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Seasonality of particle-associated trace element fluxes in the deep northeast Atlantic Ocean

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ABSTRACT

In the framework of the German contribution to the Joint Global Ocean Flux Study (JGOFS), deep-water fluxes of particle-associated trace elements were measured in the northeast Atlantic Ocean. The sinking particles were collected almost continuously from 1992 to 1996 at three time-series stations, L1 (33°N/22°W), L2 (47°N/20°W), and L3 (54°N/21°W), using sediment traps. The focus of the present study is the temporal variability of the particle-associated elemental fluxes of Al, Ca, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, Ti, V, and Zn at a depth of 2000 m.

A clear seasonality of the fluxes that persisted for several years was documented for the southernmost station (L1) at stable oligotrophic conditions in the area of the North Atlantic Subtropical Gyre East (NASTE). At L2 and L3, an episodic nature of the elemental fluxes was determined. Mesoscale eddies are known to frequently cause temporal and spatial variability in the flux of biogenic components in that area. These events modified the simple seasonal pattern controlled by the annual cycle at L2, in the North Atlantic Drift Region (NADR), and at L3, which was influenced by the Atlantic Arctic province (ARCT). All stations were characterized by an additional episodic lithogenic atmospheric supply reaching the deep sea.

The integrated annual fluxes during the multi-year study revealed similar flux magnitudes for lithogenic elements (Al, Co, Fe, Ti, and V) at L2 and L3 and roughly twofold fluxes at L1. Biogenic elements (Cd, P, and Zn) showed the opposite trend, i.e., two to fourfold higher values at L2 and L3 than at L1. For Mn, Ni, and Cu, the spatial differences were smaller, perhaps because of the intermediate behavior, between lithogenic and biogenic, of these elements. Similarly, among the three study sites, there were no noticeable differences in the total annual flux of Pb.

The respective lithogenic fractions of the deep-sea fluxes of Cd, Co, Cu, Mn, Ni, V, and Zn were subtracted based on the amount of Al, with the average composition of the continental crust as reference. This procedure allowed estimation of the labile trace element fraction (TE_{exc}) of the particles, i.e., TE taken up or scavenged during particle production and sedimentation. The ratios of TE_{exc}/P clearly demonstrated an enrichment of TE over labile P from biogenic surface material to the deep sea for Zn (factor 4–6), Mn (12–27), Ni (3–5), and Cu (9–25); an intermediate status for Co (0.5–2.2); and depletion for Cd vs. P (0.2–0.4). Surprisingly, the recycling behavior of excess Co was found to be similar to that of P. Hence, Co_{exc} behaved like a biogenic element; this is in contrast to total Co, which is dominated by the refractory lithogenic fraction.

Moreover, it is argued that these excess elemental fluxes caused a loss of the dissolved elements in upper waters, since their transport reaches the deep-sea waters at 2000 m, a depth far below of deep-winter mixing and upwelling. The annual amount of excess TE exported from surface waters was estimated to be 1.3×10^9 mol Zn y^{-1}, 4.4×10^9 mol Mn y^{-1}, 4.9×10^8 mol Ni y^{-1}, 2.2×10^7 mol Cd y^{-1}, 7.4×10^8 mol Cu y^{-1}, and 2.7×10^7 mol Co y^{-1} for the whole North Atlantic Ocean. Important primary sources that could replenish these losses are the aeolian and fluvial supply processes.

1. Introduction

Understanding on a quantitative basis the transport link from the atmosphere, the upper ocean, and the ocean's interior to the deep seafloor is not trivial (Honjo, 1996) and its exploration requires enormous logistical and analytical efforts. In 1980, the first direct measurement of the seasonality of particle flux and of the flux of organic carbon in the deep sea was published (Deuser and Ross, 1980). In the same year, the first major, minor, and trace elemental fluxes determined by sediment traps were reported as well (Brewer et al., 1980). However, since then, only a few studies

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have analyzed the flux of particle-associated trace elements in the deep ocean (Jickells et al., 1984; Kremling and Streu, 1993; Kuss and Kremling, 1999a; Lamborg et al., 2008). Nonetheless, such studies are urgently needed, in order to understand the role of trace elements within the oceanic cycles of matter fluxes. Recently, a new large international study was initiated by the GEOTRACES Science Plan. Its aim is to expand what is known about the marine biogeochemical cycles of trace elements (TE) and their isotopes (SCOR, 2006). This highlights the current importance of marine TE studies.

Within the framework of the German contribution to the Joint Global Ocean Flux Study, "Carbon-associated trace element fluxes in the deep northeast Atlantic," several fundamental conclusions have been deduced from the data set covering the years 1992/1993 (Kuss and Kremling, 1999a). This data set in combination with other particle flux studies (Jickells et al., 1984; Jickells et al., 1990; Kremling and Streu, 1993) comprises the interpretation of spatial gradients in the North Atlantic, from the west to the east and from the north to the south. Also, a detailed discussion of the compositional changes of TE associated with the particles during sedimentation was provided based on data obtained from sediment traps located at different depths and a comparison of these data to those describing surface particulate material and bottom sediments (Kuss and Kremling, 1999a). In the present study, subsequent to publications in which the major constituent fluxes (Waniek et al., 2005b) were evaluated and the results integrated with those of other particle flux studies (Antia et al., 2001), we focus on the particle-associated TE fluxes in the deep sea during the years 1992–1996 in three different provinces of the eastern North Atlantic. The seasonality and the interannual variability of these fluxes at a depth of 2000 m were analyzed.

In addition to the export of organic carbon to the deep sea via "the biological carbon pump" (Deuser and Ross, 1980; Lampitt and Antia, 1997), the associated fluxes of other elements are essential as well. Mineral phases contribute important ballasting material, which causes suspended particles to sink (Honjo, 1996; Klaas and Archer, 2002). Moreover, TE constitutes important micronutrients that are prerequisites for biological carbon fixation. A famous and well-studied example is iron (e.g., Martin and Fitzwater, 1988; Martin et al., 1994). Since, in the oxygenated surface water the solubility of iron is very low, an important pathway of iron supply is via the atmosphere (Jickells et al., 2005). Similarly, the export of other TE to depth is of great interest. These losses have to be replenished by supply mechanisms in the elemental cycle, as discussed herein.

Marine particles consist of organic matter and lithogenic or biogenic mineral phases (Brewer et al., 1980; Deuser and Ross, 1980; Honjo et al., 1982). Each major constituent has a typical composition of major and trace elements (Turekian and Wedepohl, 1961; Taylor, 1964; Sherrell and Boyle, 1992; Kuss and Kremling, 1999b). The lithogenic fraction is often well represented by the average crustal composition whereas the biogenic fraction is characterized by the so-called Redfield ratio (Redfield et al., 1963). Other mineral phases comprise opal or carbonate shells consisting of relatively pure silicate or calcium carbonate. Hence, the major and trace element composition of a single particle or an ensemble of particles can be formally separated according to these major carriers. This allows elemental ratios to be well estimated, even in aggregates of diverse composition. Here, we have used this approach to calculate the non-lithogenic (excess) elemental ratios of marine particles collected in the northeast Atlantic Ocean at a depth of 2000 m.

In summary, the aims of this study were: (1) to determine the seasonality and interannual variability of the elemental fluxes at 2000 m depth for each element based on the sediment trap data from 1992 to 1996; (2) to compare the mean annual fluxes of TE in three biogeochemical provinces; (3) to interpret these mean annual fluxes with respect to atmospheric TE deposition; (4) to elucidate the change in the inter-elemental ratios of the labile particulate fraction between surface waters and a depth of 2000 m; (5) to balance the excess TE export flux to the deep ocean with supply sources in terms of an assumed "steady state" of the TE biogeochemical cycle; and, finally, (6) to determine the amount of non-lithogenic (excess) TE exported to the deep ocean by using the algorithm of Antia et al. (2001) with the primary production values of the North Atlantic and the element to carbon ratios derived in this study.

1.1. Hydrography of the study sites

The study sites L1, L2, and L3 (Fig. 1) are located in different biogeochemical provinces of the northeast Atlantic and the prevailing physical, chemical, and biological conditions determine the timing and the amount of the particle flux (Waniek et al., 2005b).

L1: The L1 mooring at 33°N, 22°W is located 240 nm west of Madeira, in the eastern part of the North Atlantic Subtropical (NASTE) gyre province (Longhurst, 1998), where the Gulf Stream

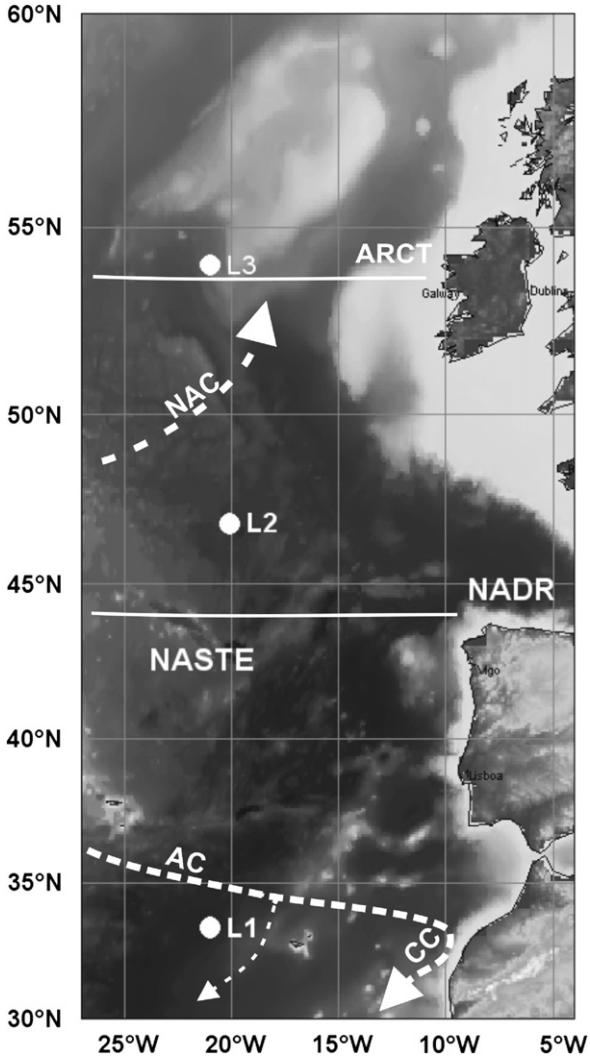

Fig. 1. Map showing the location of the deep-sea moorings of sediment traps at stations L1, L2, and L3 in the Northeast Atlantic during the German contribution to JGOFS (see also Table 1), in addition, the biogeochemical provinces ARCT, NADR, and NASTE, and the currents NAC, AC, and CC are indicated (for details see text).