



Source composition and seasonal variation of particulate trace element fluxes in Prydz Bay, East Antarctica



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HIGHLIGHTS

- Mineral debris derived from Antarctic continent account for the particulate fluxes of Al, Fe, Mn, Pb and Co.
- The fluxes of Cu, Zn and Cd are dominated by marine biogenic sources.
- The seasonality of Cu, Zn and Cd is related to the ice coverage and biological production.
- The seasonality of crustal elements is most likely controlled by ice melting and freezing process, and partly influenced by scavenging and uptake.
- The coupling between TE and C_{org} are regulated by source composition and non-lithogenic input from atmospheric or upwelling.

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ABSTRACT

Particulate fluxes of trace elements (Al, Fe, Mn, Cu, Pb, Zn, Cd and Co) in the polynya area of Prydz Bay were measured using time series sediment trap lasting from December 16th 2010 to December 16th 2011. The comparison of annual fluxes from different regions, the seasonality and sources of trace element, and their association with organic matters were investigated. The fluxes of Cu, Zn and Cd in the polynya area of Prydz Bay are dominated by marine biogenic sources. Their similar seasonality with the export of biological materials (biogenic silica, organic carbon, and calcite carbonate) is strongly related to the ice coverage and biological production. Mineral debris derived from Antarctic continent is suggested to account for the particulate fluxes of Al, Fe, Mn, Pb and Co in the polynya. Their seasonal variations are most likely controlled by ice melting and freezing process. Furthermore, their fluxes are also influenced by scavenging onto biogenic material for Pb and uptake by phytoplankton for Co. The excess fluxes of Cu, Zn and Cd have good relationship with organic carbon export. The coupling patterns are mainly regulated by source composition of trace elements and non-lithogenic input from atmospheric deposition or upwelling, and partly influenced by biological uptake process.

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1. Introduction

Marine biological pump plays an important role in fixing and burying of atmospheric carbon dioxide. Once this carbon is fixed by planktonic phototrophs in the euphotic zone, it continues to export to deep oceans in the form of sinking particles. The application of sediment traps makes continuous and long-term collection of marine sinking particles achievable. Subsequently estimates of primary production and organic carbon sinking out of the euphotic zone are possible even in remote Polar Regions (Fischer et al., 1988; Wefer et al., 1988; Honjo, 1990; Hebbeln and Wefer, 1991; Wefer

and Fischer, 1991; Smith and Dunbar, 1998; Honjo et al., 2000; Nelson et al., 2002). The vertical transport of particulates is associated with a sequence of biogeochemical processes (e.g. decomposition, dissolution and adsorption) of chemical compounds such as trace elements besides organic carbon. Thus particulate trace elements can provide important information about surface productivity, atmospheric deposition, ocean circulation and particle cycling processes (Dymond and Collier, 1996; Henderson, 2002). Since the first report of trace element fluxes determined by sediment trap in 1980 (Brewer et al., 1980) considerable studies have been carried out. Most of the investigations are conducted in the North Atlantic aiming at elucidating the sources (Brewer et al., 1980; Grousset et al., 1995; Huang and Conte, 2009; Kremling and Streu, 1993), seasonality and its driving (Jickells et al., 1984; Kuss and Kremling, 1999; Kuss et al., 2010; Pohl et al., 2004), and

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the association with major biogenic phases (Kuss and Kremling, 1999; Kumar et al., 1996) of particulate trace elements. Furthermore, the preservation of proxy signal is also evaluated to test the utility of trace metal as a proxy of export production (Kumar et al., 1996; Sun et al., 2013a). Few studies have reported particulate trace elements from high latitude regions (Schüßler et al., 1997; Sun et al., 2013a), where the physical and biological conditions differ widely from other ocean regions. Polynyas are the typical meso-scale phenomenon in the Polar Regions, which remain either partially or totally ice free at times and under climatological conditions generally associated with full ice coverage. They are of interest for a number of reasons encompassing both biology and physics (Smith et al., 1990). Here we present the export fluxes of trace elements in the polynya area of East Antarctica. We aim to identify the sources of these particulate trace elements and to discuss the possibility of utilizing trace element fluxes as the tracers of marine production in high latitude ocean regions.

2. Material and methods

2.1. Study area and sampling

Prydz Bay is the largest shelf sea on the east margin of Antarctica (Harris et al., 1998). The inner continental shelf is dominated by Amery Depression, which is bordered by two shallow banks (<200 m): Fram Bank to the north-west and Four Ladies Bank to the north-east, forming a spatial barrier to water exchange with the outer oceanic water (Smith and Tréguer, 1994). Surface circulation is characterized by a closed cyclonic gyre centered on the mid to western part of the bay (Smith et al., 1984; Vaz and Lennon, 1996) (Fig. 1). It is associated with a narrow coastal current along Amery Ice Shelf (Vaz and Lennon, 1996) (Fig. 1). The sampling stations of mooring (M1, 68.48°S; 76.57°E) and surface sediments (P4-10, P4-11 and P4-12) are located at the seasonal polynya area on the continental shelf of Prydz Bay (Fig. 1). As other high latitude regions, the annual opening of the polynya provides a high localized biological productivity which leads to considerable particle fluxes out of the surface waters (Schüßler et al., 1997).

The sediment trap was deployed from December 16th 2010 to December 16th 2011 at 460 m depth with a water depth of 620 m. It is a 20-cup time series trap (Mark78H-21) consisting of large diameter cones with baffled, 0.5 m² collection surface areas. The trap cups were pre-poisoned with saturated mercury bi-chloride solution in filtered in-situ seawater to prevent biodegradation of

the trapped materials. The cups collected particles over time periods ranging from 10 days during spring/summer to a maximum of 34 days in winter time. There are 19 samples around the year. According to Pilskaln et al. (2004), the collected samples were sieved through a 1 mm Nylon mesh to remove swimmers. Then the <1 mm particulate materials were filtered onto pre-weighed 0.45 µm pore size polycarbonate filters by vacuum filtration equipment and were flushed with Milli-Q water during filtration to eliminate remaining sea salt (Wefer and Fischer, 1991; Pohl et al., 2004; Stanley et al., 2004). Particles together with filters were freeze dried, weighed and then the dried particles were removed from the filters using a stainless scraper for geochemistry analysis.

Three surface sediment samples were collected in the vicinity of M1 (Fig. 1) using a stainless steel grab. Immediately after collection, sediment samples were placed into plastic bags and stored at −20 °C, and then freeze dried in the laboratory before chemical analysis.

2.2. Analytical procedures

Trace elements were determined by ICP-MS (Agilent 7000) after microwave-assisted digestion (CEM Mars) according to the USEPA Method 3052. In brief, about 0.2 g dried samples were digested with a HNO₃–HF mixture (7:3 v/v), and then heated in the microwave. Because of the limited amount of collected materials during winter time, only 0.02–0.1 g dried samples were used for digestion. Reference material (MESS-3, Canada) was used to test the analytical accuracy and RSD to indicate the repeatability of the data. The recovery ranged from 99% to 110% and the RSDs were generally <8.9%. The content of organic carbon (C_{org}) was determined by Element Analyzer (Elementar, Germany). In brief, about 0.05 g dried sample was treated with dilute HCl (1:3 v/v) and rinsed with Milli-Q water. This procedure was carried out three times for carbonate removal, and then dried overnight at 60 °C before analysis by Element Analyzer. Biogenic silica (Si_{bio}) content was determined using a sodium carbonate leaching analysis procedure (Mortlock and Frölich, 1989). The RSDs were generally <6% for C_{org} and <8.5% for Si_{bio}.

2.3. Calculations and statistical analysis

Total mass flux (TMF) was determined by dividing the dry weight (mg) of the particles by the collection surface area of the trap cup (0.5 m²) and collection intervals (d). The daily flux of each element was calculated by multiplying the content of the component in the dried samples by TMF. The annual fluxes were the sum of all the daily flux multiplied by collection intervals.

Basing upon the average crustal composition (Taylor, 1964), the proportion of the lithogenic input of trace metal (TE_{lith}) can be estimated as follows:

$$TE_{lith} = AI_{sample} \times (TE/AI)_{crust} \quad (1)$$

The excess trace metal (TE_{ex}) (non-lithogenic) is then obtained as follows:

$$TE_{ex} = TE_{total} - TE_{lith} \quad (2)$$

The enrichment factor is calculated as follows:

$$EF = (TE/AI)_{sample} / (TE/AI)_{crust} \quad (3)$$

The accumulation rate is calculated from the trace metal content in the surface sediment as following:

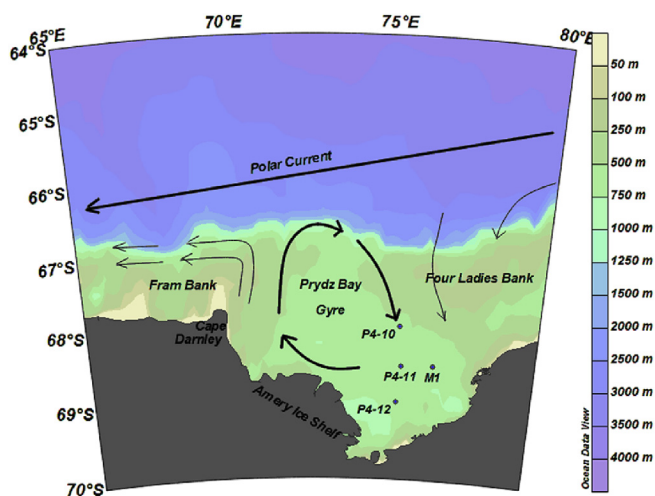


Fig. 1. Study area and sampling stations.

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