

BGD

10, 6065–6092, 2013

**Trace metal
solubilities over the
Southern Ocean**

A. Heimburger et al.

Solubility of iron and other trace elements over the Southern Indian Ocean

A. Heimburger, R. Losno, and S. Triquet

Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR7583, CNRS – Université Paris Diderot, Université Paris Est-Créteil, 94010 Créteil Cedex, France

Received: 5 March 2013 – Accepted: 14 March 2013 – Published: 28 March 2013

Correspondence to: A. Heimburger (alexie.heimburger@lisa.u-pec.fr)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

The fraction of soluble aerosols that is deposited on the open ocean is vital for phytoplankton growth. It is believed that a large proportion of this dissolved fraction is bioavailable for marine biota and thus plays an important role in primary production, especially in HNLC oceanic areas where this production is limited by micronutrient supply. There is still much uncertainty surrounding the solubility of atmospheric particles in global biogeochemical cycles and it is not well understood. In this study, we present the solubilities of seven elements (Al, Ce, Fe, La, Mn, Nd, Ti) in rainwater on Kerguelen Islands, in the middle of the Southern Indian Ocean. The solubilities exhibit high values, generally greater than 70 %, and Ti remains the least soluble element. Because the Southern Indian Ocean is remote from its dust sources, only the fraction of smaller aerosols reaches Kerguelen Islands after undergoing several cloud and chemical processes during their transport resulting in a drastic increase in solubility. Finally, we deduced an average soluble iron deposition flux of $23 \mu\text{g m}^{-2} \text{d}^{-1}$ ($0.4 \mu\text{mol m}^{-2} \text{d}^{-1}$) for the studied oceanic area, taking into account a median iron solubility of $82 \% \pm 18 \%$.

1 Introduction

The Southern Ocean is known to be the largest High-Nitrate Low-Chlorophyll (HNLC) oceanic area (de Baar et al., 1995). Such zones are characterized by a lack of micronutrients and trace metals in surface waters limiting phytoplankton growth (Martin 1990; Boyd et al., 2000, 2007; Blain et al., 2007). In HNLC area, primary production is especially limited by iron supply (Boyd et al., 2007) and could be co-limited by other transition metals, such as manganese (Middag et al., 2011), copper (Annett et al., 2008), cobalt (Saito et al., 2002), zinc (Morel et al., 1991) and nickel (Price and Morel, 1991). Atmospheric deposition is recognized to play an essential role in biogeochemical cycles in remote ocean areas (Duce and Tindale, 1991; Fung et al., 2000; Jickells et al., 2005), even at extremely low levels (Morel and Price, 2003): it brings new external trace

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



metals into surface waters and thus vital bioavailable nutrients for marine biota. Since the bioavailability of trace metals cannot be accurately measured, it is often assumed that the dissolved forms of metals in atmospheric deposition are bioavailable (e.g. Shi et al., 2012). The percentage which this dissolved fraction represents is referred to as “solubility”. Numerous studies have been carried out on iron solubility and its controlling factors. Soluble iron in soil represents 0.5 % of the total iron (Hand et al., 2004) while it ranges from 0.1 % to 90 % in aerosols, rains and snows, sampled at different places and times (e.g. Losno 1989; Colin et al., 1990; Zhuang et al., 1992; Guieu et al., 1997; Edwards and Sedwick, 2001; Kieber et al., 2003; Chen and Siefert, 2004; Baker et al., 2006; Buck et al., 2010b; Theodosi et al., 2010; Witt et al., 2010). Most of the solubility values are summarized in Mahowald et al. (2005) and Fan et al. (2006). Variability of iron solubility in the atmosphere is controlled by interactions such as photochemical reactions, cloud processes and organic complexation (e.g. Losno 1989; Zhuang et al., 1992; Kieber et al., 2003; Hand et al., 2004; Chen and Siefert, 2004; Desboeufs et al., 2001, 2005; Paris et al., 2011), as well as mineralogy of dust sources (Journet et al., 2008) and the element’s enrichment factor relative to its natural crustal abundance. Baker and Jickells (2006) also suggested that dust iron solubility may instead be controlled by particle size but this hypothesis was contradicted in Buck et al. (2010a) and Paris et al. (2010). Other studies have observed that the soluble part of other trace elements is highly variable and heterogeneous too. For example, reported solubility ranges from 0.1 % to 90 % for aluminium and from 10 % to 100 % for manganese (e.g. Jickells et al., 1992; Colin et al., 1990; Losno et al., 1993; Lim et al., 1994; Guieu et al., 1997; Desboeufs et al., 2005; Baker et al., 2006; Buck et al., 2010b; Hsu et al., 2010; Theodosi et al., 2010; Witt et al., 2010).

Compared to the North Hemisphere, micronutrient atmospheric supply is believed to be small over the Southern Ocean (Fung et al., 2000; Prospero et al., 2002; Jickells et al., 2005; Mahowald et al., 2005) due to its remote distance from dust sources. In a previous paper, Heimburger et al. (2012a) demonstrated that atmospheric inputs have to be re-evaluated in the Indian part of the Southern Ocean: the authors found that

direct measured dust flux is 20 times higher than the previous estimation calculated by Wagener et al. (2008). Therefore, it is highly probable that variation of atmospheric deposition in such an area may strongly influence marine biology and thus carbon sequestration since the Southern Ocean is depicted as the largest potential sink of anthropogenic CO₂ in the global ocean (Sarmiento et al., 1998; Caldeira and Duffy, 2000; Schlitzer, 2000). In this paper, we present measurements of soluble and insoluble composition for crustal elements, including iron, in rainwater samples collected on Kerguelen Islands in the Southern Indian Ocean. To our knowledge, such measurements have never been taken before over this ocean.

2 Materials and methods

2.1 Sampling site

The studied area was located on Kerguelen Archipelago (48°35′ S–49°54′ S; 68°43′ E–70°35′ E), in the Southern Indian Ocean, approximately 3800 km south-east of South Africa and 2000 km from the Antarctic coast. Rain sampling was carried out during four summer campaigns, one under the program KEFREN (“Kerguelen: Erosion and Fallout of tRace Elements and Nitrogen”) and three under the FLATOCOA one (“Flux Atmosphérique d’Origine Continentale de l’Océan Austral”). Both programs were supported by IPEV (“Institut polaire française Paul Emile Victor”). A total of 14 single rain events were collected; they are divided as follows: (i) two rains were collected from 30 January to 13 February 2005 (named P1/2_05 and P5_05), (ii) three rains from 3 to 11 December 2008 (P3_08, P5_08, P6_08), (iii) four rains from 5 December 2009 to 4 January 2010 (P2_09, P3_09, P6_09, P7_09) and (iv) five rains from 24 November to 11 December 2010 (from P1_10 to P5_10). The sampling site (49°21′10.3″ S, 70°12′58.3″ E) was installed near the chapel *Notre Dame des Vents*, north-west of the only permanently-occupied base of the archipelago *Port-aux-Français* (PAF) (Fig. 1a, b).

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.2 Materials and washing

Rains were sampled using a collector placed on top of a 100 mm diameter and 2 m high vertically erected PVC pipe (Fig. 2). This collector is made from a 24 cm diameter low density polyethylene (PE) funnel attached to an on-line filtration device. The filtration device is composed of several parts: a machined high density PE cable fitting holds the bottom end of the funnel and supports a Teflon[®] filter holder equipped with a 0.2 µm porosity clipped polycarbonate membrane (PC) filter. The soluble fraction is defined here as the amount which passes through this membrane. The filter holder is placed on the top of a 30 cm high closed section of tubing that is fitted to a 500 mL polypropylene (PP) bottle. A small Teflon[®] pipe lets filtered water flow freely into the bottle. The insoluble fraction of rainwater remains on the surface of the PC filter while the soluble fraction flows into the PP bottle (Nalgene[®]). The only pieces of equipment that touch the rainwater are the funnel, the Teflon[®] filter holder, the PC filters, the PC filter supporting grid and the PP bottles.

All the sampling materials were thoroughly washed in the laboratory before the campaign. The 500 mL PP bottles and Teflon[®] parts underwent the same washing protocol as described in Heimburger et al. (2012a) for total deposition devices. All of the other materials were: (i) washed using ordinary dish detergent in an ISO 8 controlled laboratory room, (ii) soaked from two days to one week in a bath of 2 % Decon[®] detergent diluted with reverse-osmosed water (purified water) and (iii) soaked from two to three weeks in 2 % *v/v* Normapur[®] analytic grade hydrochloric acid. Extensive rinsing was performed between each step with reverse-osmosed water. Materials were then transferred to an ISO 5 clean room and: (iv) rinsed in Elga[™] Purelab ultra[®] pure water and (v) soaked in a high purity hydrochloric acid solution (2 % Merk[™] Suprapur[®]), except for the funnels, which were too large for our soaking baths. In an ISO 1 laminar flow bench, these materials were finally: (vi) rinsed once (three times for the funnels)

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with 2 % high purity hydrochloric acid solution, (vii) five times with ultra pure water and (viii) left until dry (two to four hours). Once all the materials had been washed and dried, the funnels were mounted on their high density PE cable fittings under the ISO 1 laminar flow bench and the last three steps of the washing protocol were repeated. They were then individually placed in bags that had been washed in the same way as the materials, and were stored until being used only once in the field. The Nuclepore[®] PC filters (0.2 µm porosity) were washed in a bath of 2 v/v Romil-UpA[™] HCl for almost 2 h in the ISO 1 laminar flow bench, then rinsed with ultra pure water, clipped with special rings (FilClip[®]) and stored individually in washed polystyrene Petri dishes until use.

2.3 Rain sampling

A clean hood (AirC2, ISO 2 quality), which provided an ultra-clean work zone, was installed inside a dedicated clean area (ISO 6–ISO 7 quality) in the PAF scientific building (see Heimburger et al. (2012a) for more details). It allowed us to prepare rain devices before sampling: (i) a clipped filter was placed in the Teflon[®] filter holder, (ii) a 500 mL PP bottle without its cork was introduced into the 30 cm high closed tubing (the cork was stored in a clean box intended for this purpose) and (iii) a funnel with its cable fitting + Teflon[®] filter holder were screwed on to the top of the closed tubing. The plastic bag protecting the funnel's aperture had to be kept in place; a crack was made at the level of the cable fitting.

The sampling started at the beginning of a rain event. A prepared rain device was placed on the top of the PVC pipe; the plastic bag protecting the funnel was removed and conserved. Once the rain event had finished, the funnel was covered by its plastic bag and the device was brought into the clean hood in the scientific building. A vacuum was applied to the section of tubing to help the last rain drops to pass through the filter. The funnel was then removed and no longer used (a new one was used for each sampling). The clipped filter was stored in a clean Petri dish and the 500 mL bottle

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



was weighed. A certain quantity of the sampled rain was stored in a 60 mL Teflon[®] bottle, which had undergone the same washing protocol as the 500 mL bottles, containing enough *Romil-UpA*[™] HNO₃ to give a 1 % concentration of acid when filled. This fraction was then used for trace metal analyses. During the 2008 campaign, the pH of samples was immediately measured after sampling: it is equal to 5.4 ± 0.2 (mean \pm σ , σ : standard deviation) for all the samples. The Teflon[®] filter holder was then rinsed once with 2 % *Merk*[™] *Suprapur*[®] hydrochloric acid solution, five times with ultra pure water and allowed to dry in the clean hood before being used for the next sampling. Four laboratory blanks and eight field blanks were performed by simulating a rain event with *Elga*[™] *Purelab ultra*[®] pure water in an ISO 5 clean room and in the field respectively.

2.4 Sample preparation and analyses

Back in the laboratory, the soluble fractions of rains (stored in 60 mL Teflon[®] bottles) were transferred into PE sampling vials that had been thoroughly washed (see Heimburger et al. (2012a) for details of the washing protocol). These soluble fractions were then analyzed using High Resolution – Inductively Coupled Plasma – Mass Spectrometry (HR-ICP-MS, *Thermo Fisher Scientific*[™] Element 2), which was installed in an ISO 5 clean room and calibrated by diluted acidified multi-element external standards. The sample introduction system was protected by an ISO 1 box.

The contours of the clipped filters, which contained the insoluble fractions of rains, were cut using a new clean stainless steel scalpel blade. The filters of rain samples, laboratory blanks and field blanks were then digested using 4 mL of a HNO₃ / H₂O / HF solution (proportion: 3 / 1 / 0.5 of pure *Romil-UpA*[™] HNO₃ / ultra pure water / *Merk*[™] *Ultrapur*[®] HF) during 14 h in an air oven at 130°C in closed Savillex[™] PFA digestion vessels. Vessels had undergone the same washing protocol as described in Heimburger et al. (2012a) followed by a trial digestion. These vessels were then rinsed and

Trace metal solubilities over the Southern Ocean

A. Heimbürger et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

filled with 2 % *Romil-UpA*TM HCl until being used. At the end of digestion, the HF was completely evaporated on a heater plate. 5 mL of 1 % *Romil-UpA*TM HNO₃ plus 0.5 mL of *Romil-UpA*TM H₂O₂ were then added and left on the plate for 30 min. Finally, the content of each vessel was transferred into a 60 mL PP bottle (same washing protocol as for the bottles containing rain samples) with the 1 % *Romil-UpA*TM HNO₃ solution used to rinse the vessel walls. The samples were then analyzed by HR-ICP-MS too. Seven blank Nuclepore[®] PC filters underwent the digestion protocol in order to estimate possible contamination from the filters and the digestion experiments. 6 mg of BE-N (from SARM, France) and 8.6 mg of SDC-1 (from USGC, USA) geostandards, crushed prior to use, also underwent this protocol in order to estimate the yield and accuracy of our digestion method.

Analytical blanks ($n = 7$) were carried out using 1 % *v/v* *Romil-UpA*TM HNO₃ in order to determine the analytical detection limits (DL) of the HR-ICP-MS method. The accuracy (expressed as recovery rate: RR % = mean of measured standard concentrations / certified or published values) and reproducibility (expressed as relative standard deviation: RSD % = σ / mean) of measurements were checked using the certified reference material (CRM) SLRS-5 (Heimbürger et al., 2012b) commonly used to control trace metals analysis. This CRM was diluted ten times using 1 % *v/v* *Romil-UpA*TM ultra-pure nitric acid in ultra-pure water in order to find more similar concentrations between the SLRS-5 and the ones found in samples, allowing calculation of significant RR % and RSD % (Feinberg, 2009). All the measured concentrations including blanks turned out to be above DL: they are three times higher than DL in samples, except for Nd for the soluble fraction. Reproducibility of SLRS-5 measurements is under or equal to 10 % for all the elements; accuracy is between 94 % and 109 % (Table 1). Measured concentrations in BE-N and SDC-1 geostandards are fairly consistent with the certified ones: RR % are generally equal to 100 % \pm 30 % (Table 1).

3 Results and discussion

3.1 Solubility uncertainties

The solubility in rainwater is expressed as follows:

$$S_X \% = \frac{[X]_{\text{soluble}}}{[X]_{\text{total}}} \quad (1)$$

where S_X % is the solubility of an element X, $[X]_{\text{soluble}}$ is the soluble concentration of X, $[X]_{\text{insoluble}}$ is the insoluble concentration of X and $[X]_{\text{total}}$ is the sum of $[X]_{\text{soluble}}$ and $[X]_{\text{insoluble}}$. To determine $[X]_{\text{soluble}}$ and $[X]_{\text{insoluble}}$, we took into account the contamination observed in the different blanks performed (laboratory blanks, field blanks, blank filters; see Sect. 2) for both soluble and insoluble fractions respectively. This contamination is caused by elements remaining in sampling devices, including filters and the walls of equipment in contact with samples. For a given element X, we computed its quantities (Q_j) in each blank by multiplying measured blank concentrations by blank volumes. These quantities are found to be similar for both laboratory and field blanks; the quantities in filter blanks are also equivalent to the ones in laboratory and field insoluble blanks. Therefore, all the blanks were pooled together for both fractions respectively in order to extract a global blank defined as the median quantity of all the blank quantities. Figure 3 represents ratios of this median quantity in blanks relative to the one in rainwater, for all the analysed elements in the soluble and insoluble fractions respectively. Expressed as a percentage, these ratios are under 10 % for Ce, La, Mn and Nd for both fractions, under 20 % for Al and Fe for both fractions, and reach 35 % for Ti for the insoluble fraction only. This median quantity was then subtracted from the ones found in rain samples for each element. $[X]_{\text{soluble}}$ and $[X]_{\text{insoluble}}$ are consequently

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



given by the following formulas:

$$[X]_{\text{soluble}} = \frac{[X]_{\text{analytical}} V_{\text{rain}} - \text{median}(Q_i)}{V_{\text{rain}}} \quad (2)$$

$$[X]_{\text{insoluble}} = \frac{[X]_{\text{analytical}} V_{\text{insoluble}} - \text{median}(Q_i)}{V_{\text{rain}}} \quad (3)$$

5 where $[X]_{\text{analytical}}$ represents measured concentrations, V_{rain} the volumes of collected rainwater, and $V_{\text{insoluble}}$ the dilution volumes of the digested insoluble fraction. Uncertainties associated with $[X]_{\text{analytical}}$ ($\sigma([X]_{\text{analytical}})$) are computed using standard deviations and the mathematical approach of exact differential (Feinberg, 2009). Because the quantities of all the blanks are not normally distributed, we used robust statistics for
 10 a better estimation of the blank distribution range (Feinberg, 2009).

$$\sigma([X]_{\text{analytical}}) = \sqrt{\text{DL}^2 + ([X]_{\text{analytical}} \text{RSD}\%)^2 + ([X]_{\text{analytical}} (1 - \text{RR}\%))^2} \quad (4)$$

where $(1 - \text{RR}\%)$ is the accuracy error from SLRS-5 measurements. Standard deviations of $[X]_{\text{soluble}}$ and $[X]_{\text{insoluble}}$ are then computed as follows:

$$15 \quad \sigma([X]_{\text{soluble}}) = \frac{\sqrt{\sigma([X]_{\text{analytical}})^2 V_{\text{rain}}^2 + (1.483 \text{MAD})^2}}{V_{\text{rain}}} \quad (5)$$

$$\sigma([X]_{\text{insoluble}}) = \frac{\sqrt{\sigma([X]_{\text{analytical}})^2 V_{\text{insoluble}}^2 + (1.483 \text{MAD})^2}}{V_{\text{rain}}} \quad (6)$$

with median absolute deviation $\text{MAD} = \text{median}(|Q_i - \text{median}(Q_i)|)$ representing the dispersion of blank distribution. Finally, solubility uncertainties are given by the Eq. (7):

$$20 \quad \Delta S_X \% = k S_X \% \frac{[X]_{\text{insoluble}}}{[X]_{\text{soluble}}} \sqrt{\frac{\left(\frac{\sigma([X]_{\text{soluble}})}{[X]_{\text{soluble}}}\right)^2 + \left(\frac{\sigma([X]_{\text{insoluble}})}{[X]_{\text{insoluble}}}\right)^2}{1 + \frac{[X]_{\text{insoluble}}}{[X]_{\text{soluble}}}}} \quad (7)$$

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with the coverage factor of $k = 2$ (Feinberg, 2009), which allows us to obtain an expanded uncertainty representing a confidence level of 95 %, i.e. this expanded uncertainty includes 95 % of possible solubility values.

3.2 Local contamination issues

5 Rain samples may be contaminated by local soil erosion. Heimbürger et al. (2012a) demonstrated that Ti/Al ratio is a suitable tracker for such contamination: the authors reported that these ratios are equal to 0.15 ± 0.05 (mean $\pm \sigma$) and 0.04 ± 0.01 in soil and atmospheric deposition samples, respectively. Consequently, the $[\text{Ti}]_{\text{total}}/[\text{Al}]_{\text{total}}$ ratio was computed for each rain sample (Fig. 4): only three rains (P3_08, P1_10 and
10 P3_10) exhibit the same Ti/Al ratios as the one in deposition samples and so can be considered free of contamination by local soil emissions. The rest of the samples exhibit a higher ratio that points out local contamination by soil, which is not compatible with pure long range transported particles; these samples were not taken into account afterwards. To complete the validation of the three remaining rains, we used gdas re-analyzed archives (Draxler and Rolph, 2012; Rolph, 2012) to compute wind roses. For
15 the three rains, wind roses show that wind came from south-west directions for P3_08 and north-west directions for P1_10 and P3_10, excluding direct contamination from PAF.

3.3 Rain event fluxes

20 Deposition fluxes generated by single rain events were computed by dividing the quantities found in each validated rain sample by the surface of the funnel aperture (0.045 m^2). In Heimbürger et al. (2012a), the authors found that atmospheric total deposition fluxes are equal to $54 \pm 42 \mu\text{g m}^{-2} \text{ d}^{-1}$ (mean $\pm \sigma$ of 41 samples) and $28 \pm 22 \mu\text{g m}^{-2} \text{ d}^{-1}$ for Al and Fe respectively. We found averaged event basis rain fluxes
25 equal to $32 \pm 42 \mu\text{g m}^{-2}$ and $17 \pm 12 \mu\text{g m}^{-2}$ (Table 2). Taking into account meteorological data that we recorded 8 km from PAF, the average frequency of such rain events

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimbürger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



is between one and two days. Measured rain fluxes are then consistent with the atmospheric total deposition fluxes. We can conclude that the rains studied in this paper are representative of average rain events on Kerguelen Islands.

3.4 Solubility

5 Solubilities in rains are reported in Table 3: they are higher than 70 % for all the elements (Al, Ce, Fe, La, Mn, Nd, Ti) for the three rains, except for Ti ($33 \% \pm 44 \%$) and Fe ($57 \% \pm 17 \%$) in P1_10. The rare earth elements (La, Ce and Nd) also exhibit high solubility values ranging from 79 % to 96 %. In contrast, solubilities measured for the rejected rain samples show much lower values, for example with a median of 17 %
10 for Ti. High solubilities were already observed for some of these elements in the literature. Siefert et al. (1999) wrote that “labile Fe” solubility in the fine dust fraction is more than 80 % in aerosols collected on-board, while Edwards and Sedwick (2001) reported a Fe solubility ranging from 9 % to 89 % in snow samples collected in Antarctica and Baker and Croot (2010) modelled a Fe solubility between 0.2 % and 100 %
15 over the Southern Indian Ocean. Witt et al. (2010) found that Al solubility can reach $91 \% \pm 66 \%$ when the soluble fraction of aerosols collected in the North Indian Ocean was extracted with a pH 1 solution. Mn solubility can reach more than 90 % in oceanic areas (Baker et al., 2006) and is known to be highly variable (Losno, 1989; Desboeufs et al., 2005; Buck et al., 2010b). Nonetheless, Ti solubility generally exhibits a lower value ($< 15 \%$) (Buck et al., 2010b; Hsu et al., 2010) than the ones found on Kerguelen
20 Islands (median = $76 \% \pm 13 \%$) although Ti remains the least soluble element in our samples. We did not find any previously published solubility values for La, Ce or Nd.

Several studies demonstrate that aerosol solubility increases during particle transport, especially due to cloud processes (Zhuang et al., 1992; Gieray et al., 1997; Desboeufs et al., 2001): it is believed that during their transport in the atmosphere aerosols
25 typically undergo around 10 condensation/evaporation cloud cycles (Pruppacher and Jaenicke, 1995), in which trace gases such as HNO_3 , SO_2 and NH_3 can be present, can modify the pH of cloud droplets and consequently can increase the soluble fraction of

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mineral particles. Organic molecules can also increase solubility, e.g. oxalate complexation promoting iron solubility (Paris et al., 2011), as well as photochemistry processes, as reviewed in Shi et al. (2012). Moreover, the average size of mineral aerosols decreases with distance from dust sources, as a result of higher deposition rates for larger particles (Duce et al., 1991). When mineral aerosol size becomes smaller, a greater proportion of their volume is exposed to surface processes (Baker and Jickells, 2006) and is therefore available for dissolution. Ito (2012) support the hypothesis that smaller dust particles yield increased iron solubility relative to larger particles as a result of acid mobilization in smaller particles. In consequence, the smaller the aerosols are and the further they are from their source area, the more soluble they are. Taking into account both of these hypotheses, we can explain the high solubilities observed on Kerguelen Islands by long range transport from dust sources, which have been identified as South America, South Africa and/or Australia (Prospero et al., 2002; Mahowald et al., 2007; Bhattachan et al., 2012). Indeed, Wagener et al. (2008) and Heimbürger et al. (2012a) noted that particles observed on Kerguelen Islands at sea or ground level exhibit 2 μm median diameters, suggesting that only the fine dust fraction, which is more soluble than the larger dust fraction, reaches Kerguelen Islands. In addition, air mass back trajectories computed from a Hybrid Single Particle Lagrangian Integrated trajectory from the NOAA Air Resource Laboratory (HYSPLIT) model (Draxler and Rolph, 2012; Rolph, 2012) with re-analysed archived meteorological data (gdas) show that air masses travelled for at least five days over the ocean before arriving at our sampling location during the three rain collection period. These air masses did not pass over continents and so did not gain new less soluble continental aerosols. In consequence, continental aerosols coming to Kerguelen Islands underwent several cloud processes during their long range transport in the atmosphere and over the ocean, which probably dramatically increased their solubilities.

Trace metal solubilities over the Southern Ocean

A. Heimbürger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Conclusions

Out of a total of 14 single rain events collected on Kerguelen Islands, three samples free of local contamination were validated and are representative of average rain events. Soluble and insoluble fractions of rainwater were immediately separated during sampling allowing chemical evolution of some elements, such as Fe, to be kept to a minimum. We found very high solubilities ($> 70\%$) for all the analysed elements, even the rare earth elements, for which these are the first solubility values to be measured in an oceanic area, to our knowledge. Consistently, Ti remains the least soluble element and we can suppose that other elements not measured here and of importance in biogeochemical cycles, such as Co, Ni and Cu, have solubilities at least equal to the solubility value of Ti ($76\% \pm 26\%$). Heimburger et al. (2012a) reported an iron deposition flux of $28 \pm 22 \mu\text{g m}^{-2} \text{d}^{-1}$ on Kerguelen Islands. Applying the median ($\pm \sigma$) iron solubility of $82\% \pm 18\%$ (Table 3), the deduced soluble iron flux is equal to $23 \mu\text{g m}^{-2} \text{d}^{-1}$ for this oceanic area. This value is three times higher than the dissolved iron flux in the Southern Indian Ocean according to the model proposed by Fan et al. (2006) taking into account solubility processes with a 17% average solubility calculated for modelled wet deposition, the predominant atmospheric deposition type on Kerguelen Islands (Heimburger et al., 2012a). To conclude, this experiment produced results for three validated samples only but strongly suggests that solubility processes should be re-evaluated, as should soluble depositions simulated by current atmospheric models for remote oceanic areas such as the Southern Ocean.

Acknowledgements. We would like to thank the *Institut polaire Paul Emile Victor* (IPEV), which provided funding and enabled us to run KEFREN and FLATOCOA programs. We also thank the *Terres Australes et Antarctiques Françaises* (TAAF) team and Elisabeth Bon Nguyen for their help. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (<http://ready.arl.noaa.gov>) used in this publication.

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The publication of this article is financed by CNRS-INSU.

References

- 5 Annett, A. L., Lapi, S., Ruth, T. J., and Maldonado, M. T.: The effects of Cu and Fe availability on the growth and Cu : C ratios of marine diatoms, *Limnol. Oceanogr.*, 53, 2451–2461, doi:10.4319/lo.2008.53.6.2451, 2008.
- Baker, A. R. and Croot, P. L.: Atmospheric and marine controls on aerosol iron solubility in seawater, *Mar. Chem.*, 120, 4–13, doi:10.1016/j.marchem.2008.09.003, 2010.
- 10 Baker, A. R. and Jickells, T. D.: Mineral particle size as a control on aerosol iron solubility, *Geophys. Res. Lett.*, 33, L17608, doi:10.1029/2006GL026557, 2006.
- Baker, A. R., Jickells, T. D., Witt, M., and Linge, K. L.: Trend in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean, *Mar. Chem.*, 98, 43–58, doi:10.1016/j.marchem.2005.06.004, 2006.
- 15 Bhattachan, A., D'Odorico, P., Baddock, M. C., Zobeck, T. M., Okin, G. S., and Cassar, N.: The Southern Kalahari: a potential new dust source in the Southern Hemisphere?, *Environ. Res. Lett.*, 7, 024001, doi:10.1088/1748-9326/7/2/024001, 2012.
- 20 Blain, S., Quéguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., Bowie, A., Brunet, C., Brussard, C., Carlotti, F., Christaki, U., Corbière, A., Durand, I., Ebersbach, F., Fuda, J.-L., Garcia, N., Gerringa, L., Griffiths, B., Guigue, C., Guillermin, C., Jacquet, S., Jean-del, C., Laan, P., Lefevre, D., Monaco, C. L., Malits, A., Mosseri, J., Obernosterer, I., Park, Y.-H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., Savoye, N., Scouarnec, L., Souhaut, M., Thuiller, D., Timmermans, K., Trull, T., Uitz, J., van Beek, P., Veldhuis, M., Vincent, D., Viollier, E., Vong, L., and Wagener T.: Effect of natural iron fertilization on carbon sequestration in the Southern Ocean, *Nature*, 446, 1070–1074, doi:10.1038/nature05700, 2007.
- 25

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Boyd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R., Bakker, D. C.,
Bowie, A. R., Buesseler, K. O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R.,
Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R.,
Maldonado, M., McKay, R. M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K.,
5 Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., and Zeldis, J.: A mesoscale
phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, *Nature*,
407, 695–702, doi:10.1038/35037500, 2000.

Boyd, P. W., Jickells, T. D., Law, C. S., Blain, S., Boyle, E. A., Buesseler, K. O.,
Coale, K. H., Cullen, J. J., de Baar, H. J. W., Follows, M., Harvey, M., Lancelot, C., Lev-
10asseur, M., Owens, N. P. J., Pollard, R., Rivkin, R. B., Sarmiento, J., Schoemann, V.,
Smetacek, V., Takeda, S., Tsuda, A., Turner, S., and Watson, A. J.: Mesoscale iron en-
richment experiments 1993–2005: synthesis and future directions, *Science*, 315, 612–617,
doi:10.1126/science.1131669, 2007.

Buck, S. C., Landing, W. M., and Resing, J. A.: Particle size and aerosol iron
15 solubility: a high-resolution analysis of Atlantic aerosols, *Mar. Chem.*, 120, 14–24,
doi:10.1016/j.marchem.2008.11.002, 2010a.

Buck, C. S., Landing, W. M., Resing, J. A., and Measures, C. I.: The solubility and de-
position of aerosol Fe and other trace elements in the North Atlantic Ocean: observa-
tions from the A16N CLIVAR/CO₂ repeat hydrography section, *Mar. Chem.*, 120, 57–70,
20 doi:10.1016/j.marchem.2008.08.003, 2010b.

Caldeira, K. and Duffy, P. B.: The role of the Southern Ocean in uptake and storage of anthro-
pogenic carbon dioxide, *Science*, 287, 620–622, doi:10.1126/science.287.5453.620, 2000.

Chen, Y. and Siefert, R. L.: Seasonal and spatial distributions and dry deposition fluxes of
atmospheric total and labile iron over the tropical and subtropical North Atlantic Ocean, *J.*
25 *Geophys. Res.*, 109, D09305, doi:10.1029/2003JD003958, 2004.

Colin, J.-L., Jaffrezo, J.-L., and Gros, J. M.: Solubility of major species in precipitation: factors
of variation, *Atmos. Environ.*, 24, 537–544, doi:10.1016/0960-1686(90)90008-B, 1990.

de Baar, H. J. W., de Jong, J. T. M., Bakker, D. C. E., Loscher, B. M., Veth, C., Bathmann, U.,
and Smetacek, V.: Importance of iron for plankton blooms and carbon dioxide drawdown in
30 the Southern Ocean, *Nature*, 373, 412–415, doi:10.1038/373412a0, 1995.

Desboeufs, K. V., Losno, R., and Colin, J.-L.: Factors influencing aerosol solubility during cloud
processes, *Atmos. Environ.*, 35, 3529–3537, doi:10.1016/S1352-2310(00)00472-6, 2001.

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



- Desboeufs, K. V., Sofikitis, A., Losno, R., Colin, J. L., and Ausset, P.: Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter, *Chemosphere*, 58, 195–203, doi:10.1016/j.chemosphere.2004.02.025, 2005.
- Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY website, NOAA Air Resources Laboratory, Silver Spring, MD, available at: <http://ready.arl.noaa.gov/HYSPLIT.php>, 2012.
- Duce, R. and Tindale, N. W.: Chemistry and biology of iron and other trace metals, *Limnol. Oceanogr.*, 36, 1715–1726, 1991.
- Edwards, R. and Sedwick, P.: Iron in East Antarctic snow: implications for atmospheric iron deposition and algal production in Antarctic waters, *Geophys. Res. Lett.*, 28, 3907–3910, doi:10.1029/2001GL012867, 2001.
- Feinberg, M.: Labo-stat – Guide de Validation des Méthodes d'Analyse, Lavoisier, Basse Goulaine, France, 361 pp., 2009.
- Fung, I. Y., Meyn, S. K., Tegen, I., Doney, S. C., John, J. G., and Bishop, J. K. B.: Iron supply and demand in the upper ocean, *Global Biogeochem. Cy.*, 14, 281–295, 2000.
- Gieray, R., Wieser, P., Engelhardt, T., Swietlicki, E., Hansson, H. C., Mentes, B., Orsini, D., Martinsson, B., Svenningsson, B., Noone, K. J., and Heintzenberg, J.: Phase partitioning of aerosol constituents in cloud based on single-particle and bulk analysis, *Atmos. Environ.*, 31, 2491–2502, doi:10.1016/S1352-2310(96)00298-1, 1997.
- Guieu, C., Chester, R., Nimmo, M., Martin, J.-M., Guerzoni, S., Nicolas, E., Mateu J., and Keyse, S.: Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean, *Deep-Sea Res. II*, 44, 655–674, doi:10.1016/S0967-0645(97)88508-6, 1997.
- Hand, J. L., Mahowald, N. M., Chen, Y., Siefert, R. L., Luo, C., Bubranianiam, A., and Fung, I.: Estimates of atmospheric-processed soluble iron from observations and a global mineral aerosol model: biogeochemical implications, *J. Geophys. Res.*, 109, D17205, doi:10.1029/2004JD004575, 2004.
- Heimburger, A., Losno, R., Triquet, S., Dulac F., and Mahowald, N. M.: Direct measurements of atmospheric iron, cobalt and aluminium-derived dust deposition at Kerguelen Islands, *Global Biogeochem. Cy.*, 26, GB4016, doi:10.1029/2012GB004301, 2012a.
- Heimburger, A., Tharaud, M., Monna, F., Losno, R., Desboeufs, K., and Bon Nguyen, E.: SLRS-5 elemental concentrations of thirty-three uncertified elements deduced from SLRS-5/SLRS-4 ratios, *Geostand. Geoanal. Res.*, 37, 77–85, doi:10.1111/j.1751-908X.2012.00185.x, 2012b.

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Hsu, S.-C., Wong, G. T. F., Gong, G.-C., Shiah, F.-K., Huang, Y.-T., Kao, S.-J., Tsai, F., Lung, S.-C. C., Lin, F.-J., Lin, I.-I., Hung, C.-C., and Tseng, C.-M.: Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea, *Mar. Chem.*, 120, 116–127, doi:10.1016/j.marchem.2008.10.003, 2010.

Ito, A.: Contrasting the effect of iron mobilization on soluble iron deposition to the ocean in the Northern and Southern Hemispheres, *J. Meteorol. Soc. Jpn.*, 90A, 167–188, doi:10.2151/jmsj.2012-A09, 2012.

Jickells, T. D., Davies, T. D., Tranter, M., Landsberger, S., Jarvis, K., and Abrahams, P.: Trace elements in snow samples from Scottish Highlands: sources and dissolved/particulate distributions, *Atmos. Environ.*, 26A, 393–401, doi:10.1016/0960-1686(92)90325-F, 1992.

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P. W., Duce, R. A., Hunter, K. A., Kawahata, H., Kubilay, N., LaRoche, J., Liss, P. S., Mahowald, N., Prospero, J. M., Ridgwell, A. J., Tegen, I., and Torres, R.: Global iron connections between desert dust, ocean biogeochemistry, and climate, *Science*, 308, 67–71, doi:10.1126/science.1105959, 2005.

Journet, E., Desboeufs, K. V., Caquineau, S., and Colin, J.-L.: Mineralogy as a critical factor of dust iron solubility, *Geophys. Res. Lett.*, 35, L07805, doi:10.1029/2007GL031589, 2008.

Kieber, R. J., Willey, J. D., and Avery Jr., G. B.: Temporal variability of rainwater iron speciation at the Bermuda Atlantic Time Series Station, *J. Geophys. Res.*, 108, 3277, doi:10.1029/2001JC001031, 2003.

Lim, B., Jickells, T. D., Colin, J.-L., and Losno, R.: Solubilities of Al, Pb, Cu, and Zn in rain sampled in the marine environment over the North Atlantic Ocean and Mediterranean Sea, *Global Biogeochem. Cy.*, 8, 349–362, doi:10.1029/94GB01267, 1994.

Losno, R.: *Chimie d'éléments minéraux en trace dans les pluies méditerranéennes*, Ph. D. Thesis, Université de Paris 7, Paris, France, 1989.

Losno, R., Colin, J.-L., Lebris, N., Bergametti, G., Jickells, T., and Lim, B.: Aluminium solubility in rainwater and molten snow, *J. Atmos. Chem.*, 17, 29–43, doi:10.1007/BF00699112, 1993.

Mahowald, N. M., Baker, A. R., Bergametti, G., Brooks, N., Duce, R. A., Jickells, T. D., Kubilay, N., Prospero, J. M., and Tegen, I.: Atmospheric global dust cycle and iron inputs to the ocean, *Global Biogeochem. Cy.*, 19, GB4025, doi:10.1029/2004GB002402, 2005.

Mahowald, N. M.: Anthropocene changes in desert area: sensitivity to climate model predictions, *Geophys. Res. Lett.*, 34, L18817, doi:10.1029/2007GL030472, 2007.

Martin, J. H.: The iron hypothesis, *Paleoceanography*, 5, 1–13, 1990.

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Middag, R., de Baar, H. J. W., Laan, P., Cai, P. H., and van Ooijen, J. C.: Dissolved manganese in the Atlantic sector of the Southern Ocean, *Deep-Sea Res. Pt. II*, 58, 2661–2677, doi:10.1016/j.drs2.2010.10.043, 2011.
- Morel, F. M. M. and Price, N. M.: The biogeochemical cycles of trace metals in the oceans, *Science*, 300, 944–948, doi:10.1126/science.1083545, 2003.
- Morel, F. M., Hudson, R. J. M., and Price, N. M.: Limitation of productivity by trace metals in the sea, *Limnol. Oceanogr.*, 36, 1742–1755, doi:10.4319/lo.1991.36.8.1742, 1991.
- Paris, R., Desboeufs, K. V., Formenti, P., Nava, S., and Chou, C.: Chemical characterisation of iron in dust and biomass burning aerosols during AMMA-SOP0/DABEX: implication for iron solubility, *Atmos. Chem. Phys.*, 10, 4273–4282, doi:10.5194/acp-10-4273-2010, 2010.
- Paris, R., Desboeufs, K. V., and Journet, E.: Variability of dust iron solubility in atmospheric waters investigation of the role of oxalate organic complexation, *Atmos. Environ.*, 45, 6510–6517, doi:10.1016/j.atmosenv.2011.08.068, 2011.
- Price, N. M. and Morel, F. M. M.: Colimitation of phytoplankton growth by nickel and nitrogen, *Limnol. Oceanogr.*, 36, 1071–1077, doi:10.4319/lo.1991.36.6.1071, 1991.
- Prospero, J. M., Ginoux, P., Torres, O., Nicholson, S. E., and Gill, T. E.: Environmental characterization of global sources of atmospheric soil dust identified with the NIMBUS 7 TOMS absorbing aerosol product, *Rev. Geophys.*, 40, 2–31, doi:10.1029/2000RG000095, 2002.
- Pruppacher, H. R. and Jaenicke, R.: Processing of water-vapor and aerosols by atmospheric clouds, a global estimate, *Atmos. Res.*, 38, 283–295, doi:10.1016/0169-8095(94)00098-X, 1995.
- Rolph, G. D.: Real-time Environmental Applications and Display sYstem (READY) Website. NOAA Air Resources Laboratory, Silver Spring, MD, available at: <http://ready.arl.noaa.gov>, 2012.
- Saito, M. A., Moffett, J. W., Chisholm, S. W., and Waterbury, J. B.: Cobalt limitation and uptake in *Prochlorococcus*, *Limnol. Oceanogr.*, 47, 1629–1636, doi:10.4319/lo.2002.47.6.1629, 2002.
- Sarmiento, J. L., Hughes, T. M. C., Stouffer, R. J., and Manabe, S.: Simulated response of the ocean carbon cycle to anthropogenic climate warming, *Nature*, 393, 245–249, doi:10.1038/30455, 1998.
- Schlitzer, R.: Applying adjoint method for biogeochemical modeling: export of particulate organic matter in the world ocean, *Geoph. Monog. Series*, 114, 107–124, 2000.
- Shi, Z., Krom, M. D., Jickells, T. D., Bonneville, S., Carslaw, K. S., Mihalopoulos, N., Baker, A. R., and Benning, L. G.: Impacts on iron solubility in the mineral dust by pro-

Trace metal solubilities over the Southern OceanA. Heimburger et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

cesses in the source region and the atmosphere: a review, *Aeolian Res.*, 5, 21–42, doi:10.1016/j.aeolia.2012.03.001, 2012.

Siefert, R. L., Johansen, A. M., and Hoffmann, M. R.: Chemical characterization of ambient aerosol collected during the south-west monsoon and inter-monsoon seasons over the Arabian sea: labile-Fe(II) and other trace metals, *J. Geophys. Res.*, 104, 3511–3526, doi:10.1029/1998JD100067, 1999.

Theodosi, C., Markaki, Z., Tselepidis, A., and Mihalopoulos, N.: The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater, *Mar. Chem.*, 120, 154–163, doi:10.1016/j.marchem.2010.02.003, 2010.

Wagener, T., Guieu, C., Losno, R., Bonnet, S., and Mahowald, N.: Revisiting atmospheric dust export to the Southern Hemisphere ocean: biogeochemical implications, *Global Biogeochem. Cy.*, 22, GB2006, doi:10.1029/2007GB002984, 2008.

Witt, M. L. I., Mather, T. A., Baker, A. R., De Hoog, J. C. M., and Pyle, D. M.: Atmospheric trace metals over the south-west Indian Ocean: total gaseous mercury, aerosol trace metal concentrations and lead isotope ratios, *Mar. Chem.*, 121, 2–16, doi:10.1016/j.marchem.2010.02.005, 2010.

Zhuang, G., Yi, Z., Duce, R. A., and Brown, P. R.: Chemistry of iron in Marine aerosols, *Global Biogeochem. Cy.*, 6, 161–173, doi:10.1029/92GB00756, 1992.

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Table 1. Detection limits, accuracy and reproducibility of SLRS-5 measurements, estimated recovery rate of BE-N and SDC-1.

Element	<i>m/z</i> (res.)	DL (ngL ⁻¹)	SLRS-5 measured values ± σ (μgL ⁻¹)	SLRS-5 RSD %	SLRS-5 RR %	BE-N RR %	SDC-1 RR %
Al	27 (m)	26.4	51 ± 3	6 %	102 %	112 %	74 %
Ce	140 (l)	0.036	0.257 ± 0.014	5 %	109 %	121 %	
Fe	56 (m)	5.2	93.0 ± 4.6	5 %	102 %	129 %	105 %
La	139 (l)	0.039	0.199 ± 0.011	5 %	101 %	111 %	
Mn	55 (m)	0.62	4.50 ± 0.20	5 %	104 %	143 %	111 %
Nd	146 (l)	0.11	0.183 ± 0.008	4 %	99 %	112 %	
Ti	47 (m)	1.7	2.14 ± 0.22	10 %	94 %	151 %	109 %

m/z = mass of the considered isotope; res. = resolution; m = medium resolution (≈ 4000), l = low resolution (≈ 300); DL = detection limit; RSD % = reproducibility, RR % = recovery rate.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Table 2. Rain event fluxes ($\mu\text{g m}^{-2}$) \pm uncertainties.

Element	P1_10	P3_10	P3_08
Al	12 ± 3	51 ± 7	31 ± 5
Ce	0.024 ± 0.005	0.11 ± 0.02	0.048 ± 0.010
Fe	8.4 ± 3.4	30 ± 4	13 ± 3
La	0.010 ± 0.001	0.041 ± 0.004	0.025 ± 0.003
Mn	0.82 ± 0.11	1.3 ± 0.2	0.34 ± 0.06
Nd	0.0069 ± 0.0015	0.043 ± 0.004	0.017 ± 0.002
Ti	0.81 ± 0.65	2.3 ± 0.8	2.2 ± 0.8

Uncertainties are computed by propagating standard deviations of Eqs. (5) and (6).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Table 3. Solubility (%) in rainwater.

Element	P1_10	P3_10	P3_08	Median $\pm \sigma$
Al	70 % \pm 8 %	96 % \pm 1 %	92 % \pm 2 %	92 % \pm 14 %
Ce	84 % \pm 3 %	96 % \pm 1 %	94 % \pm 1 %	94 % \pm 7 %
Fe	57 % \pm 17 %	91 % \pm 2 %	82 % \pm 5 %	82 % \pm 18 %
La	83 % \pm 2 %	96 % \pm 1 %	95 % \pm 1 %	95 % \pm 7 %
Mn	89 % \pm 3 %	94 % \pm 2 %	88 % \pm 4 %	89 % \pm 3 %
Nd	79 % \pm 4 %	96 % \pm 1 %	95 % \pm 1 %	95 % \pm 10 %
Ti	33 % \pm 44 %	79 % \pm 13 %	76 % \pm 14 %	76 % \pm 26 %

Absolute uncertainties (\pm) are computed using Eq. (7) for each rain sample; median $\pm \sigma$ = median of the three solubility values for an element \pm associated standard deviations, which is representative of (an) average solubility.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





Fig. 1. (a) Kerguelen Islands in the Southern Indian Ocean.

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



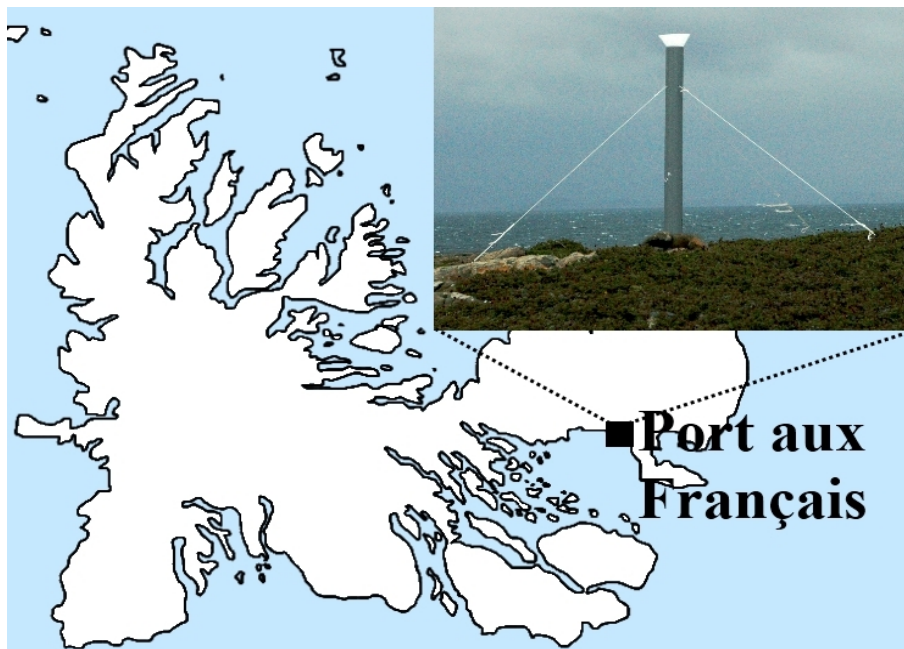


Fig. 1. (b) *Port-aux-Français* on Kerguelen Islands plus picture of rainwater sampling device on PAF.

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





Fig. 2. Rainwater sampling device on the top of its PVC tube.

BGD

10, 6065–6092, 2013

Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Trace metal solubilities over the Southern Ocean

A. Heimburger et al.

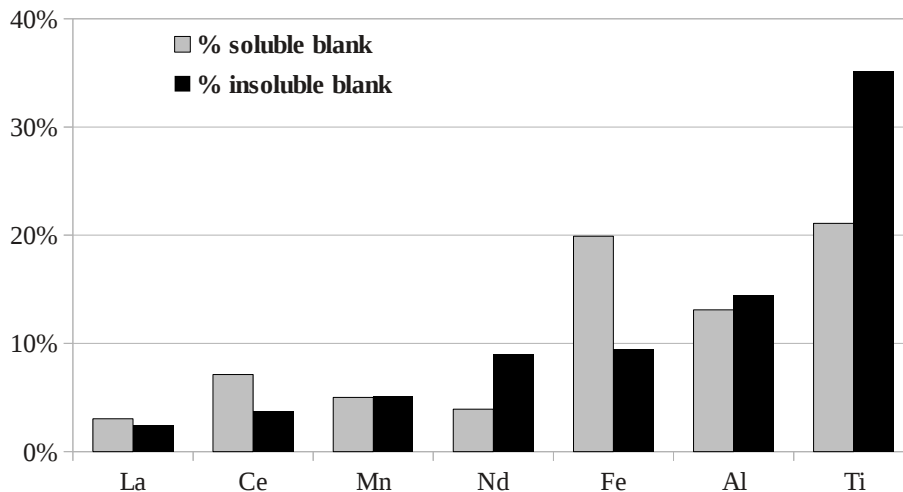


Fig. 3. Ratio, expressed in percentage, of the median quantities in blanks (all the blanks pooled together) relative to both median soluble (grey) and median insoluble (black) quantities in rain-water samples for all the measured elements.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Trace metal solubilities over the Southern Ocean

A. Heimbürger et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

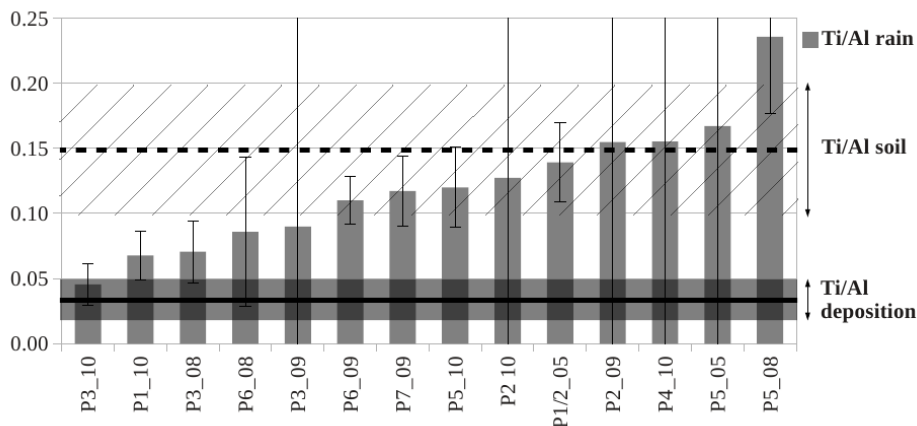


Fig. 4. Ti/Al ratios in rainwater samples (grey histogram), in soil samples (dotted black line + hatched rectangle for uncertainties; Heimbürger et al., 2012a) and in deposition samples (black line + grey rectangle for uncertainties; Heimbürger et al., 2012a). Ti/Al in P3.10, P1.10 and P3.08 are equal to Ti/Al in deposition samples.