



# Distribution of dissolved aluminium in the high atmospheric input region of the subtropical waters of the North Atlantic Ocean

J. Kramer<sup>a,\*</sup>, P. Laan<sup>a</sup>, G. Sarthou<sup>b</sup>, K.R. Timmermans<sup>a</sup>, H.J.W. de Baar<sup>a</sup>

<sup>a</sup>Department of Marine Chemistry and Geology, Royal Netherlands Institute for Sea Research (Royal NIOZ), P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands

<sup>b</sup>CNRS/UBO/IUEM, UMR 6539 LEMAR, Technopole Brest Iroise, F-29280 Plouzané, France

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## Abstract

Concentrations of dissolved Al (0.2 µm filtered) have been determined in the Canary basin and on a transect towards the Strait of Gibraltar, in order to allow sampling across the Saharan dust plume. The highest surface water concentrations of up to 25 nM were observed in the northwest part of the studied region, indicating substantial atmospheric input from the Sahara desert. This observation was supported by relatively pronounced Al surface maxima of the shallow casts performed in this region. The positive covariance between dissolved Al and dissolved Fe concentrations on the transect from the Canary Islands towards the Strait of Gibraltar suggests a common atmospheric source of the two metals. Outside the Canary basin, the Al concentrations rapidly dropped to values below 10 nM, coherent with lower aeolian inputs. A good correlation has been found between dissolved Al surface seawater concentrations and dissolved orthosilicic acid (Si(OH)<sub>4</sub>), which can most likely be attributed to conservative mixing of warm, more saline Al- and Si-rich water masses with colder waters of lower salinity which are more depleted in both elements. In spite of the oligotrophic waters that were met most of the cruise, a strong minimum in dissolved Al was observed at the chlorophyll *a* maximum at a few stations, suggesting rapid Al scavenging or biological uptake in this region.

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## 1. Introduction

During the last decade, atmospheric dust input into the open ocean has become recognised as a very important source of trace elements, such as Al and Fe, the latter of which is well known to be essential

for the growth and metabolism of all marine organisms (de Baar et al., 1995; Morel and Price, 2003; Turner and Hunter, 2001). Aluminium is an ideal tracer for the indication of dust input into the surface ocean seawater, for several reasons:

- (1) It is a major and relatively invariant component of continental materials; the composition of aluminosilicate dust has been assumed to be relatively invariant, and the generally accepted value is 8.0% Al by weight (Wedepohl, 1995). Further-

\* Corresponding author. Tel.: +31-27-21-8082699; fax: +31-27-21-8083342.

E-mail address: [kramer@sun.ac.za](mailto:kramer@sun.ac.za) (J. Kramer).

more, the solubility of aeolian dust has been investigated. Estimates of dust solubility upon contact with rainwater and/or seawater range from 1.5% up to 10%, and the ratio of dissolved to particulate Al in rain events ranges between 1.5% and 5% (Gehlen et al., 2003; Maring and Duce, 1987; Measures and Vink, 2000).

- (2) Surface seawater Al concentrations appear to be driven primarily by dust deposition, as evidenced by the coincidence of the highest Al concentrations with regions of greatest dust deposition. Concentrations in regions devoid of atmospheric input are extremely low ( $< 1$  nM) (Jickells et al., 1994; Measures and Vink, 2000).
- (3) Little of the significant amounts of fluvial Al, delivered into the oceans, escapes the intense scavenging of the estuarine and coastal zones (Hydes and Liss, 1977).

Al does not undergo redox reactions, and removal from the upper water column has been proposed to take place either passive or active. Passive scavenging is thought to occur via inorganic adsorption onto particle surfaces (Hydes, 1983; Orians and Bruland, 1985). Alternatively, numerous examples of a nutrient-like distribution of dissolved aluminium in the water column demonstrate biological uptake of Al, in other words, active Al removal (Chou and Wollast, 1997; Hydes et al., 1988; Stoffyn, 1979). As a result of these removal processes, the residence time of Al in ocean surface waters is relatively short, and has been estimated to be 3–4 years (Orians and Bruland, 1986). In the deep ocean, scavenging rates are considerably reduced, and residence times have been estimated to be between 100 and 200 years (Orians and Bruland, 1985). Deep-water concentrations are semiconservative over short periods of time, since hardly any of the Al scavenged in surface waters is biologically recycled, and there appears to be little input from sedimentary sources (Measures and Edmond, 1990).

Fe, on the other hand, is a recycled trace metal, and may be supplied to the upper water column via atmospheric input. Both wet deposition (rainfall) and dry deposition (dust) contribute largely to local Fe enrichments. Other important Fe sources are rivers and sediments. On the other hand, rapid removal of Fe takes place via biological uptake; particle scavenging

and export to the deeper ocean, and very short residence times ranging from 2 to 4 weeks in surface waters (de Baar and de Jong, 2001; Sarthou et al., 2003) to a few years in deeper waters, are the result (Bowie et al., 2002; de Baar and de Jong, 2001).

Summarising, since Fe supply sources and removal sinks are difficult to ascertain, the quantification of Al levels in the surface and upper ocean is of great significance especially in quantifying Fe atmospheric input.

To date, information on Al distributions in surface open ocean water and the upper water column is still limited on the world ocean scale, and a clear overview of the few publications discussing dissolved Al distributions is given by Gehlen et al. (2003). The equatorial Atlantic region is best described, as the Saharan dust plume is well established to be one of the most important sources of trace metals to the open ocean of the Tropical North Atlantic (Duce and Tindale, 1991). Most of the publications report on Al surface distributions determined during long-range transects, giving rise to clear distribution differences on a large scale, arising from different oceanic regimes and highly variable atmospheric input (Bowie et al., 2002; Helmers and Rutgers van der Loeff, 1993; Kremling, 1985; Measures, 1995; Rutgers van der Loeff et al., 1997; Vink and Measures, 2001). In contrast, the Al distribution in each individual region is much less extensively studied. To our knowledge, only two publications exist to date on Al distribution in a small region of the Saharan dust plume in the Atlantic Ocean. Hydes (1983) reported on only six stations sampling the whole water column with Al surface concentrations ranging from 16 to 32 nM. Somewhat more recently, Gélado-Caballero et al. (1996) sampled close to one of the Canary Islands during spring 1991 and observed surface concentrations that were highly variable, owing to proximity to upwelling regions, dust input and a strong influence of the Canary Islands.

The substantial small-scale differences both groups observed, as well as the lack of an Al/Fe comparison, provided an extra impetus for us to thoroughly map the Canary basin, a region that is highly influenced by Saharan desert input but, surprisingly, hardly described in terms of surface and upper water column Al distributions. We provide new data on Al surface and upper water column distribu-

tions in the Canary basin region, as well as further north towards the Strait of Gibraltar, collected during the IRONAGES III shipboard expedition. The data are compared with distributions of dissolved Fe and major nutrients, and a connection with deposition events is presented.

## 2. Methods

### 2.1. Sampling and filtration

Samples were collected aboard the *R. V. Pelagia* between October 3 and October 29, 2002, during the IRONAGES III shipboard expedition between Ponta Delgada (Azores, Portugal) and Valencia (Spain), shortly interrupted by a port call to Funchal (Madeira) on October 25–26. Samples of the upper water

column (0–150 m) were collected at 20 vertical profile stations. In addition, two deep casts (0–4000 m) were performed during the cruise. Underway surface sampling was conducted during transit between the stations in a box roughly from latitude 25°N to 32°N and longitude 17°W to 25°W, and an additional transect between Madeira (16.91°N, 32.64°W) and the Strait of Gibraltar. The cruise track and positions of the sampling stations are depicted in Fig. 1, and additional station details are listed in Table 1.

For the CTD sampling, an ultraclean rosette sampler attached to an all-Kevlar cable with internal signal cables was used. Seawater samples were collected from Teflon coated PVC General Oceanics 12 l Go-Flo sampler bottles in a class 1000 clean container. At one of the deep casts, the ultraclean CTD Rosette sampling system was successfully verified for DFe versus individual Go-Flo samples mounted on a 6 mm

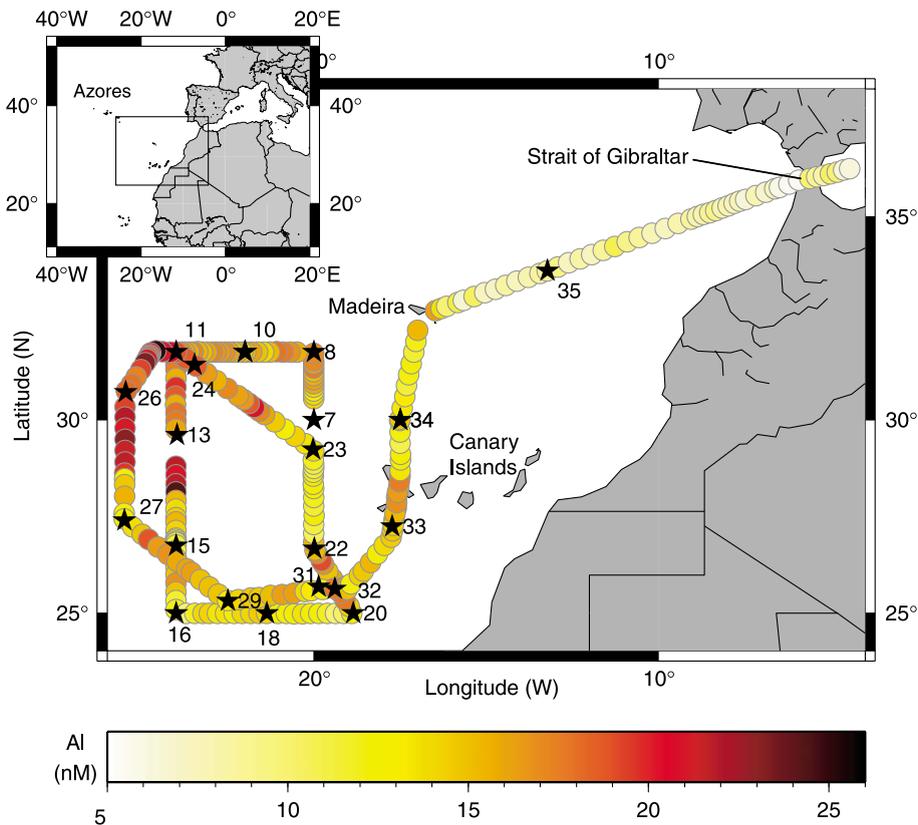


Fig. 1. Contour map showing sea-surface dissolved Al concentrations during the IRONAGES III cruise from October 7–29 aboard *R. V. Pelagia* in October 2002. All stations are labelled as stars in the figure. A smaller scale of the research area is given in the inset map.

Table 1  
Listing of station details

Station, cast	Date	Latitude (N)	Longitude (W)	Type of sample
7, 4	07/10/2002	30.00	20.00	CTD 0–150 m
8, 1	08/10/2002	31.71	20.00	CTD 0–150 m
10, 1	09/10/2002	31.71	22.00	CTD 0–150 m
10, 2	09/10/2002	31.71	22.00	CTD 0–4000 m
11, 1	10/10/2002	31.71	24.00	CTD 0–150 m
13, 1	11/10/2002	29.62	23.98	CTD 0–150 m
15, 1	12/10/2002	26.78	24.00	CTD 0–150 m
16, 1	13/10/2002	25.00	24.00	CTD 0–150 m
18, 1	14/10/2002	25.00	21.37	CTD 0–150 m
20, 1	15/10/2002	25.00	18.86	CTD 0–150 m
22, 1	16/10/2002	26.70	19.99	CTD 0–150 m
23, 1	17/10/2002	29.25	20.03	CTD 0–150 m
24, 1	18/10/2002	31.39	23.47	CTD 0–150 m
26, 1	19/10/2002	30.70	25.47	CTD 0–150 m
27, 1	20/10/2002	27.43	25.50	CTD 0–150 m
29, 1	21/10/2002	25.33	22.50	CTD 0–150 m
31, 1	22/10/2002	25.70	19.87	CTD 0–150 m
32, 1	22/10/2002	25.64	19.39	CTD 0–150 m
33, 1	23/10/2002	27.27	17.73	CTD 0–150 m
34, 1	24/10/2002	30.00	17.50	CTD 0–150 m
34, 2	24/10/2002	30.00	17.50	CTD 0–4000 m
35, 1	27/10/2002	33.70	13.22	CTD 0–150 m

Kevlar hydrowire. The water was filtered through Sartobran 0.2  $\mu\text{m}$  cartridge filters and acidified manually to pH 1.8 by the addition of 100  $\mu\text{l}$  three times quartz-distilled (3QD)  $\text{HNO}_3$  per 100 ml sample.

Underway surface seawater samples ( $\sim 1$ – $2$  m depth) were collected every 1–2 h when the Rosette sampler was not in use, through a towed torpedo-shaped ‘fish’ fitted with a Teflon FEP nose tube and deployed off the crane arm of a hydrographic winch at a distance of  $\sim 5$  m from the ship’s starboard side. The water was pumped on-board through acid-washed braided PVC tubing and filtered in-line through a Sartobran-P polypropylene cartridge unit with 0.2  $\mu\text{m}$  cellulose acetate filter membrane (Sartorius, Epsom, UK) in a class-1000 clean container laboratory and acidified manually to pH 1.8 by the addition of 100  $\mu\text{l}$  3QD  $\text{HNO}_3$  per 100 ml sample (de Jong et al., 2000).

## 2.2. Al analysis

Dissolved Al determinations were conducted based on a method developed by Resing and Measures (1994). All acidified samples were left for at least 1

h before further processing. The samples were then manually buffered to  $\text{pH } 4.7 \pm 0.1$  with ultraclean ammonium acetate. In a continuous flow system, Al was preconcentrated (180 s) on a column containing TSK HW-40C gel (TosoHaas, Germany) modified with 8-hydroxyquinoline (Landing and Bruland, 1987). Next, the column was rinsed (60 s) with MQ water (Millipore Milli-Q deionised water  $>18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) to remove possibly interfering salts. The Al was subsequently eluted (250 s) from the resin and released into the FIA system with a 0.075 M HCl (Suprapure, Merck) solution in MQ.

The eluted Al reacted with a lumogallion solution in ammonium acetate to form an Al-lumogallion chelate complex, which is detected by its fluorescence. The complex was mixed in a 10 m mixing coil placed in a water bath ( $60^\circ \text{C}$ ). Further mixing in a 3 m mixing coil was performed with a 2.5% Brij-35 solution in MQ, a detergent used to increase the sensitivity (Resing and Measures, 1994). After mixing, the emission of the fluorescent complex was detected on a flow-through 470 Waters fluorometer. The excitation and emission wavelengths were set to 484 and 552 nm, respectively. Dissolved Al concentrations (measured in duplicate) were calculated from the peak heights, measured from a Kipp BD111 recorder.

Calibration lines were obtained using standard additions (0–30 nM Al, obtained from a 5000 nM Al stock solution) to a filtered and acidified (pH 1.8) seawater batch of low concentration Al, collected underway. Everyday a new calibration was performed with freshly prepared calibration solutions. Blank correction (instrumental and MQ blank) was done by subtracting an acidified, non-buffered seawater sample blank. The reagent blank obtained via double spiking of a seawater sample with acid and buffer was lower than the detection limit. The limit of detection was observed to be about 0.7 nM (defined as three times the standard deviation of the blank) and the typical precision at the average surface concentration of 14.2 nM was 2.3%.

## 2.3. Additional analyses

The salinity (conductivity), temperature and depth (pressure) were measured using a CTD Seabird mounted in the Rosette sampler. While passing a

transect, the salinity and temperature of the surface water were recorded with an automated thermosalinograph coupled to a computer for data storage (de Baar et al., 1999).

The concentrations of dissolved Fe (DFe) in filtered samples from the fish and Go-Flo bottles were measured according to a chemiluminescence method adapted from Obata et al. (1993). Samples were acidified to pH 2.0 using 100  $\mu\text{l}$  of HCl (ultrapure, Merck) per 100 ml of sample at least 1 h before analysis. The detection limit defined as three times the standard deviation of the blank was equal to 0.03 nM. A complete data set of DFe will be presented elsewhere (Sarthou et al., in preparation).

Inorganic major nutrients ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Si}(\text{OH})_4$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ) were determined following standard procedures (Grashoff et al., 1983). The samples were collected in a high-density polyethylene sample bottle, filtered over a 0.20  $\mu\text{m}$  acrodisc filter and stored in the dark at 4 °C in a polyethylene cup. All samples were analysed within 8 h on a Technicon TrAAcs 800 autoanalyser, except for some silicate samples, which were analysed within 24 h. The detection limit was 0.03  $\mu\text{M}$  for  $\text{NO}_3^-$ , 0.03  $\mu\text{M}$  for  $\text{NO}_2^-$ , 0.1  $\mu\text{M}$  for  $\text{Si}(\text{OH})_4$ , 0.1  $\mu\text{M}$  for  $\text{NH}_4^+$  and 0.01  $\mu\text{M}$  for  $\text{PO}_4^{3-}$ . Cell counts and cell properties (size, chlorophyll *a* fluorescence and spines/cell surface) were determined using a bench top flow cytometer (Coulter XL-MCL).

Two dust samplers containing acid washed filters were mounted on top of the bridge of Pelagia.

### 3. Results and discussion

#### 3.1. General characteristics of the studied site

The Canary Basin occupies a large part of the NW African margin, and its boundaries are roughly defined by a triangle between the Azores and the African coast between 10N and 30N. In most of the mapped box in the basin between 17–25W and 25–32N, as well as the transect from the Canary basin via Madeira to the Strait of Gibraltar, the following low surface concentrations of the major nutrients were observed: 0.2–0.5  $\mu\text{M}$   $\text{Si}(\text{OH})_4$  (hereafter abbreviated as Si), 0.01–0.04  $\mu\text{M}$   $\text{PO}_4^{3-}$ , 0.1–0.4  $\mu\text{M}$   $\text{NH}_4^+$ , <0.05  $\mu\text{M}$   $\text{NO}_3^-$ , <0.03  $\mu\text{M}$   $\text{NO}_2^-$ . These values are typical for

the oligotrophic North Atlantic Gyre, and even somewhat lower than previous observations in this region (Bowie et al., 2002; Rutgers van der Loeff et al., 1997). As a consequence, very low phytoplankton numbers were observed. However, a chlorophyll *a* maximum was found at greater depth between 70 and 100 m.

The Canary Current, which flows along the African coast from 30N towards 10N and offshore to 20 W and entrains upwelled coastal water, might play a significant role in the east/southeast part of our study area. The temperature distributions of the upper water column have been determined at all stations, which have been depicted in E–W transects at various latitudes (Fig. 2a–c). The transects at latitude 25.0–25.7N and latitude 30.7–31.7N (Fig. 2a and c) clearly indicate a wind-mixed layer of some 40–60 m depth. Below the mixed layer, a sharp thermocline exists at higher latitude, which becomes weaker towards the south of the studied site. Moreover, the isotherms do not suggest strong upwelling in most of the mapped region, and temperatures gradually decreased with increasing depth. Only the E–W transect at latitude 26.7–27.4N (Fig. 2b) shows shoaling of warmer water going from west to east. Probably the water masses are more influenced by the close proximity of the Canary Islands. Besides, the N–S Transect at 24W (Fig. 2d) shows a conservative trend from warmer waters in the south of the mapped region, towards cooler waters up north.

#### 3.2. Surface water

##### 3.2.1. Al distributions

Underway sea-surface concentrations of dissolved aluminium are shown in Fig. 1. The highest concentrations of 22–25 nM Al were observed in the northwest part of the Canary basin, whereas the values in the south region were considerably lower (ca. 12–14 nM). North of Madeira, the Al concentrations dropped rapidly below 10 nM, reaching values as low as 6–7 nM just before the Strait of Gibraltar. After a small increase in this region (to around 10 nM), the values decreased again to similar values as before the Strait of Gibraltar.

The above mentioned concentrations in the Canary basin are in concordance with most of the reported values (unfiltered samples, Al concentrations 10–20

nM) in this region (Bowie et al., 2002; Helmers and Rutgers van der Loeff, 1993; Hydes, 1983). The high concentrations observed southwest of Madeira and west of the Canary Islands are indicative of substantial atmospheric input. Still, deposition events were only

sporadic during a month's cruise, as only once dust was clearly detectable on the filters. Besides, little rain was met. A few isolated showers were crossed, and on one occasion more substantial amounts of rain were collected (30 ml). Unfortunately, these quantities were

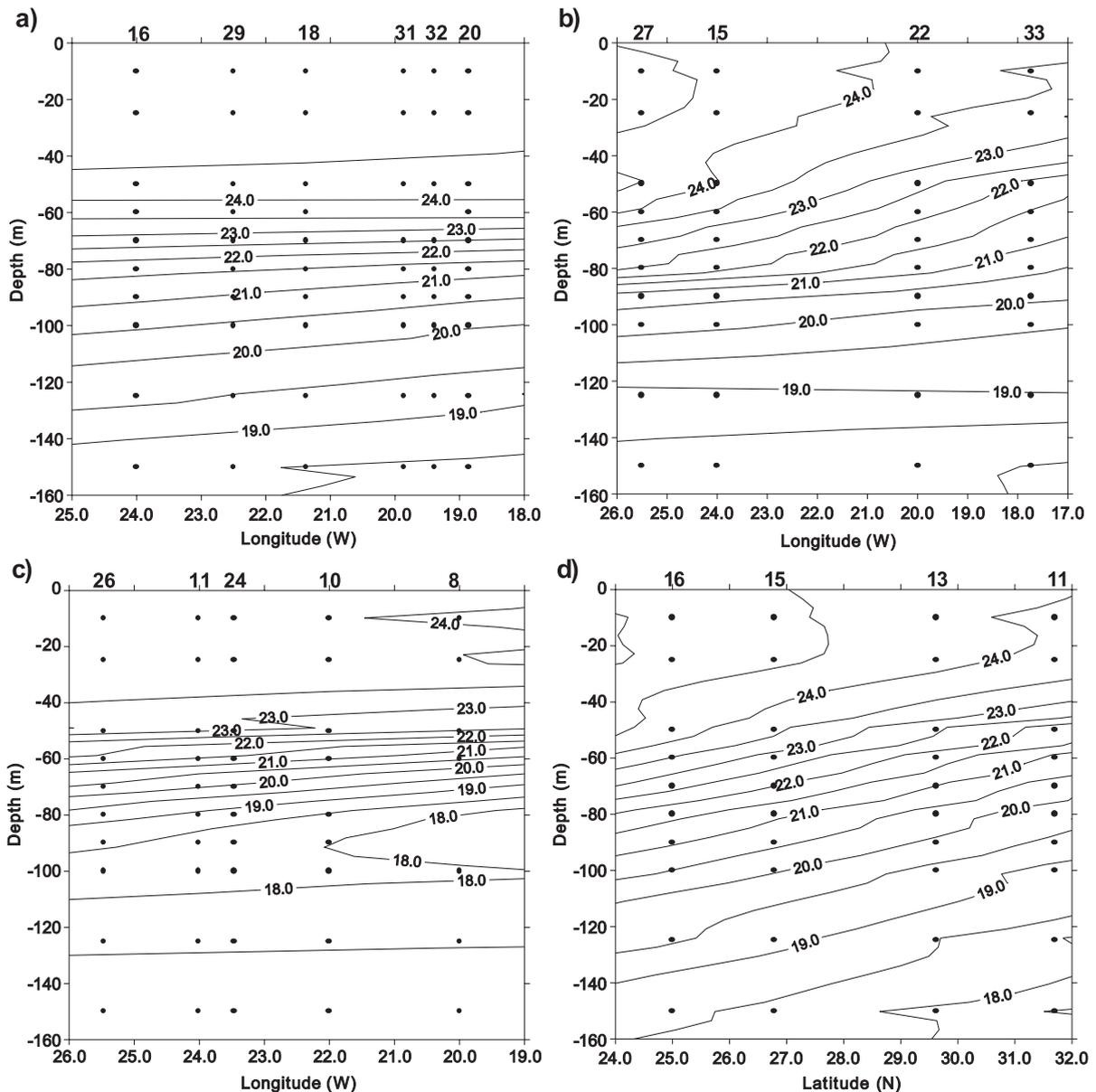


Fig. 2. The upper water column (0–150 m) temperature distribution for an E–W Transect (a) at latitude 25.0–25.7N (stations 16, 18, 20, 29, 31, 32), (b) at latitude 26.7–27.4N (stations 15, 22, 27, 33), (c) at latitude 30.7–31.7N (stations 8, 10, 11, 24, 26) and (d) for a N–S Transect at 24.0W (stations 11, 13, 15, 16). Measured depths are marked • and bold numbers above the figures indicate the stations of the depth profiles.

too small to have any effect on the Al concentration in surface seawater. The levels of dissolved Fe, Si and salinities also remained unaffected, proving the strong dilution in the wind mixed layer in this region. The coincidence of a wet deposition event with dust storms, a situation that would most likely have led to Al enrichments, was not observed.

The slight increase in Al surface concentrations we observed while sailing very close to the Canary Islands (Fig. 3), as well as close to Madeira, might be attributable to some coastal run-off from the islands.

The dramatic drop of dissolved Al once north of Madeira indicates a much lower dust input, typical of the depleted North Atlantic Seawater, and Al concentrations were much alike earlier reported values (Helmers and Rutgers van der Loeff, 1993).

Concluding, on a large scale the mapped region can be divided into two separate zones, with the Canary basin clearly receiving higher atmospheric input than the region between Madeira and the Strait of Gibraltar. Using these dissolved Al surface water concentrations, a rough estimation of the average annual dust deposition can be made, apply-

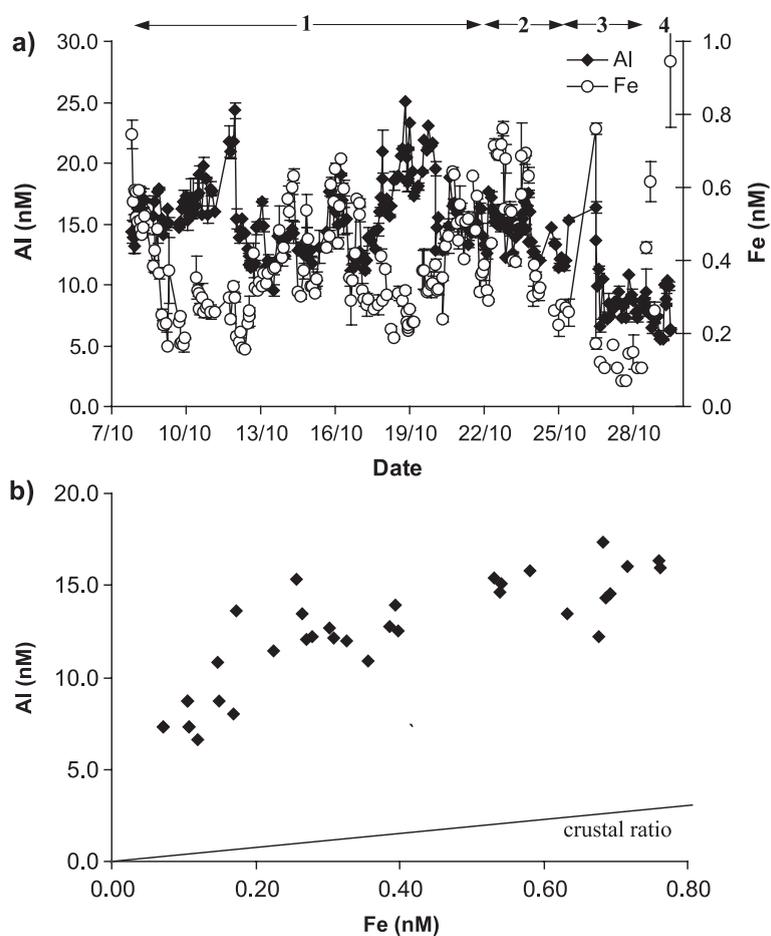


Fig. 3. (a) The surface water distribution of dissolved Al (nM) and dissolved Fe (nM) during the IRONAGES III cruise from October 7–29, 2002. The dates 7/10–22/10 (section ← 1 →) depict the transect in the Canary basin. The dates 22/10–25/10 (section ← 2 →) depict the transect through the Canary Islands to Madeira. The dates 25/10–28/10 (section ← 3 →) depict the transect from Madeira to the Strait of Gibraltar and the transect through the Strait of Gibraltar is marked 4. The very high concentrations of Fe (~ 7 nM), recorded in the Strait of Gibraltar fall outside the scale of the figure. (b) The relationship between dissolved Al and Fe in surface waters between the Canary Islands and the Strait of Gibraltar (sections ← 2 → and ← 3 →). The crustal ratio (Al/Fe=3.8 mol/mol) is plotted for comparison.

ing the model of Measures and Brown (1996) and Measures and Vink (2000). Assuming 3.25% average dust dissolution, a residence time of 5 years and a surface-mixed layer of 50 m, average annual fluxes in the studied region range from 0.7–0.9 g dust  $\text{m}^{-2} \text{year}^{-1}$  in the region between Madeira and the Strait of Gibraltar to 1.0–2.2 g dust  $\text{m}^{-2} \text{year}^{-1}$  in the Canary basin. These values are similar to the dust deposition rates as calculated in the model by Duce et al. (1991), forecasting values close to 1 g dust  $\text{m}^{-2} \text{year}^{-1}$  in the former region and between 1 and 10 g dust  $\text{m}^{-2} \text{year}^{-1}$  in the latter region.

### 3.2.2. Al versus Fe

The clear differentiation between different zones in terms of atmospheric input is also supported by the observed DFe concentrations (Fig. 3a). The highest concentrations of both Al and Fe were found in the Canary basin (12 to 25 nM Al, 0.16 to 0.76 nM Fe) and much lower concentrations in the other region between Madeira and Gibraltar (6 to 10 nM Al, 0.07 to 0.17 nM Fe). A strong elevation of DFe levels in the Strait of Gibraltar ( $\sim 7.0$  nM, Sarthou et al., in preparation), coinciding with highly elevated levels of all the nutrients and a decrease of sea-surface temperatures (from 21 to 17 °C) and salinity, may be associated with upwelling of Fe-rich waters probably due to a strong input from shelf sediment, together with high river discharge from the Tinto and Odiel rivers (Elbaz-Poulichet et al., 2001).

On the transect north of the Canary Islands and, more pronounced, north of Madeira, a reasonably strong positive correlation was observed between Fe and Al distributions (Fig. 3b). The assumption of congruent dissolution of Al and Fe from dust particles (applying an average Fe dissolution from mineral dust of 6.2%; Zhu et al., 1997, and 5% for Al) containing 8.0% Al and 4.3% Fe (Wedepohl, 1995) would result in a theoretical Al/Fe ratio of  $\sim 3.1$ . We observed large deviations from this theoretical ratio, with Al/Fe varying roughly from 20 in the southwest to about 100 in the northeast of the Canary basin. Previous observations of similar ratios were done in regions of high deposition (Bowie et al., 2002; Vink and Measures, 2001). The large differences between theoretical and ob-

served Al/Fe ratios can be explained in different ways; the rapid removal of dissolved Fe from aerosol particles due to scavenging or biological uptake will lead to higher Al/Fe ratios. On the other hand, higher dissolution of Al than Fe from dust is likely to occur and will have the same effect on the Al/Fe ratio (Bowie et al., 2002; Maring and Duce, 1987; Measures and Vink, 1999; Vink and Measures, 2001) and large dust inputs in the surface will not necessarily lead to a linear increase in both Al and DFe concentrations (Guieu et al., 2002; Zhu et al., 1997). Additionally, since the proportion of Fe in soils and rocks varies significantly (Taylor and McClennan, 1985) whereas Al proportions are more constant (Wedepohl, 1995), a much higher Al/Fe molar ratio than 3.8 in the dust source of our study site cannot be ruled out.

On a smaller scale, in the Canary basin, no correlation can be found between the dissolved Al and Fe surface concentrations. The abovementioned differences in biological uptake and residence times of the two elements, combined with the observation that deposition events were scarce during the time of the cruise, provide a good explanation for the lack of covariance in the Canary basin between Al and Fe. Other groups also observed that deposition events in this region are highly episodic and irregular in magnitude (Jickells and Spokes, 2001; Spokes et al., 2001; Torres-Padron et al., 2002).

### 3.2.3. Al versus Si

Dissolved Al surface concentrations have been compared with dissolved Si and the continuous transect surface distributions have been plotted against the date in Fig. 4a. There appears to be a good correlation (Fig. 4b) between dissolved Al surface seawater concentrations and Si in the Canary basin and during the transect from the Canary basin and the Strait of Gibraltar.

This Al/Si relationship might be explained in terms of the well-known structural association of Al and Si in biogenic siliceous particles (Dixit et al., 2001; Gehlen et al., 2002; van Bennekom et al., 1991). Partial redissolution of biogenic Si also induces an increase in dissolved Al. A strong contribution of Al redissolution from biogenic silica implies that the Al/Si observed in diatom frustules (ranging from  $<10^{-3}$  to a maximum of 0.011 (van Benne-

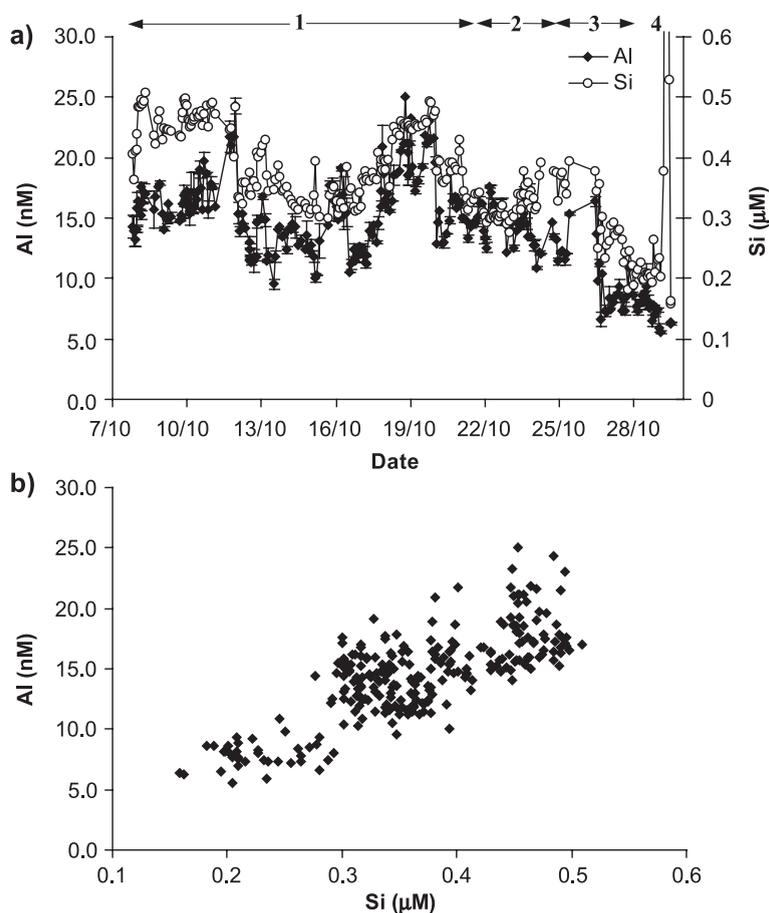


Fig. 4. (a) The surface water distribution of dissolved Al (nM) and Si ( $\mu\text{M}$ ) during the IRONAGES III cruise from October 7–29, 2002. The dates 7/10–22/10 (section  $\leftarrow 1 \rightarrow$ ) depict the transect in the Canary basin. The dates 22/10–25/10 (section  $\leftarrow 2 \rightarrow$ ) depict the transect through the Canary Islands to Madeira. The dates 25/10–28/10 (section  $\leftarrow 3 \rightarrow$ ) depict the transect from Madeira to the Strait of Gibraltar. The high concentrations of Si ( $\sim 1.1 \mu\text{M}$ ), recorded in the Strait of Gibraltar, fall outside the scale of the figure. (b) The relationship between dissolved Al and Si in surface waters along the whole transect, except for section 4 (the transect through the Strait of Gibraltar).

kom et al., 1991; van Beusekom et al., 1997)) be reflected in the dissolved Al/Si ratios. A clear example comes from Chou and Wollast (1997) who observed a very strong positive correlation between Al and Si through the upper 1000 m of the water column in the western Mediterranean which could be explained in terms of biologically related processes. However, even the highest reported Al/Si ratios in biogenic silica are at least three times lower than the Al/Si ratios we observed in our surface water, which were  $\sim 0.04$  on average. This observation, together with the very low surface concentrations of phytoplankton (and consequently diatom frustules) throughout most of our studied

region further preclude an important contribution of structurally associated Al/Si in explaining our Al/Si covariance.

To our knowledge, the only other report of a positive covariance between Al and Si in open ocean surface waters of the Atlantic Ocean comes from Rutgers van der Loeff et al. (1997). They observed a positive relationship of similar magnitude to our findings (Al/Si  $\sim 0.04$ ) on a cruise from 10N to 35N in the North Atlantic. They attributed the relationship to mixing of relatively Al- and Si-rich water masses of tropical origin with Al- and Si-depleted waters from the Canary Current. Clearly, they covered a much larger range in latitudes than we did, giving rise to

much bigger regional differences. It is therefore surprising that we find such a strong covariance in a relatively small region as well.

Conservative mixing of different water masses requires the presence of this covariance throughout the entire mixed layer (~50–60 m). Indeed, in the mixed layer of the shallow vertical stations a, somewhat weaker, positive correlation between Al and Si with a similar ratio ( $\text{Al/Si} \sim 0.04$ ) was observed. Below the mixed layer, no correlation between the two was found. The positive relationships between both surface Al and Si concentrations and salinity (Fig. 5) and, less pronounced, between Al and Si and temperature (not shown) also suggest a conservative mixing correlation. Based on these observations, a rough estimation of two mixing end members (EM) has been proposed with the follow-

ing composition: EM 1 is composed of highly saline (close to 38‰) and warm ( $>25\text{ }^{\circ}\text{C}$ ) waters most likely from the Canary Current, whereas EM 2 possibly consists of North Atlantic Central Water which is cooler (ca  $18\text{ }^{\circ}\text{C}$ ) and somewhat less saline (ca. 36.7‰) close to the surface (Tomczak and Godfrey, 1994).

### 3.3. Upper water column

The vertical profile of Al at all shallow (0–150 m) stations is listed in Table 2, along with the corresponding depths, dissolved Si and salinity data. Relatively high salinities were found in the mixed layer, ranging from 36.6 to 37.3, characteristic of this North Atlantic region with high evaporation and little rainfall. The Si concentrations follow a

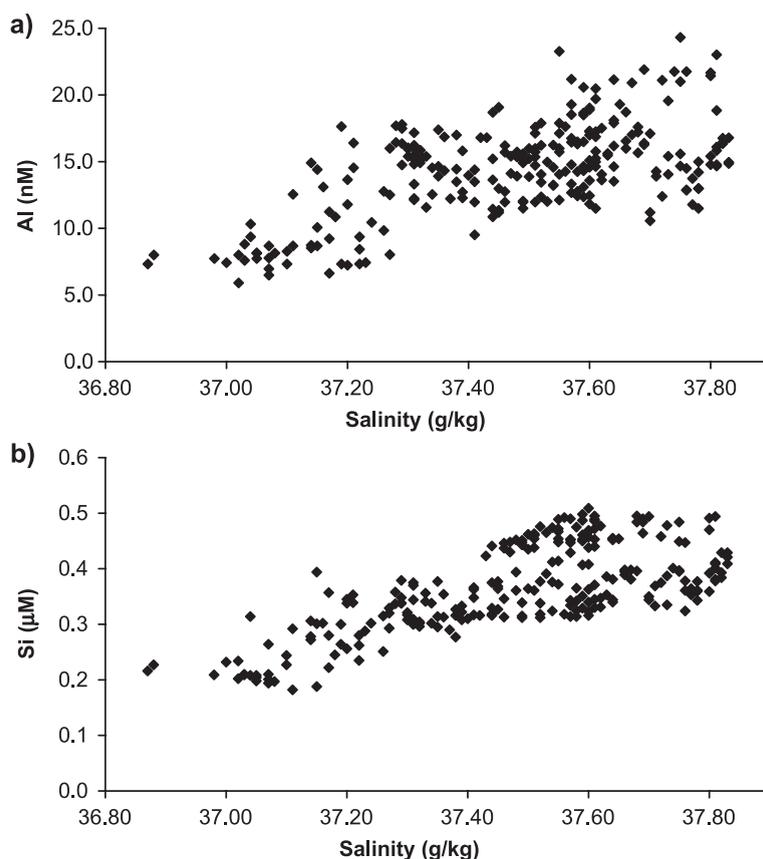


Fig. 5. (a) The relationship between dissolved Al and salinity in surface waters along the whole transect, except for section 4 (the transect through the Strait of Gibraltar). (b) The relationship between Si and salinity in surface waters along the whole transect, except for section 4.

Table 2

Vertical profile (0–150 m depth) listing of determinations of Al (nM), Si ( $\mu\text{M}$ ) and salinity ( $\text{g}/\text{kg}$ ) with respect to sampling depth

Station	Depth (m)	Al (nM)	Si ( $\mu\text{M}$ )	Salinity ( $\text{g}/\text{kg}^{-1}$ )	Station	Depth (m)	Al (nM)	Si ( $\mu\text{M}$ )	Salinity ( $\text{g}/\text{kg}^{-1}$ )
7	10	20.5	0.36	37.024	23	10	11.4	0.36	36.949
	25	19.6	0.45	37.022		25	11.0	0.36	36.948
	50	25.5	0.43	36.787		50	11.1	0.35	36.919
	60	17.1	0.40	36.761		60	12.0	0.38	36.738
	80	19.4	0.52	36.734		70	12.4	0.41	36.700
	90	20.0		36.714		80	12.8	0.43	36.665
	100	17.8	0.60	36.656		90	12.2	0.45	36.645
	125	17.4	0.73	36.575		100	11.8	0.49	36.637
	150	23.6	0.79	36.466		125	12.6		36.531
	8	10	19.5	0.52		37.128	24	150	14.8
25		17.6	0.52	37.127	10	16.8		0.46	37.007
50		14.7		36.946	25	17.0		0.43	37.006
60		15.1	0.51	36.720	50	14.4		0.48	36.708
100		14.2	0.61	36.590	60	13.9		0.48	36.662
125		14.5	0.79	36.509	70	16.1			36.653
10	10		0.44	37.002	26	80	17.5	0.56	36.683
	25	11.2	0.43	37.001		90	15.4	0.69	36.655
	50	12.2	0.48	36.694		100	16.0	0.74	36.610
	60	9.3	0.47	36.554		150	18.9	1.08	36.464
	80	8.8	0.55	36.502		10	17.8	0.48	37.104
	90	10.9	0.65	36.474		25	18.6	0.47	37.103
	100	9.3	0.78	36.448		50	21.7	0.46	37.098
	125	11.7	1.14	36.359		60	15.6	0.47	36.868
11	150	11.4		36.322	70	16.3	0.48	36.751	
	10	19.9	0.51	37.017	80	15.9	0.52	36.656	
	25	18.3	0.48	37.017	90		0.56	36.600	
	60	18.9	0.49	36.710	100	14.7	0.61	36.570	
	70	24.2		36.723	125	18.7		36.503	
	80	18.4		36.727	150	20.3	1.10	36.415	
	90	17.4	0.56	36.741	10	15.4	0.43	37.280	
	100		0.58	36.663	25	15.1	0.38	37.279	
	125	18.0	0.82	36.534	50	16.0	0.39	37.275	
	150	19.0	1.00	36.473	60	15.8	0.40	37.205	
13	10	19.2	0.50	37.286	70	15.0	0.41	37.104	
	25	20.2	0.48	37.282	80	14.7	0.47	36.939	
	50	19.6	0.48	37.217	90	16.0	0.49	36.911	
	60	19.8	0.52	37.002	100	17.4	0.52	36.874	
	70	20.3	0.54	36.981	125	19.5	0.49	36.708	
	80	22.5		36.941	150	18.5	1.09	36.618	
	90	18.7	0.55	36.916	10	13.5	0.38	37.046	
	100	18.5	0.56	36.864	25	15.0	0.35	37.052	
	125	19.1	0.63	36.774	50	11.8	0.36	37.019	
	150	19.2	0.69	36.714	60	11.2	0.37	37.072	
15	10	12.4	0.39	37.293	70	11.0	0.36	37.062	
	25	14.3	0.37	37.304	80	12.5	0.46	36.983	
	50	12.7	0.37	37.302	90	13.5	0.51	36.954	
	60	14.2	0.39	37.153	100	14.2	0.52	36.920	
	70	15.4	0.41	37.058	125	17.3		36.841	
	80	13.7	0.44	36.965	150	15.9	0.85	36.767	
	90	14.0	0.50	36.911	25	12.3	0.33	36.798	
	100	13.3	0.54	36.861	50	11.4	0.34	36.711	

(continued on next page)

Table 2 (continued)

Station	Depth (m)	Al (nM)	Si ( $\mu\text{M}$ )	Salinity ( $\text{g}/\text{kg}^{-1}$ )	Station	Depth (m)	Al (nM)	Si ( $\mu\text{M}$ )	Salinity ( $\text{g}/\text{kg}^{-1}$ )	
15	125	15.1	0.75	36.757		70	11.0	0.34	36.688	
	150	15.8	1.05	36.654		80	11.4	0.34	36.668	
16	10	8.9	0.40	36.781	32	90	11.5	0.34	36.690	
	25	9.1	0.39	36.788		125	9.6	0.36	36.717	
	60	11.8	0.41	37.122		150	11.6	0.91	36.609	
	70	11.8	0.42	37.059		10	14.2	0.30	36.820	
	80	12.2	0.48	37.038		25	12.6	0.31	36.819	
	90	13.7	0.52	37.008		50	13.0	0.32	36.792	
	100	13.4	0.6	36.944		70	11.8	0.32	36.733	
	125	15.9	0.87	36.836		80	14.8	0.31	36.738	
	150	16.2	1.44	36.656		90	13.8	0.32	36.726	
	18	10	15.8	0.35		37.059	33	100	12.5	0.31
25		15.7	0.34	37.054	125	12.0		0.37	36.733	
50		14.6	0.34	37.051	150	10.3		0.53	36.696	
60		12.0	0.37	36.982	25	13.9		0.37	36.717	
70		13.6	0.39	37.001	60	15.4		0.42	36.752	
80		11.0	0.47	36.875	70	15.1		0.43	36.740	
90		12.8	0.63	36.856	80	13.5		0.42	36.723	
100		13.6	0.79	36.810	90	12.2		0.41	36.699	
125		14.7	0.76	36.669	100	13.1		0.44	36.672	
150		16.7	1.45	36.568	125	15.2		0.44	36.665	
20	10	12.4	0.36	36.663	34	10	15.2	0.41	37.040	
	25	11.3	0.33	36.654		25	15.4	0.42	37.046	
	50	9.3	0.33	36.472		50	15.0	0.41	37.080	
	60	7.2	0.43	36.448		60	15.2	0.48	36.764	
	70	6.7	0.55	36.419		70	13.9	0.50	36.706	
	80	6.1	0.61	36.393		80	13.6	0.51	36.735	
	90	7.0	0.68	36.377		90	13.6	0.54	36.704	
	100	8.1	0.77	36.454		100	13.2	0.61	36.653	
	125	12.2	0.32	36.623		125	14.8	0.8	36.530	
	150	14.4	1.52	36.549		150	13.3	1.13	36.420	
22	10	16.7	0.36	37.008	35	25	11.2	0.32	36.658	
	25	15.6	0.33	37.016		50	8.9	0.30	36.652	
	50	16.6	0.38	36.912		70	8.9	0.39	36.443	
	60	17.2	0.41	36.844		80	9.8	0.49	36.394	
	70	19.0	0.48	36.812		90	10.2	0.55	36.372	
	80	18.1	0.52	36.809		100	12.2	0.71	36.356	
	90	18.8	0.6	36.833		125	13.8	1.04	36.268	
	100	18.5	0.62	36.782		150	12.8	1.26	36.212	
	150	18.9	1.04	36.552						

gradual trend with values less than  $0.5 \mu\text{M}$  in the mixed layer gradually increasing with depth to values  $>1 \mu\text{M}$ .

The vertical profiles of Al range roughly from 8 to 24 nM. These values are in good agreement with published data by Hydes (1983) and by Measures (1995) in this region but much lower than those reported by Gélado-Caballero et al. (1996) close to the Canary Islands. Presumably, the Al concentrations close to the islands were more elevated due to runoff

input from the islands. Additionally, during their sampling in springtime, they observed strong upwelling effects of Al-rich warmer waters in the southwest of their mapped region ( $27-27.5\text{N}$ ,  $16-17\text{W}$ ). As was already mentioned in Section 3.1, we did not observe these strong upwelling effects in the region that is most influenced by the Canary Current, neither reflected in the temperature distributions (Fig. 2a), nor in the Al distributions (Fig. 6a) of the upper water column. Moreover, the temperature distribution

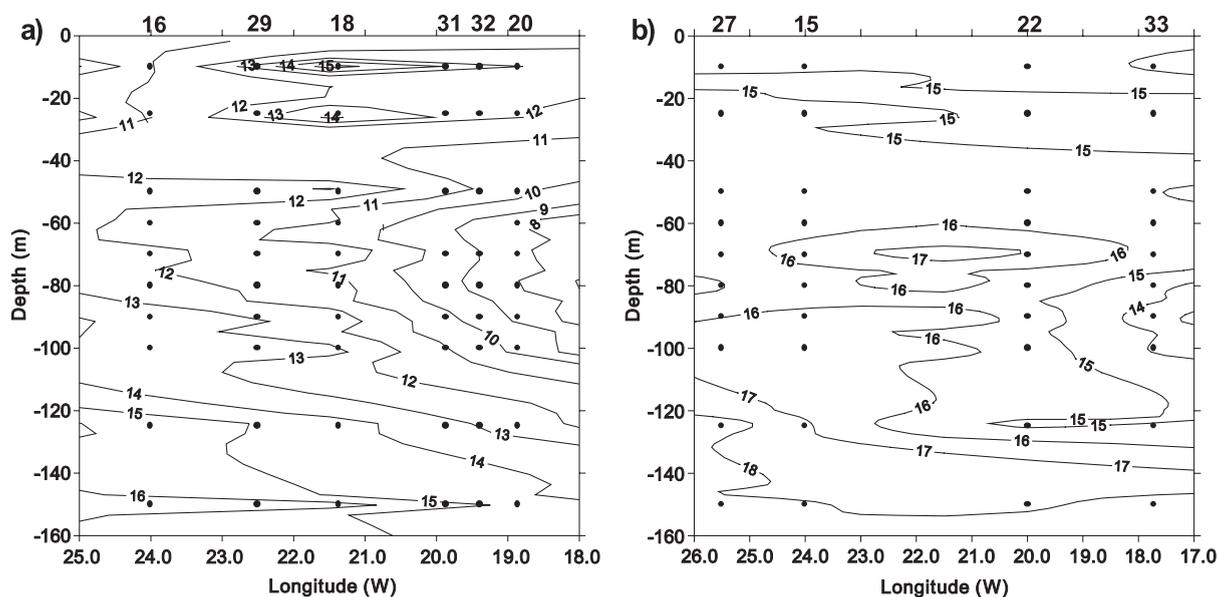


Fig. 6. The upper water column (0–150 m) Al distribution for an E–W transect (a) at latitude 25.0–25.7N (stations 16, 18, 20, 29, 31, 32), (b) at latitude 26.7–27.4N (stations 15, 22, 27, 33). Measured depths are marked • and bold numbers above the figures indicate the stations of the depth profiles.

around the Canary Islands, which showed signs of upwelling of colder water (Fig. 2b), was not related with Al concentrations, as can be seen in Fig. 6b.

About half of the stations show maximum Al levels at the surface (Table 2). The surface maximum is most pronounced at stations 7, 8, 24 and 26, all of which lie in the region with highest surface concentrations, in concordance with our earlier assessment of higher atmospheric input in this region. Still, the surface enrichments observed during this cruise were much lower than those reported by Hydes (1983) for this region, pointing again towards the highly periodical nature of dust input and rapid scavenging to particles after a deposition event.

Stations 18 and 20 show a maximum at the surface and a subsurface minimum at 80–100 m. The minimum is closely related to the chlorophyll *a* maximum (see Fig. 7), which has been found to lie between 70 and 100 m depth for all stations. At most stations, the chlorophyll *a* max is not very pronounced ( $<0.3 \mu\text{g l}^{-1}$ ) as a result of the low phytoplankton values, but at station 20, deployed in the region which was richest in phytoplankton, a maximum of  $0.54 \mu\text{g l}^{-1}$  was measured. The scavenging of Al via inorganic adsorption onto particle

surfaces is a well-known process (Gehlen et al., 2003; Orians and Bruland, 1986) and Al removal appears to be particularly effective at station 20, reducing Al levels by more than 50% to a mere 6 nM at 80 m depth.

### 3.4. Deep water column

Two deep casts have been conducted both in the north of the mapped region, and Al concentrations together with Si concentrations and salinities are depicted in Fig. 8. At both stations 10 and 34, the Si levels increase almost linearly with depth, typical of this strongly recycled major nutrient. Both casts show a very similar Al pattern, with the lowest values (9–16 nM) in the upper 200 m. The concentrations reach a maximum (23–25 nM) at mid-depth (1000–1300 m). Closer to the bottom, the Al concentrations stabilise to 19–22 nM. The maximum around 1 km depth is closely coincident with a salinity maximum, and is caused by Mediterranean Outflow Water (MOW) (Cabeçadas et al., 2002; Hydes, 1983; Measures, 1995). The MOW water, containing Al from subducted surface water and dissolved from detrital particles (Hydes et al., 1988), is rich in Al and Si and

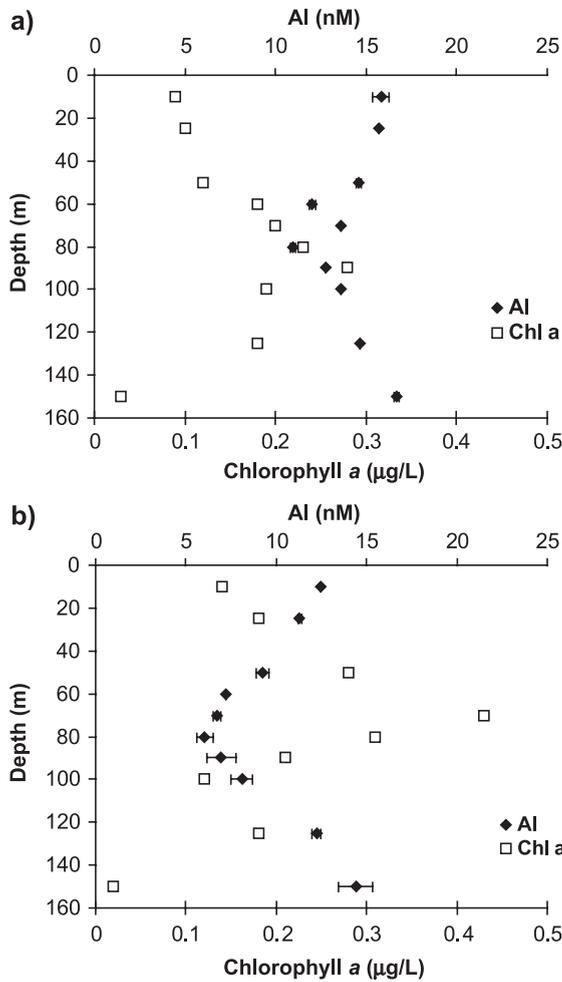


Fig. 7. Vertical profile of Al and chlorophyll *a* in the upper water column at (a) station 18 and (b) station 20.

the MOW end member contains a salinity of 38.4 and Al concentrations of  $>100$  nM (Measures and Edmond, 1988). This Al-rich MOW mixes with the overlying North Atlantic Central Water, which contains a salinity of 35.5 at this depth, and the underlying North Atlantic Deep Water (with an observed salinity of 34.9) (Measures, 1995; Tomczak and Godfrey, 1994). Mixing with MOW gives rise to the observed maximum, since both these water masses are much lower in Al. The profile is much alike previously published profiles (Hydes, 1983; Measures, 1995), but less pronounced, as our stations 10 and 34 were taken at a much larger distance from the Strait of Gibraltar. Our results demonstrate the re-

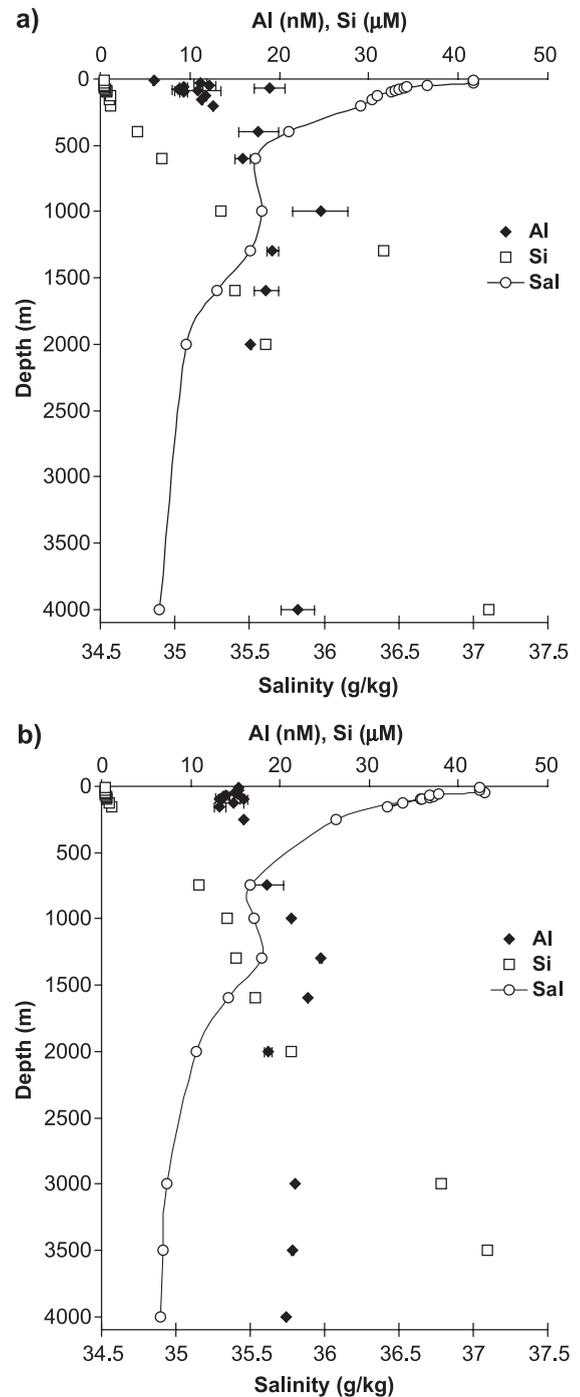


Fig. 8. Deep vertical profile of Al, Si and salinity at (a) station 10 and (b) station 34.

markably long-range influence of MOW at the time of the cruise, as generally this highly saline water, does not quite reach the Canaries (Johnson and Stevens, 2000). The concentrations closer to the bottom do not suggest substantial regeneration of Al from the sediments as no increase is observed. Still, care must be taken not to rule out any Al elevation very close to the bottom (~4300 m at station 34) as a result of diagenetic input.

#### 4. Conclusions

The distribution of dissolved Al in surface seawater in the Canary basin between 17–25W and 25–32N revealed Al concentrations of 12–25 nM, indicative of the well-known high atmospheric input in this region. Concentrations in the basin were highest in the northwest (22–25 nM) and lower (12–14 nM) in the south and concentrations north of Madeira were much lower (6–10 nM), in concordance with a decreased influence of the Sahara dust plume in this region. On a large scale, a supporting argument for this conclusion comes from the coincidence of highest dissolved Al and Fe values in the Canary basin and much lower concentrations between Madeira and the Strait of Gibraltar. Within the Canary basin, no clear correlation could be seen between the two trace elements, which can be explained by the irregularity of aeolian input observed in the region, and the fact that both elements differ significantly in residence times, solubility and scavenging/biological uptake.

The strong positive covariance between surface Al and Si may be the result of conservative mixing of warm, more saline Al- and Si-rich waters with colder waters of lower salinity and poorer in both Al and Si. About half of the shallow stations show an Al surface maximum, with the most pronounced maximum found in the northwest region, where atmospheric input was most prominent. At two stations, a very clear subsurface minimum in Al concentrations was observed at 70–100 m depth. This minimum coincides with the chlorophyll *a* maximum, which was strongest at these two stations, and reflects the apparent effective removal of Al via scavenging onto particles. Deeper down the water column, a maximum is observed at 1000–1300 m, characteristic of the trace metal-rich and nutrient-rich MOW.

Our findings show that on a large-scale the Al concentrations are similar with previously published work. In a smaller region, the possibility to find a covariance of Al with Fe or the major nutrients appears highly dependent on both the season, the time between atmospheric deposition and sample collection and the magnitude of the deposition event.

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