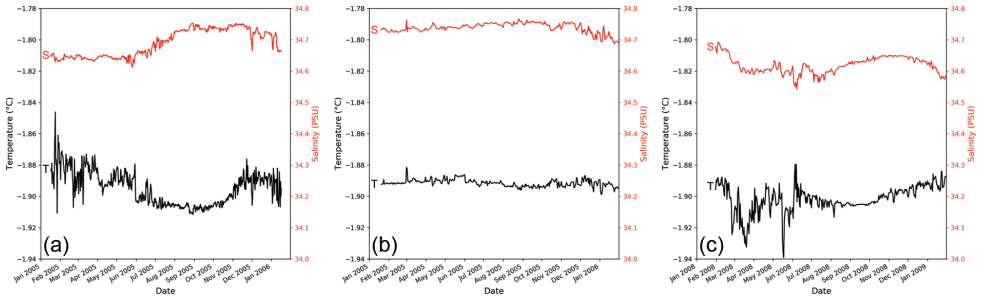

Figure 5. Temperature (T) and salinity (S) values **a** at the top and **b** at the bottom levels in 2005 and **c** the surface level measure in 2008.

tained only passive flux. The swimmers were few also in the bottom trap samples. From February to the end of September 2005, many empty and broken shells of *L. helicina* were found. The period of maximum abundance of swimmers did not coincide with that of maximum particulate fluxes.

During 2008, in the top trap, the period of maximum abundance of swimmers was from March to April. During the same period, many specimens of *L. helicina* were found with the maximum flux in March (700 specimens m^{-2} d^{-1}).

Chlorophyll-*a*

Chl-*a* concentrations are reported in Figure 6. During 2004–2005, chl-*a* concentrations gradually increased up to the highest value reached from 18 December 2004 to 25 December 2004 (1.4 mg m^{-3}), then they decreased to ~0.2 mg m^{-3} from January to March 2005 (Fig. 6a). During 2007–2008 (Fig. 6b), the data series showed a maximum chl-*a* concentration of 4.5 mg m^{-3} (between 1 January and 8 January 2007) and values generally higher than those of the 2004–2005 period. It should be noted that, while the presence of chl-*a* in the area was constant from November 2004 to January 2005, the satellite did not record the presence of chl-*a* from 18 December 2007 until 3 January 2008 (value marked with a star in Fig. 6b).

Discussion

Variability in particles fluxes

During the present study, the maximum mass fluxes at the top and at the bottom sampling levels were detected in the year 2005 just before the onset of maximum sea ice concentration and during sea ice formation (between the beginning of February and the end of March). During winter, a period of high and stable sea ice cover, the

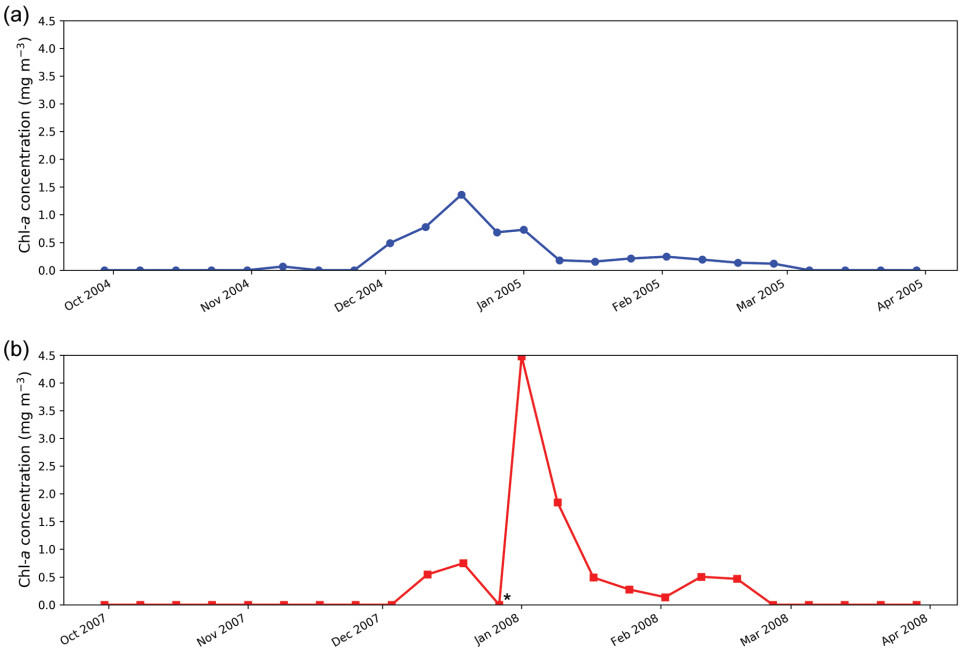

Figure 6. Chl-*a* concentrations in the periods **a** 01 November 2004 – 15 March 2005 and **b** 01 November 2007 – 15 March 2008.

trap at 360 m collected very few materials, whereas abundant material was detected near the seafloor. We interpreted these results with the possible presence of resuspension and/or lateral advection processes occurring during cold periods. As previously mentioned, in 2005 Iceberg B-15 was present near Mooring A area (less than 20 km distant). The satellite images in 2005 showed an anomalous, wide stripe of thick sea ice present between the iceberg and the shoreline in the austral summer (Fig. 7a), whereas in 2008, a more typical ice-free area was present (Fig. 7b). We hypothesise that this iceberg provided a great amount of both lithogenic and organic materials, according to previous studies that documented an increase in the export fluxes near icebergs (Shaw et al. 2011; Sherman et al. 2011; Smith et al. 2011). In addition, the material increase in the bottom sediment trap may have also been due to lateral advection induced by the modified oceanographic pattern in this area. In fact, Iceberg B-15A influenced the oceanographic pattern by blocking the inflow of Antarctic Surface Water (AASW) (Robinson and Williams 2012).

The maximum mass flux registered in 2008, from both the top and bottom traps, was detected during January – March, when the sea ice concentration begun to rise. During winter, both traps collected about the same amount of material, which may suggest that the collected material could have originated from gravitational sinking along the water column and no or very low post-depositional processes were active. It is also worth noting the presence of significant oscillations in the sea ice cover (minimum and maximum values of 56.8% and 97.2%, respectively) in 2005 and the higher concentration (minimum and maximum values of 66.8% and 100.0%, respectively) with less intense changes in 2008. This may be explained with the recent mass balance of the ice sheets observations by Zwally et al. (2015) who reported that, during the years 2003 – 2008, the Antarctic mass gain from snow accumulation exceeded the mass loss from ice discharge.

The interpretation of the BioSi/OC and OC/N molar ratios may help in understanding the processes which occurred in the sampling years, particularly at the bottom trap. Generally, SiO_2/OC values were higher at the bottom than at the top trap in both

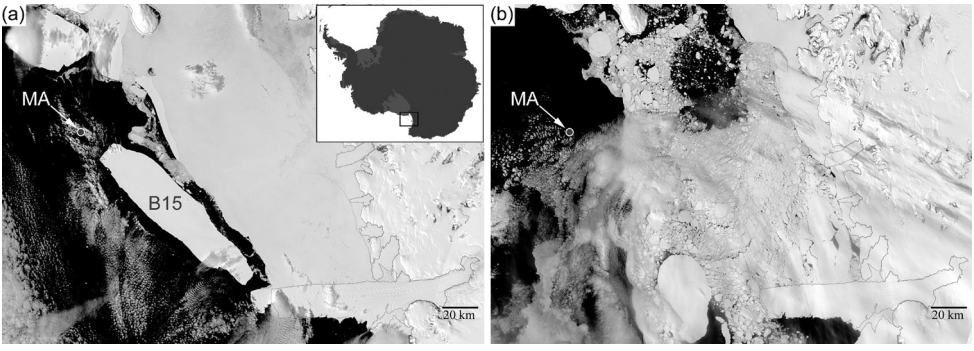

Figure 7. True-colour imagery of the area near Mooring A on 02 January 2005 **a** and 02 January 2008 **b** The location of Iceberg B-15 is also shown (**a**).

years. This indicated the decoupling of Si and C cycles during both years, probably due to a different preservation of biogenic silica compared to organic carbon along the water column. Consequently, the hypothesis of rapid sinking phenomena during 2008 is weakened. On the other hand, the average of the C/N molar ratio was about the same at both depths and in 2005 (with an average of 7.0 at the top and 7.2 at the bottom) and in 2008 (7.5 and 7.6, respectively, at the top and bottom). As introduced in the Materials and Methods section, diatoms are the dominant primary producers in the Ross sea area, and the observed C/N ratios suggest that diatom assemblages varied more than carbonates in the later years. This ratio is slightly lower than the Redfield ratio (an empirical stoichiometric ratio calculated for carbon, nitrogen and phosphorous for phytoplankton and deep-ocean sediments) estimated at about 8 for Antarctic diatoms (DeMaster et al. 1996). In fact, the C/N molar ratio commonly increases along the water column, because nitrogen degrades more quickly than carbon. In addition, according to Collier et al. (2000), if the area is subjected to resuspension processes, the material from the seafloor (with high carbon and low nitrogen contents) may drive this ratio even higher. Our BioSi/OC and OC/N data showed almost constant values at both depths. This might suggests that either: i) the resuspension processes were negligible during both years and the collection of particles in the seafloor trap was then driven only by lateral advection processes or ii) resuspension processes occurred (raising BioSi content) together with an increase in both carbon and nitrogen due to the exports from Iceberg B-15A (2005) and high productivity and preservation along the water column (2008).

Our data document that mass flux peaks occurred in mid-February and in mid-March during 2005, whereas only one peak was detectable during 2008. However, in the Ross Sea, the peak of primary productivity is usually in December or early January (Nelson et al. 1996; Smith et al. 2000; Arrigo and van Dijken 2004) as evidenced by the chl-*a* concentrations, suggesting a time lag of about two - three months between the productivity peak and the higher mass fluxes measured. This observation has already been reported by studies performed in this area (Dunbar et al. 1998; Collier et al. 2000; Langone et al. 2003), but it does not have a unique explanation at the moment. As hypothesised in previous studies, the main driving force(s) responsible for the observed time lag could be: i) the time lag between the growth of phytoplankton and zooplankton community development (Dunbar et al. 1998; Smith and Dunbar 1998; Boyd and Newton 1999); ii) a late diatom bloom associated with winds or a pulse of iron (Collier et al. 2000; Peloquin and Smith 2007), and iii) small or low density aggregates or particles that sink at a slower rate in the water column (Smith and Dunbar 1998; Becquevort and Smith 2001). However, the available data do not seem to support unequivocally one or more of these hypotheses. For example, the chl-*a* concentrations in 2008 seemed to support hypothesis ii), because they showed the presence of some productivity in late summer (between February and March).

It is well known that iron plays a fundamental role in the development of the phytoplankton community, as it is one of the micro-nutrients needed for the synthesis of chl-*a*. In the Ross Sea, this element is mainly supplied by two sources (Collier et al. 2000): dust released into the ocean, with different origins (melting of sea ice,

transported by winds from local and/or distant sources) and resuspension processes due to currents (e.g., Modified Circumpolar DeepWater current, MCDW). However, very recent studies of Winton et al. (2016) suggest that only dust as a source is not enough to regulate phytoplankton growth in the SW Ross Sea. As reported by a recent work (Castagno et al. 2017), also the intrusion of CDW could be pointed as one of the drivers for the benthic development, in addition to being a source of heat and salt. According to the data available, we may suggest that, in the sampling years, the CDW intrusion did not occur because the temperature values were constantly below -1.0 °C.

In 2005, the delay in vertical mass flux that followed the peak of production was likely related to zooplankton grazing, since this area was dominated by diatoms that are important component of the diet of many zooplankters, while *Phaeocystis antarctica* is less grazed (Smith et al. 2003). Indeed, we observed abundant faecal pellets during the period of high flux of particulate material. In 2008, the shift of the mass flux peak of about a month later may be explained by a late reduction in sea ice cover. Consequently, the major algal growing period was also delayed.

In 2008, the extent of the area with high chl-*a* concentration was very limited, probably due to the presence of the sea ice. Chl-*a* concentrations were high only during 20 days in January and the algal bloom did not have a wide extension also in the neighbouring areas. Additionally, in comparison with 2005, the extension and concentration of chl-*a* were significant by the end of November until the first week of January, when the extension remained the same, even if the concentration was much lower. It can therefore be inferred that the phytoplankton bloom in 2005 started at the end of November and that it lasted more than a month, while in 2008 its extension was greatly reduced, although the time length of the bloom was about the same when considering the whole area.

The area of the Ross Sea considered in the present study has a substantial component of diatoms and Nelson et al. (1996) calculated an average SiO_2/OC production ratio of about 0.60–0.65 in the ice edge diatom bloom. The 2005 SiO_2/OC values measured at 360 m were about twice this production ratio, while in 2008, the average ratio was only 0.4. This could be due, in addition to low productivity, to a very limited diatom bloom and to the predominance of non-siliceous algae.

Quantification of particles fluxes

The availability of particle fluxes from two levels of sampling during 2005 and 2008 allowed us to carry out an approximated mass balance to investigate the processes along the water column (Figures 8 and 9). As previously discussed, the fluxes of 2005 could have been influenced by the contribution of different processes (resuspension, lateral advection, presence of Iceberg B-15A). Indeed, we obtained a lithogenic contribution from these processes of 38.7 g m^{-2} yr^{-1}, which is 2.4 times the vertical flux. To evaluate the expected values of biogenic silica and organic carbon fluxes at the bottom, we consider an external input 2.4 times the top flux. This means an input of 36.28 g Bio-Si m^{-2} yr^{-1} and 5.56 g OC m^{-2} yr^{-1}, respectively. Balancing the BioSi and the OC fluxes, we

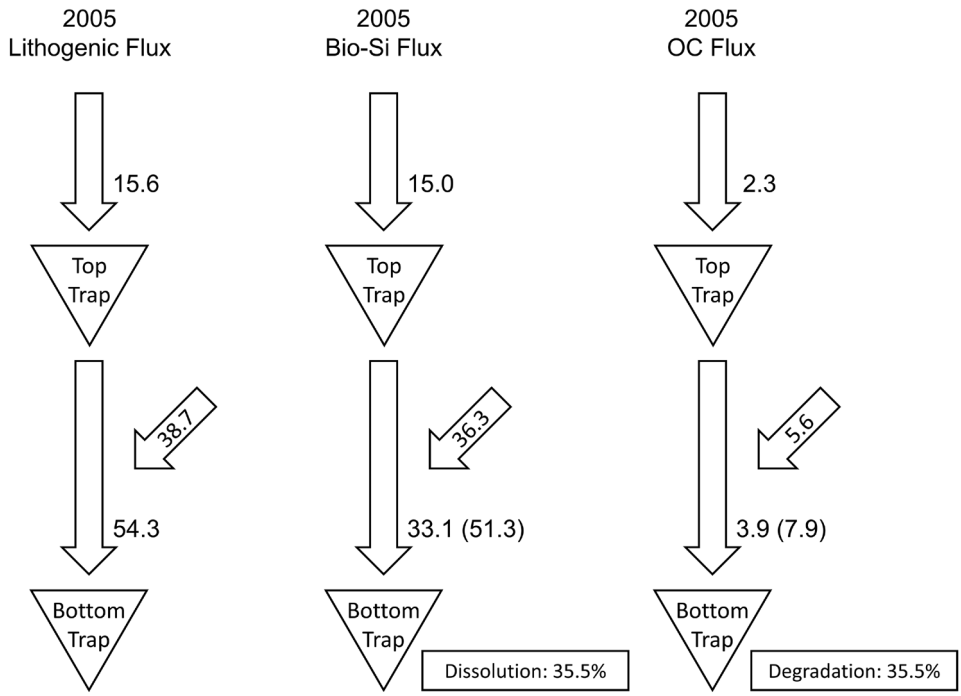

Figure 8. Mass balance and processes of lateral advection in 2005. The numbers near the vertical arrows represent lithogenic, biogenic silica and organic carbon annual integrated fluxes (g m^{-2} yr^{-1}) at the top and bottom trap during 2005. The values near the sideways arrows represent the amount from external inputs and numbers in brackets are the expected fluxes.

get an expected value of silica of 51.28 g m^{-2} yr^{-1} against a measured value of 33.1 g m^{-2} yr^{-1}, which would denote there was a dissolution of about 36% of the biogenic silica in transit from the upper to the bottom trap (DeMaster et al. 1992; Nelson et al. 1996; Collier et al. 2000; Langone et al. 2000; Greenwood et al. 2001). Considering organic carbon, the expected value is 7.86 g m^{-2} yr^{-1} against a measured value of 3.9 g m^{-2} yr^{-1} and thus a degradation of about 50% (Figure 8). These results underline the decoupling of carbon and silica cycles with a higher rate of carbon degradation compared to silica dissolution in this area in line with the results provided by literature (Nelson et al. 1996; Dunbar et al. 1998).

Since the time series of samples was not complete in 2005, the balance was recalculated considering only the periods in which samples at the top and at the bottom levels were both available. The results showed dissolution of biogenic silica of 32% and a degradation of organic carbon of 67%, thus confirming, also in this case, the different cycling rates of OC and BioSi.

In 2008, as previously mentioned, fluxes into the bottom trap were lower than those at the upper level. Considering the measurement errors, this trend was maintained for about 293 days, during periods of high ice coverage. During the remaining 75 days of the year, when the sea was free from ice, other processes, i.e., focusing (ac-

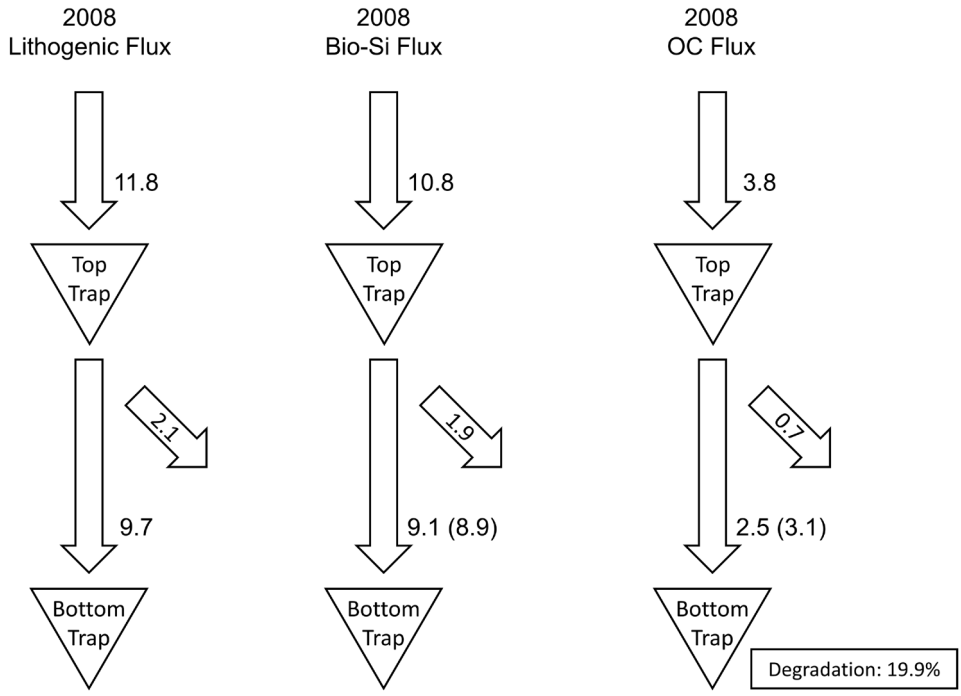

Figure 9. Mass balance and processes of lateral advection in 2008. The numbers near the vertical arrows represent lithogenic, biogenic silica and organic carbon annual integrated fluxes (g m^{-2} yr^{-1}) at the top and bottom trap during 2008. The values near the sideways arrows represent the removed amount and numbers in brackets are the expected fluxes.

cumulation of material), may have taken place. In this case, the balance showed no or negligible dissolution for the silica; in fact, the expected value was 0.2 g m^{-2} yr^{-1} less than the actual value and these two values could be considered equal, taking into account the measurement errors. Conversely, organic carbon had an expected value of 3.12 g m^{-2} yr^{-1} with an actual value of 2.5 g m^{-2} yr^{-1}, meaning that OC degradation was 19.9% (Fig. 9). Additionally, this value was much lower than the value estimated for 2005.

At the top level, particle fluxes during 2005 and 2008 did not differ much. In 2005, they were slightly higher, likely due to a higher primary productivity, as indicated from the chl-*a* values. In contrast, the comparison of the bottom levels showed that the particle fluxes values in 2005 were significantly higher than in 2008.

In 2008, external inputs from lateral advection and/or resuspension were probably negligible, as suggested by the balance of biogenic silica and organic carbon fluxes. This may be due to the low primary productivity that characterised the entire area of the Ross Sea where low chl-*a* concentrations scattered in small areas were observed. During 2008, the ice concentration was greater than in 2005 and the Ross Sea was never completely ice-free. The greater amount of sea ice that surrounded the Ross Sea during summer certainly influenced surface and bottom waters, causing reduced hydrodynamics.

Conclusions

The analysis and correlation of different variables, i.e. particle fluxes, sea ice cover and chl-*a* concentrations, collected from Mooring A, located in the Ross Sea during the years 2005 and 2008, allowed us to provide, for the first time along an extended period of time, *in situ* data on biogeochemical processes in the Ross Sea, which are still poorly understood.

The peaks of mass and biogenic fluxes were recorded in February and March, delayed by one/two months from the algal blooms that usually occur in December/January, related with the processes of ice formation and melting. This can be due to the interaction of different factors, such as the time lag between the growth of phytoplankton and zooplankton community development, the late diatom bloom associated with winds or a pulse of iron, and small or low density aggregates or particles that sink at a slower rate in the water column. The highest percentages of biogenic silica were detected from February to April in both investigated years (2005 and 2008). The mass balance between the top and bottom traps was related to different processes, such as resuspension and/or lateral advection. Also, the presence of Iceberg B-15A could have influenced the amount of sinking material.

Our results highlight the presence of high interannual variability in the biogeochemical processes in the Ross Sea and support the importance of time-series observations. Long-term data sets as in the present research can provide, indeed, sound grounds to identify the type and role of the driving forces that may explain the observed variability.

As a final remark, this study underlines the high importance of interdisciplinary long-term surveys, such as those proposed by the LTER network, in obtaining representative time-series of physical, geochemical and biological data to investigate ecosystem dynamics. In fact, since the climate change and anthropic pressure are expected to intensify, long-term research constitutes a baseline reference for the future management and conservation of the ocean and other ecosystems.

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Sea Ice Concentration Data are from EOS Distributed Active Archive Center (DAAC) at the National Snow and Ice Data Center, University of Colorado, Boulder, Colorado (http://nsidc.org/data/).

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This is contribution number 1995 of CNR-ISMAR of Bologna.

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