



Synoptic transects on the distribution of trace elements (Hg, Pb, Cd, Cu, Ni, Zn, Co, Mn, Fe, and Al) in surface waters of the Northern- and Southern East Atlantic

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ABSTRACT

Surface seawater samples were taken in the framework of the GEOTRACES program on "POLARSTERN" expedition ANT XXIII/1 in the Eastern Atlantic in 2005 to study the distribution of the trace elements Hg (mercury), Pb (lead), Cd (cadmium), Cu (copper), Ni (nickel), Zn (zinc), Co (cobalt), Mn (manganese), Fe (iron), and Al (aluminium). With the exception of Hg, results were compared to earlier datasets from 1989 to 1990. The particulate fraction averaged over the transect was calculated to be 49% for Cd, 23% for Mn and 50% for Fe indicating a release of these TEI's (trace elements and their isotopes) from a leachable SPM fraction in the stored and acidified samples.

Total Pb concentrations ranged between 5 and 20 pmol kg⁻¹ in 2005 with highest values in the ITCZ (intertropical convergence zone). In 1989 Pb concentrations were twice as high in the region of the ITCZ, while by a factor of 10–15 higher values were obtained in the North Atlantic.

Total Cd and Co are dominated, by different seasonal upwelling regimes (Equatorial upwelling, Guinea Dome, Angola Dome).

Total Cu, Ni, Fe, Mn and Al show nearly identical concentrations in 1990 and 2005. For total manganese and aluminium strong maxima (3–4 nmol kg⁻¹ and 55 nmol kg⁻¹ respectively) are observed between 23°N and 0°, while the Fe maximum (6–9 nmol kg⁻¹) is located at 7°N. Total Hg concentrations ranged between 0.5 and 4.5 pmol kg⁻¹.

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1. Introduction

The ocean is mainly impacted by the supply of anthropogenic and natural TEI's from atmospheric- and riverine input. Entering the surface waters, the transport of TEI's is closely linked to the seasonal variation of the biological production and the composition of suspended particulate matter (SPM) (Buesseler et al., 2000; Kuss and Kremling, 1999a; 1999b; Pohl et al., 2004).

Particle reactive metals such as Pb and Hg and trace metals with nutrient-like behaviour, e.g. Cd, are mostly removed from surface waters by adsorption on, or incorporation into, particles and then transported down through the water column. These metals can accumulate at horizontal interfaces/boundaries such as the pycnocline, the OMZ (oxygen minimum zone) or the redox boundary because of slow sinking rates.

However, particle fluxes are a key mechanism in regulating the ocean carbon cycle (Buesseler et al., 2007a,b) and additionally they

have a cleaning effect on the ocean, by removing elements like Pb or Hg which might otherwise build up to toxic levels in the water column.

The biological important, and therefore climate relevant, TEI's Fe, Co and Mn are essential micronutrients for ocean fertilisation (Boyd et al., 2000; Boye and van den Berg, 2000; Boyd et al., 2007). They therefore help regulate the uptake of atmospheric CO₂. The low solubility of these trace elements under oxic conditions and their high affinity to particulate phases like clay, results in a rapid vertical transport through the water column resulting in residence times of a few weeks in the surface layer (Baker and Croot, 2010; Bruland et al., 1994).

It is also assumed, that the removal of Fe, Mn, Co, and Zn from the euphotic zone is a recurrent process, induced by primary producers (Morel et al., 2004). This removal is closely connected to solubility and sinking fluxes of these elements within the geochemical cycles of C, N, S, and O.

In the framework of the JGOFS program (Joint Global Ocean Flux Study) Kuss and Kremling (1999a,b) carried out investigations on particle associated TEIs in the north-east Atlantic, showing significant variability of particulate TEI-fluxes with season and depth (1000 m and 4000 m) for the biogenic elements (Cd, Ni, Zn, and P), while the vertical transport of Co, Fe, and Mn, was strongly correlated with clay (Al).

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Aerosol dust is the major source of several key trace elements (Fe, Al, Mn and Ti) to the surface open ocean and their ultimate concentration in surface waters is governed by 3 key factors: (i) supply rate, (ii) loss terms – scavenging, particle sinking and (iii) the solubility of the element under ambient seawater conditions. For the elements present in aerosol dust in high concentrations the third term is perhaps the most crucial as it also impacts on the loss terms through particle formation causing short residence times for elements under the Saharan dust plume (Chavagnac et al., 2007; Croot et al., 2004; Jickells et al., 2005). Currently however there are few field data on the chemistry controlling solubilities of these elements. In the case of Fe, organic complexation via DOM (dissolved organic matter) is an important process by which iron solubility is enhanced over purely inorganic conditions (Liu and Millero, 1999, 2002; Millero, 1998; Rijkenberg et al., 2008). The situation is different for Mn, where photochemical processes make the more soluble Mn^{2+} species (Sunda and Huntsman, 1988, 1990, 1994) dominate over the more thermodynamically favoured higher redox species (Mn(III) and Mn(IV)) in surface seawater. At present these are central themes in the biogeochemistry of oceans in the GEOTRACES programme which has two primary objectives:

- (i) to determine global distributions of TEIs including their concentration, chemical speciation and physical form in the ocean; and
- (ii) to evaluate the oceanic sources, sinks and internal cycling of these TEIs and thereby characterize more completely their biogeochemical cycles.

To investigate some aspects of the above objectives, the Atlantic transect of “RV POLARSTERN” (ANT XXIII/1) served as a pilot study for such an integrated approach, with coordinated joint sampling techniques for surface water being integral to this.

During this expedition we passed through water masses characterized by different inputs e.g. the upwelling area of West Africa, dust inputs off Saharan and Namibian deserts by north-eastern and south-eastern trade winds and the low atmospheric inputs in the South Atlantic gyre. The analysis of filtered and unfiltered samples was performed to get information about the content of trace metals associated to the particulate fraction on the one hand. Otherwise it was done to control the contamination risk during filtration and to aid the development of further sampling techniques. We also took the chance for an intercomparison exercise of Fe determination techniques between three laboratories.

Furthermore this expedition also provided a unique opportunity to repeat parts of an earlier investigation, performed in 1989/1990, with different sampling equipment but with the same determination methods and with the same analysts. Those laboratory preconditions are a valuable background to monitor and/or to identify changes in natural and/or anthropogenic sources by comparing the two datasets within a time period of 15 years (Pohl, 1992; Pohl et al., 1993).

2. Material and methods

2.1. Sampling

Surface water samples for the determination of Hg, Pb, Cd, Cu, Ni, Zn, Co, Mn, Fe and Al were collected in high spatial resolution with the “IFM-GEOMAR” towed fish on cruise ANT XXIII-1 with RV POLARSTERN from Vigo to Cape Town between 13.10. and 17. 11. 2005 (Fig. 1).

A fish was deployed, using a winch on the working deck some, 3–4 m from the side of the ship at a depth of 2–3 m. From the fish, samples were pumped to the laboratory, via a totally enclosed system with suction provided by Teflon diaphragm pumps (Almatec, Germany). The seawater was pumped through this enclosed system to several 20 or 50 L carboys for collection as part of the coordinated GEOTRACES sampling program carried out during ANT XXIII/1.



Fig. 1. Area under investigation, stations, sampling equipment.

Filtered samples were obtained by drawing a sample from the carboys through a $0.2\ \mu\text{m}$ cartridge filter (Sartobran PH) using a second Teflon diaphragm pump. Sample bottles were then filled under laminar flow clean air in a Class 100 flow hood (Air Clean Systems AC-600) located on the same bench in the laboratory. The carboys for trace metal sampling were fitted with air vent filters to prevent contamination from laboratory air, so the entire system was nearly self enclosed.

Samples were mostly taken every 8 h over the duration of the cruise. The frequency was increased to every 6 h through the dust input region.

For the determination of the metals (Pb, Cd, Cu, Ni, Zn, Co, Mn, and Fe), samples were divided in filtered (filt) and unfiltered (tot) samples, acidified with $1\ \text{cm}^3\ \text{HNO}_3$ suprapur per litre seawater to $\text{pH} < 2$, wrapped in polyethylene bags and stored in boxes at room temperature until analysis in the laboratory. Filtration equipment and LDPE bottles were cleaned according to the methods described by Grasshoff et al. (1999; chapter 12.1.4) prior to use.

In 1989 and 1990 samples were collected from the bow boom of Polarstern on ANT VII/5 (12.3.–6.4.1989) and with the “Kieler Pumping System” (Schüssler and Kremling, 1993) on ANT VIII/7 (29.4.–22.5.1990). Detailed information on the sampling in the earlier studies is given in Pohl et al. (1993).

The determination of mercury and aluminium was performed directly after sampling onboard in unfiltered samples.

2.2. Laboratory analysis

Analysis of all samples was performed in the home laboratory under clean room conditions in clean air benches (class 100, US Federal-Standard 209b) within 3 to 6 months after sampling. The analytical materials used were also cleaned carefully as recommended by Grasshoff et al. (1999).

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