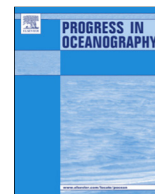




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Atmospheric deposition of soluble trace elements along the Atlantic Meridional Transect (AMT)

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ABSTRACT

We briefly review the role of atmospheric deposition measurements within the Atlantic Meridional Transect (AMT) programme and then go on to present new data on the soluble concentrations of a range of trace metals (Fe, Al, Mn, Ti, Zn, V, Ni and Cu) and major ions in aerosols collected along the AMT transect. The results allow us to identify emission sources of the trace metals particularly in terms of the relative importance of anthropogenic versus crustal sources. We identify strong gradients in concentrations and deposition for both crustal and anthropogenically sourced metals with much higher inputs to the North Atlantic compared to the South Atlantic, reflecting stronger land based emission sources in the Northern Hemisphere. We suggest anthropogenic sources of Ni and V may include an important component from shipping.

We consider the extent to which these gradients are reflected in surface water concentrations of these metals based on the GEOTRACES water column trace metal data. We find there is a clear difference in the concentrations of surface water dissolved Al and Fe between the north and south Atlantic gyres reflecting atmospheric inputs. However for Mn, V or Ni, higher inputs to the North Atlantic compared to the South Atlantic are not clearly reflected in their water column concentrations.

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1. Introduction

There is a long history of studies of the biogeochemical interactions between the atmosphere and the ocean over the North Atlantic dating at least from the Beagle expedition (Darwin, 1846) through classic studies in the early 1970s (Lovelock et al., 1972; Chester et al., 1972; Duce et al., 1975) and more recent studies (e.g. Church et al., 1991; Losno et al., 1992; Rädlein and Heumann, 1995; Norman and Leck, 2005). When the AMT consortium phase was established in 2002, one of its main research themes was the biogeochemical interaction between the surface ocean and atmosphere (Robinson et al., 2006), considering both the impact of the atmosphere on the ocean and the ocean on the atmosphere. Research on the impact of the ocean on the atmosphere within AMT has included work on air-sea exchange of important climate relevant gases such as CO₂ (Lefevre and Moore, 2000), methane and N₂O (Forster et al., 2009) and also the air-sea exchange of gases that play an important role in aerosol formation and cycling processes in the remote marine boundary layer, such as dimethyl sulphide, DMS (Bell et al., 2006; Johnson

and Bell, 2008; Lin et al., 2012) and ammonia (Johnson et al., 2008; Johnson and Bell, 2008; Lin et al., 2016). In the case of ammonia the net air-sea exchange may be from the ocean to the atmosphere or vice versa (Johnson et al., 2008).

Much of the AMT research on the biogeochemical impacts on the ocean of deposition from the atmosphere has focussed on the nutrient elements nitrogen, phosphorus and iron (e.g. Baker et al., 2006b). Although silicon is well recognised as an important nutrient for marine phytoplankton (Moore et al., 2013), it is clear that the atmospheric supply of soluble silicon along AMT is small compared to those of other nutrients, and also compared to the supply of silicon to the euphotic zone from below (Baker et al., 2006b; Krishnamurthy et al., 2010). Hence atmospheric supply of this element has little impact on water column biogeochemistry, with for example one model estimating that atmospheric Si supply is only responsible for sustaining 0.2% of export production (Krishnamurthy et al., 2010). There are important impacts of atmospheric deposition of N, P and Fe on surface water biogeochemistry, but the impact for each nutrient is different. The atmospheric deposition of phosphorus is small in comparison to the magnitude of atmospheric deposition of nitrogen and iron, and also in comparison to phytoplankton requirements for these elements (Moore et al., 2013; Baker et al., 2003, 2007). The overall impact of this N, P and Fe atmospheric deposition is to push the

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underlying water column toward P limitation from a condition of slight excess of P relative to N (Baker et al., 2003; Okin et al., 2011). The atmospheric iron supply (Baker et al., 2013) directly enhances ocean primary production in high latitude high nitrate low chlorophyll waters and also enhances primary production at low latitudes by increasing biological nitrogen fixation, and hence relieves nitrogen limitation and reduces P^* , the surface water excess of P relative to N and the Redfield ratio (Moore et al., 2009; Jickells and Moore, 2015).

The quantitative impacts of atmospheric deposition of N and Fe on ocean productivity are not particularly well constrained, but are generally considered to be significant. Atmospheric N deposition (which is predominantly anthropogenic) has been suggested to support 3–5% of ocean export productivity (Duce et al., 2008; Krishnamurthy et al., 2010).

Total iron deposition is mainly associated with soil dust deposition and predominantly natural (Jickells et al., 2005) but there is an additional input of anthropogenically sourced iron which probably contributes an important input of soluble iron in some areas particularly downwind of large emission source regions (Sholkovitz et al., 2012). The impact of atmospheric dust deposition on water column biogeochemistry depends in part the solubility of the dust-associated iron. Studies within AMT have made an important contribution to the recognition that there are systematic gradients in iron solubility, from low solubility in high dust regions to high solubility in low dust deposition regions (Baker et al., 2006c). The causes of these gradients in solubility are still debated (Baker et al., 2014; Baker and Croot, 2010).

Atmospheric iron deposition is estimated to support 30–50% of global export productivity (Krishnamurthy et al., 2010; Jickells et al., 2014). The atmospheric deposition of dust also directly affects the water column distribution of iron (and other crustally dominated metals such as aluminium), although the link between dust deposition and surface Fe concentrations is not a simple linear one, but one mediated by biological processes. This is particularly evident on the AMT transect where there are strong inter-hemispheric differences in dust loadings due to the Saharan dust plume over the tropical North Atlantic, with much lower dust loadings over the tropical South Atlantic. This leads to higher surface water dissolved iron concentrations and a shorter dissolved iron residence time in the surface waters of the North Atlantic gyre (Ussher et al., 2013), and much lower values of P^* in these waters due to increased nitrogen fixation (Moore et al., 2009).

Atmospheric deposition is a highly variable process in space and time. The spatial gradients and temporal variability within the Saharan dust plume region are particularly marked (Powell et al., 2015) with concentrations at the Cape Verde site, for instance, varying by more than an order of magnitude on time scales of a day reflecting dust storm passages through the region (Patey et al., 2015). However, repeat sampling along the AMT transect has allowed the development of a large data base with which to define the substantial systematic spatial gradients in atmospheric deposition of N, P and Fe that are due to the distribution of source regions and prevailing atmospheric transport pathways (Baker et al., 2010, 2013). This data base also allows comparisons of data and models of atmospheric deposition to the Atlantic Ocean. These reveal good agreement for nitrogen but less so for dust and iron, reflecting the difficulty of modelling the temporally variable emission and transport process for dust associated with dust storms (Baker et al., 2010, 2013).

Our previous work within the AMT programme on the influence of Atlantic atmospheric transport regimes on the distribution and deposition of aerosol trace metals has focused on elements (Fe, Al and Mn) whose major sources are dominated by mineral dust (Baker et al., 2013, 2006b). In these studies, we characterised atmospheric transport (and hence source regions) over the Atlantic

using 5-day air parcel back trajectories. Using this approach (Baker et al., 2010, 2013) we identified seven air transport types relevant to the samples collected for the present study (see Fig. 1): Air transported from the surrounding continental land masses of Europe (EUR), North Africa (and heavily influenced by mineral dust emissions from the Sahara and Sahel: SAH), Southern Africa (SAF), including air impacted by biomass burning emissions (SAB) and South America (SAM), and air that had circulated over the remote North or South Atlantic for at least 5 days prior to collection (RNA and RSA respectively). All of the continental transport types are likely have been impacted by anthropogenic emissions to some extent (Savoie et al., 1989), while marine-derived material inevitably also contributed significantly to the aerosol load in all transport types, since the air passed over the oceans for several days before reaching the ship.

The intense rain shower activity associated with the intertropical convergence zone (ITCZ) along with limited direct air flow across the ITCZ severely limits the transfer of aerosol material between the northern and southern hemispheres. The ITCZ migrates seasonally and was located at ~5–10°N at the time of the AMT cruises we report here.

The zones affected by deposition from the atmospheric transport regimes identified above (Fig. 1) overlap in part, but not completely, with oceanic biogeochemical provinces (Longhurst, 2007). This needs to be considered in assessing the impacts of atmospheric deposition on water column biogeochemistry, since within different ocean biogeochemical provinces physical forcing creates different biogeochemical environments and ecological communities (Robinson et al., 2006) which will respond differently to atmospheric deposition.

Several other trace metals beside Fe have a potential role as nutrients for phytoplankton primary production and bacterial processes (e.g. Zn, Mn, Cu), although evidence for the quantitatively significant role for these metals is currently lacking (Moore et al.,

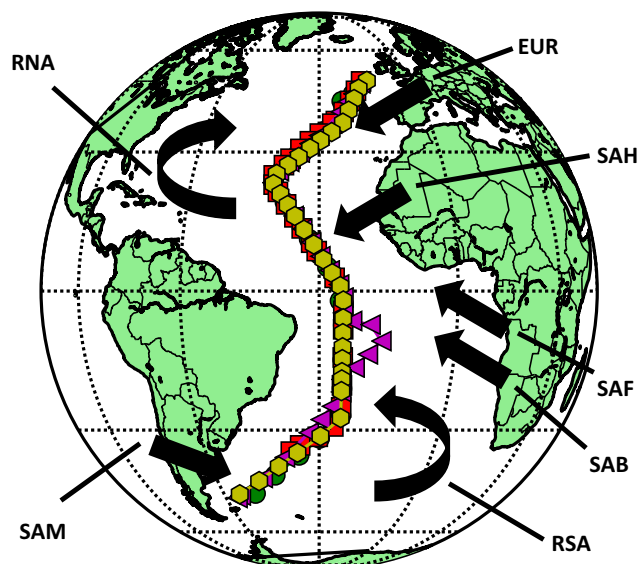


Fig. 1. Approximate tracks of cruises AMT18 (green), AMT19 (red), AMT21 (magenta) and AMT20 (yellow) through the Atlantic Ocean. Markers show the start of the collection period for each sample. Arrows indicate the general flow directions of the seven major atmospheric transport routes encountered during the cruises (see text for further discussion). Abbreviations for the air transport regimes are: continental Europe (EUR), North Africa including the Sahara and Sahel: (SAH), Southern Africa impacted by biomass burning emissions (SAB), Southern Africa not impacted by biomass burning (SAF), South America (SAM), remote North or South Atlantic i.e. not reaching crossing land for at least 5 days prior to collection (RNA and RSA respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2013). Other metals can act as valuable tracers of water column processes, for example aluminium as a tracer of dust inputs (Measures and Vink, 2000). Data on the aerosol concentrations of many of these trace metals is more limited than for iron. Here we therefore report results from four southbound AMT cruises conducted during the austral springs of the years 2008–2011 and extend our analysis to the soluble concentrations of a wider range of trace metals (including Ti, Zn, V, Ni and Cu) in aerosols, many of which have significant sources from anthropogenic emissions. The soluble fraction of these trace metals is assumed to be bioavailable to water column plankton, although this may underestimate the total bioavailable input if some material not dissolved in our leaching is subsequently solubilised within the euphotic zone. We use this data to consider sources of these metals and the potential impact of their deposition on the Atlantic surface waters.

2. Methods

We report results obtained from aerosol sampling on AMT cruises 18–21, which followed similar tracks from the UK to the southern regions of South America via the central North and South Atlantic gyres (Fig. 1). Full details of each cruise are given in Table 1. Aerosol sampling was usually conducted over periods of 24 h, except at the south of each transect where aerosol concentrations were low and sampling periods were therefore extended to 2 days.

Our methods for aerosol sampling have been previously described (Powell et al., 2015; Chance et al., 2015; Baker et al., 2007) and are only briefly summarised here. Sampling took place on the top deck of the ship. Aerosols were collected only when relative wind speed and direction conditions were favourable: i.e. there was minimal chance of contamination of samples by emissions from the ship. For AMT18 and 19, this sampling was manually controlled, while for the later cruises automatic wind sector controllers were used. Samples were collected using high volume aerosol samplers ($\sim 1 \text{ m}^3 \text{ min}^{-1}$) and Sierra-type cascade impactors. For almost all samples, stages 3 and 4 of the cascade impactor were used, together with a backup filter providing estimates of concentrations $>1 \mu\text{m}$ and $<1 \mu\text{m}$. To provide more detailed information on the size distribution of various elements, for AMT21 samples #15 and #30, stages 1–5 of the cascade impactor and a backup filter were used. For soluble trace metals analysis, aerosol collection substrates were Whatman 41 cellulose and these were pre-washed with nitric and hydrochloric acid (Baker et al., 2007). During each cruise a second collector was employed to sample for aerosol major ions. These filter substrates were (unwashed) Whatman 41 (for AMT18 and 19) or glass fibre (AMT21, a cruise with a particular focus on organic matter within the aerosol). These different filter types have comparable aerosol particle size collection efficiencies. Glass fibre substrates were washed with ultrapure water and ashed at 450°C before use. The second collector failed early during AMT20 and major ions were therefore determined on the acid-washed substrates for this cruise. Samples were frozen on the ship and stored frozen until analysed.

We focus on soluble trace metals (indicated by the prefix s, e.g. s-Al to indicate soluble aluminium) here because these will most

directly affect water column biogeochemistry as discussed above. Full details of analytical methods are reported in Chance et al. (2015) and only summarised here. Details of blanks and limits of detection are presented in Table 2. Laboratory analysis for soluble trace metals began with a 1–2 h pH 4.7 ammonium acetate leach followed by filtration through a $0.2 \mu\text{m}$ filter with all procedures conducted within a laminar flow hood housed in a trace metal clean room. Samples were subsequently analysed by ICP-OES (and ICP-MS for AMT21 samples #15 and #30 only) alongside the TMRAIN04 certified reference material (Environment Canada). Recoveries for the CRM were within the following percentages of the certified values: $\pm 10\%$ Fe, Mn; $\pm 20\%$ Ti, Zn, V, Cu; $\pm 45\%$ Ni. Soluble major ions were extracted into ultrapure water using ultrasonic agitation for a period of 1 h, and then also filtered through $0.2 \mu\text{m}$ filters. Major ions were determined by ion chromatography. Where concentrations were below detection limits, we used substitute values equivalent to 75% of the relevant detection limit (e.g. for the data plotted in Figs. 2–4 and for the calculation of descriptive statistics). For some ions (K^+ , Ca^{2+} and SO_4^{2-}), we calculated the contribution to measured concentrations arising from seaspray using the aerosol Na^+ concentrations and the ratio of the ion in question to Na in seawater. Non-seaspray (nss) concentrations were then calculated by subtracting the seaspray contribution from the measured concentration for each ion. Further details of analysis procedures can be found in Baker et al. (2007), Chance et al., 2015 and Powell et al. (2015).

3. Results and discussion

3.1. Atmospheric concentrations and deposition

In Figs. 2 and 3 we present the concentrations of aerosol soluble trace metals and major ions, respectively, sorted according to the air transport/source types encountered during AMT18–21. These figures illustrate the strong characteristic signatures of certain source types (e.g. high concentrations of nss- Ca^{2+} , s-Fe, s-Al and s-Mn in Saharan air, and of NO_3^- , NH_4^+ , s-Zn, s-V, s-Ni and s-Cu in European air). Also apparent are other traits, such as the presence of relatively high levels of anthropogenic-origin species (NO_3^- , nss- SO_4^{2-} , s-V and s-Ni) in Saharan air, the generally higher concentrations of most species (both dust- and anthropogenic-derived) in aerosols over the remote North Atlantic compared to the remote South Atlantic, and the low median concentrations for most species in samples of the SAF type relative to the other continentally-influenced transport types. We discuss these relationships in more detail below.

Overall our results for the 2008–2011 AMT cruises appear to be comparable to those obtained during our previous surveys in the Atlantic and other similar studies for aerosol major ion and trace metal concentrations (e.g. Buck et al., 2010; Baker et al., 2006b, 2010, 2013). This is illustrated by comparison to the corresponding plots for s-Fe, s-Al, s-Mn, NO_3^- and NH_4^+ , for the September–November meridional transect cruises conducted between 2000 and 2005 (Fig. 4) (data from Baker et al. (2010, 2013)), which leads us to suggest that the results for the new soluble trace metal aerosol com-

Table 1
Details of AMT cruises 18–21.

Cruise	Ports		Year	Vessel
	From	To		
AMT18	Immingham, UK	Port Stanley, Falkland Islands	2008	RRS <i>James Clark Ross</i>
AMT19	Falmouth, UK	Punta Arenas, Chile	2009	RRS <i>James Cook</i>
AMT20	Southampton, UK	Punta Arenas, Chile	2010	RRS <i>James Cook</i>
AMT21	Avonmouth, UK	Punta Arenas, Chile	2011	RRS <i>Discovery</i>

Table 2
Blanks and detection limits for aerosol soluble trace metals for each of the 4 cruises reported in this study. Values are given for fine (<1 μm) and coarse (>1 μm) aerosol size fractions. Detection limits are presented for an air volume of 1400 m³, representative of the ~24 h sample collection used for most of the samples.

	sFe	sAl	sMn	sTi	sZn	sV	sCu	sNi
<i>Blank (nmol/filter)</i>								
AMT18								
<1 μm	9.8	19	0.3	<0.2	36	<0.7	9.2	<1.5
>1 μm	3.5	12	0.2	<0.2	14	<0.7	4.2	<1.5
AMT19								
<1 μm	4.4	8.4	0.2	<0.2	19	<0.7	0.8	<1.5
>1 μm	3.2	8.1	0.2	0.2	26	<0.8	<0.4	<1.2
AMT20								
<1 μm	3.5	8.8	0.4	<0.2	33	<0.7	2.6	1.3
>1 μm	<2.2	7.2	0.2	<0.2	16	<0.7	2.9	<1.4
AMT21								
<1 μm	4.7	10	0.4	0.2	36	<0.6	1.8	0.9
>1 μm	2.3	4.6	0.1	0.1	14	<0.6	1.8	0.6
<i>Detection limit (pmol/m³)</i>								
AMT18								
<1 μm	1.3	3.6	0.1	0.1	0.8	0.5	0.3	1.0
>1 μm	3.3	2.4	0.1	0.1	0.6	0.5	0.3	1.0
AMT19								
<1 μm	2.8	2.6	0.1	0.1	0.9	0.5	0.3	1.0
>1 μm	1.8	6.3	0.1	0.2	25	0.6	0.3	0.9
AMT20								
<1 μm	2.0	1.0	0.2	0.2	22	0.5	2.1	0.8
>1 μm	2.2	6.9	0.2	0.1	8.9	0.5	3.1	1.0
AMT21								
<1 μm	1.6	2.4	0.1	0.03	11	0.5	0.2	0.3
>1 μm	1.3	1.3	0.04	0.1	11	0.5	2.4	0.7

ponents obtained during AMT18–21 are representative of this region in that season. To illustrate this similarity further for contrastingly sourced analytes and air mass regimes, the median sAl concentrations for the 2000–2005 and AMT18–21 data for the SAH air mass are 1271 and 1051 pmol m⁻³ respectively, and for the RSA air mass are 65 and 80 pmol m⁻³ respectively. In the case of nitrate, for the 2000–2005 and AMT18–21 median concentrations for SAH air mass are 32 and 16 nmol m⁻³ respectively and for the RSA air mass 3.2 and 3.5 nmol m⁻³ respectively.

The soluble metal fraction of marine aerosols has been defined using a number of methods (e.g. Buck et al., 2010; Wu et al., 2007; Baker et al., 2006c), particularly in terms of the leaching solutions used to solubilise metals from the aerosol sample collection filter papers, and the results obtained appear to be method- and element-dependent. For instance, a direct comparison of the method used here with an instantaneous leach procedure using ultrapure water yielded higher solubility values for Fe in ammonium acetate solution, but very similar solubility values for V (Morton et al., 2013). An indirect comparison of Fe solubility between these and other methods suggested that all methods gave broadly similar results particularly in terms of the relationship of solubility to dust loading (Baker et al., 2014; Sholkovitz et al., 2012). Although the biogeochemical relevance of the various leach methods is not very clear at present, it does appear that the majority of the observed variability in TM solubility is due to differences between the aerosol samples themselves, rather than differences between analytical methods (Aguilar-Islas et al., 2010). A clear conclusion from several different studies is that the solubilities of metals, such as Al, Fe and Si, which are predominantly present in the aerosol bound directly and strongly within aluminosilicate lattices, are lower than for other trace metals, such as Mn, Zn, V, Ni, Cu, Cr, Co, and Cd. One study, for example, shows Fe and Al solubilities of <3% and Mn, Co, Cu, Ni, Pb, Zn and Cd >15% (Mackey et al., 2015). The difference reflects in part the chemical form of the metals in the aerosols as discussed by Jickells et al. (2016). Metals bound

within aluminosilicate phases are less soluble than those present in more soluble metal coatings on aerosols produced by condensation from the gas phase after high temperature combustion processes, although in many aerosols metals are associated with both aluminosilicate and the more soluble phases (Desboeufs et al., 2005; Mackey et al., 2015; Chance et al., 2015; Paytan et al., 2009; Fomba et al., 2013).

It is important to note that the species identified above as being associated with either dust or anthropogenic emissions can still have different geographic sources. For instance, the proportion of Ca in mineral dust is known to vary from north to south through the Sahara/Sahel region (Chiapello et al., 1997).

Anthropogenic sources include emissions from agriculture (particularly for NH₄⁺), combustion (e.g. for SO₄²⁻, Ni, V, NO₃⁻) and other high temperature industrial processes (e.g. for Zn, Cu). Emissions of Ni and V are often associated with combustion of heavy fuel oils, particularly from shipping (Becagli et al., 2012), and in some ocean regions aerosol concentrations of these elements have been found to be highly correlated e.g. in the Mediterranean (Becagli et al., 2012) and off the coast of Peru (Baker et al., 2016). In the AMT18–21 data set there is also a strong correlation (Spearman's ρ = 0.84, p < 0.01) between the soluble concentrations of these two elements in fine mode (<1 μm) aerosols (Fig. 5), suggesting that they may also have similar emission sources from shipping on the open Atlantic, although terrestrial emissions from heavy fuel oil combustion could also be important. The significance of ship emissions as sources of atmospheric contamination is now becoming clear (Eyring et al., 2010) and, although new control measures may reduce this impact if implemented globally (Yang et al., 2016), this role of ship emissions merits further investigation.

In general, the processes by which species enter the atmosphere has a strong influence on the size of particle in which they are found in the aerosol phase (Raes et al., 2000). Particles generated by mechanical processes, such as the uplift of mineral dust, are

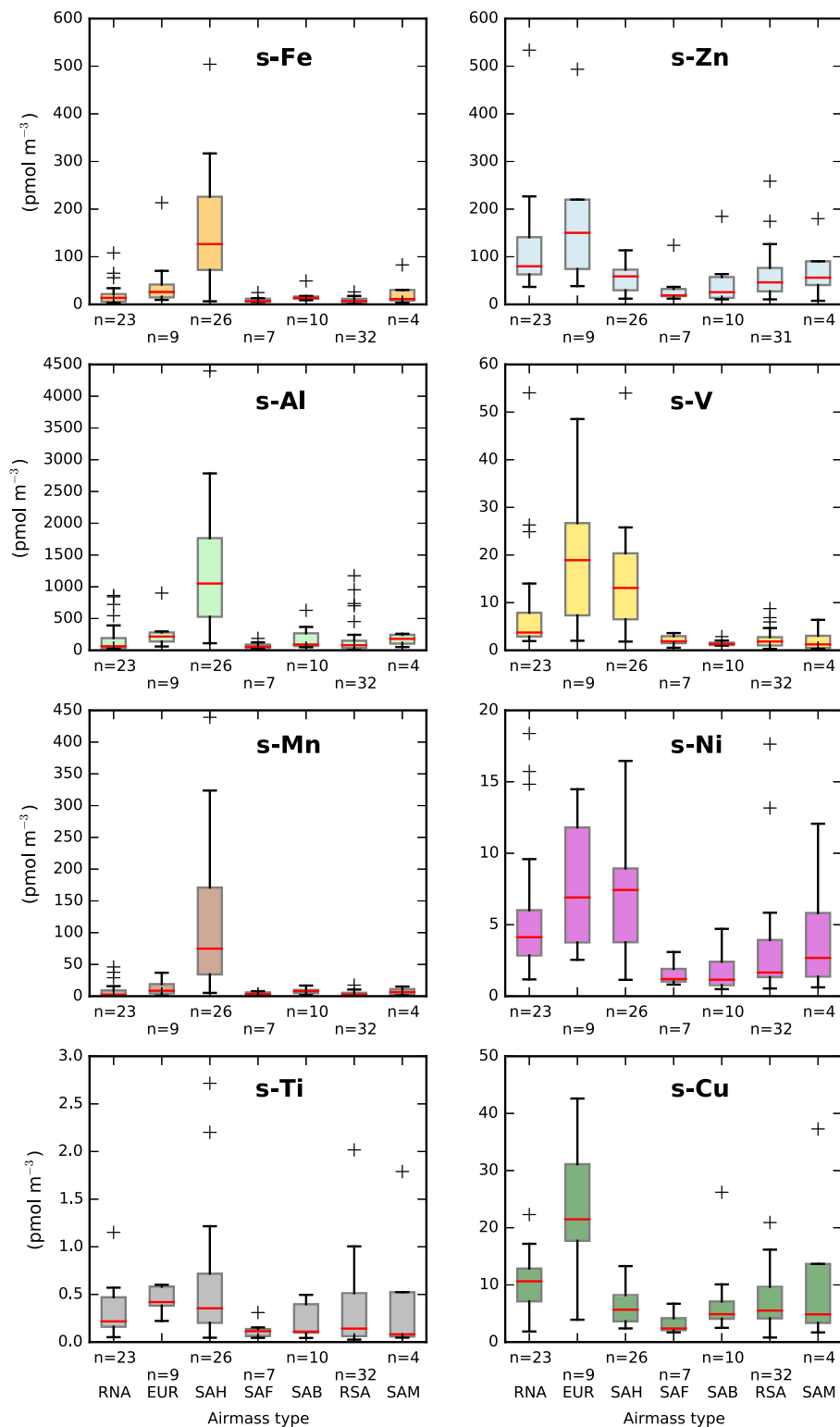


Fig. 2. Box and whisker plots showing the variations in the concentrations of (a) s-Fe, (b) s-Al, (c) s-Mn, (d) s-Ti, (e) s-Zn, (f) s-V, (g) s-Ni and (h) s-Cu with air transport/source type for the AMT18–21 cruises. Upper and lower limits of boxes represent the interquartile range of data in each category, with the median shown as bars in each box. Whiskers represent the range of the data, except where extremes (values greater than 1.5 times the interquartile range above the upper quartile) were present (crosses). Numbers of samples in each category are given.

mostly found in the coarse ($>1 \mu\text{m}$) mode, while those produced by condensation of gas phase substances associated with high temperature emissions (e.g. combustion) are most commonly found in the fine ($<1 \mu\text{m}$) mode (Seinfeld and Pandis, 1998). This pattern is seen quite generally in aerosol data from remote areas around

the world (Arimoto and Duce, 1986). In Table 3 we show the median fraction of each soluble trace metal and major ion found in the fine mode for each of the air transport types discussed above. While the elements that we assume to be dominated by mineral dust (sFe, sAl, sMn and sTi) do have lower fine mode fractions than

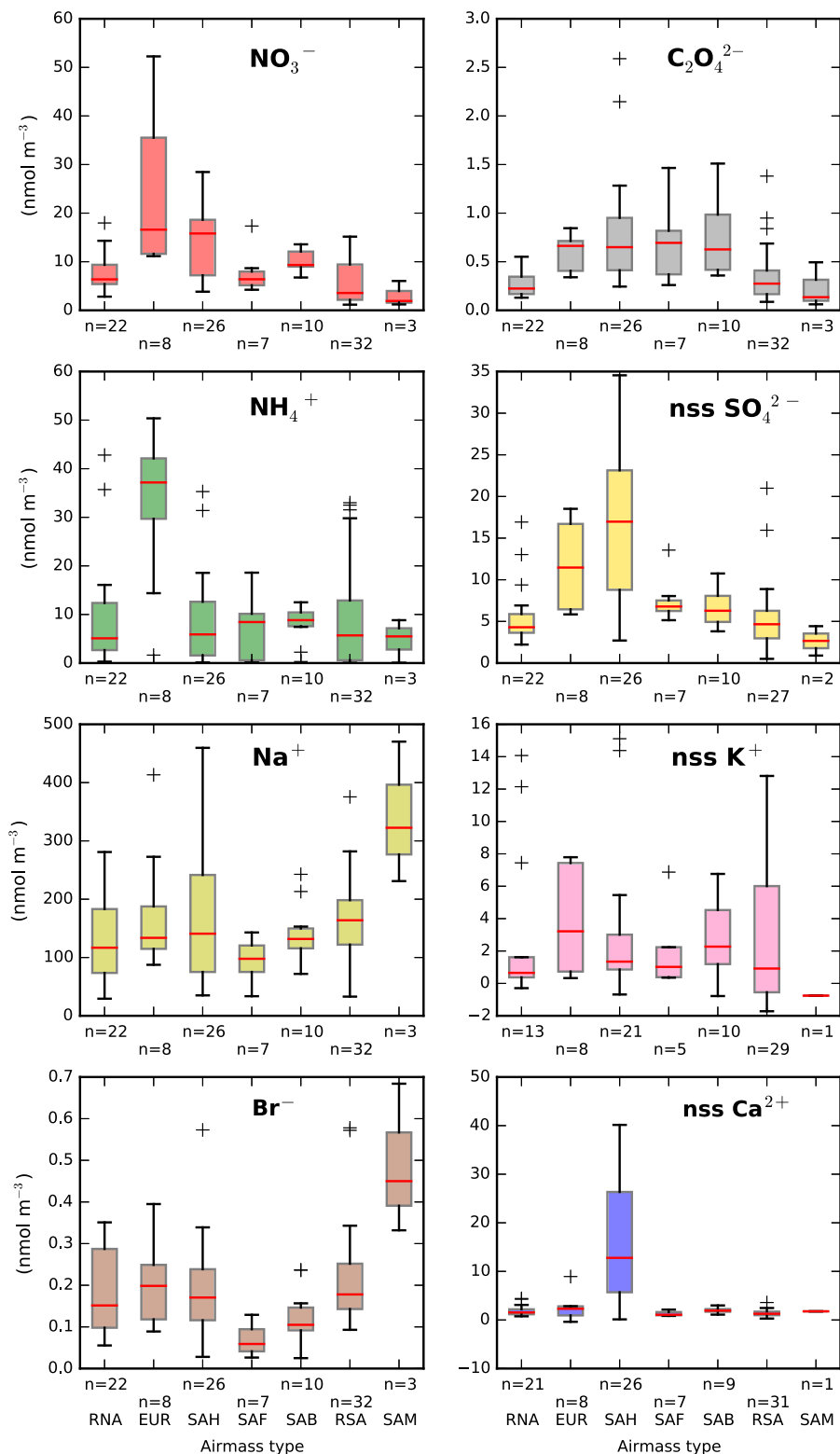


Fig. 3. Box and whisker plots showing the variations in the concentrations of (a) NO_3^- , (b) NH_4^+ , (c) Na^+ , (d) Br^- , (e) oxalate, (f) nss-SO_4^{2-} , (g) nss-K^+ and (h) nss-Ca^{2+} with air transport/source type for the AMT18–21 cruises. See Fig. 2 for explanation of box and whisker characteristics.

the anthropogenic elements (sZn, sV, sNi and sCu), they still contain significant fractions in fine mode particles (Table 3). We assume that this is due in part to the different solubility of these elements with aerosol particle size, as we have previously observed that sFe, sAl and sMn in fine mode aerosols over the Atlantic are more soluble than in the coarse mode (Baker et al.,

2006a, 2006c). Hence for trace metals the results in Table 3 reflect both the relative source strength of coarse and fine contributions for an aerosol component, and also the solubility of that metal in the coarse and fine mode. For aerosol components which are essentially completely soluble the situation is simpler to interpret. The small fine mode fraction of the mineral dust indicator nss-Ca^{2+}

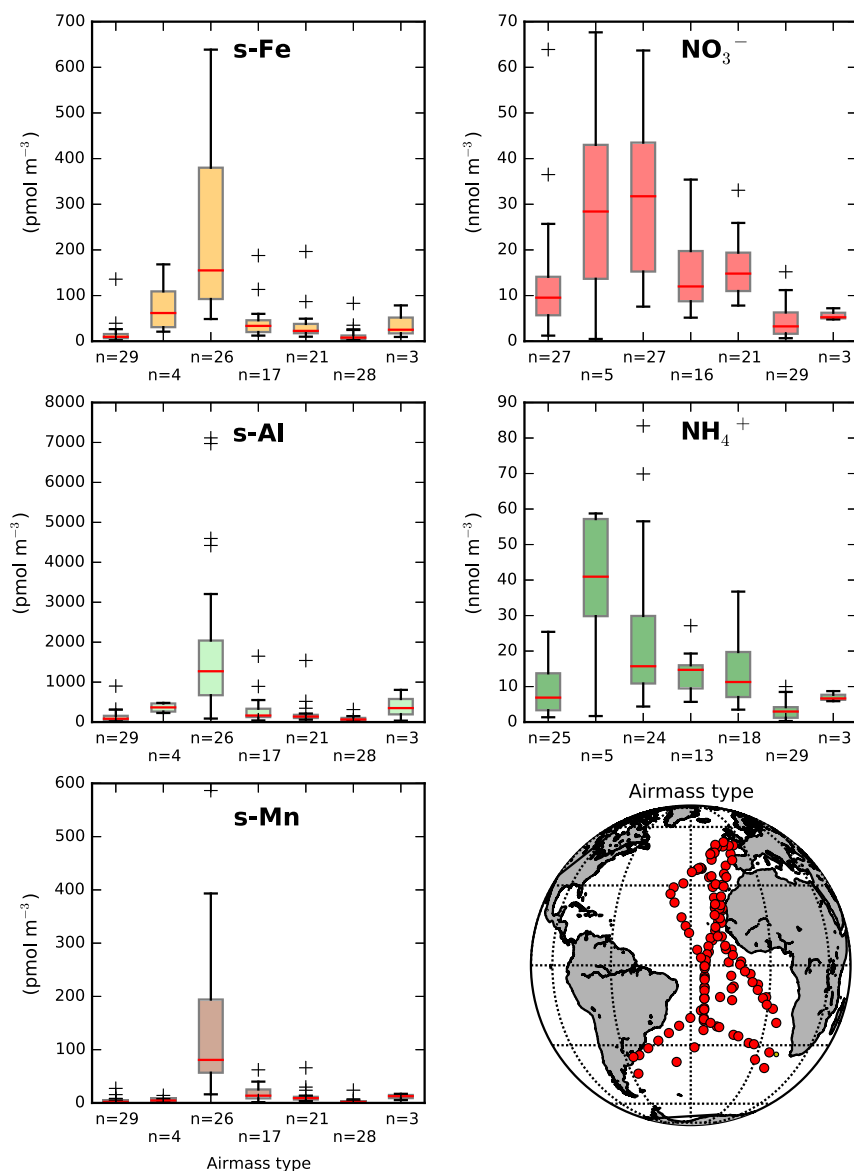


Fig. 4. Box and whisker plots showing the variations in the concentrations of (a) s-Fe, (b) s-Al, (c) s-Mn, (d) NO_3^- and (e) NH_4^+ with air transport/source type for the meridional transect cruises which took place in the months of September–November between 2000 and 2005 (Baker et al., 2010, 2013). See Fig. 2 for explanation of box and whisker characteristics. A map of the locations of these samples is also shown.

(Table 3) indicates that dust is dominantly found in coarse mode particles. The coarse mode dominance of Na^+ is due to the mechanical generation of seaspray at the ocean surface, while the major ions with predominant gas phase anthropogenic-origin (NH_4^+ and nss-SO_4^{2-}) are found chiefly in fine mode aerosol. The dominance of the coarse mode fraction for nitrate reflects the reaction of gas phase nitric acid with seasalt (Andreae and Crutzen, 1997) as discussed by Baker et al. (Baker et al., 2006b).

In Fig. 6 we show sFe, sMn and sV concentrations for the 6 size fractions collected for sample #15 in the centre of the North Atlantic gyre ($\sim 21^\circ\text{N}$, 39°W) during AMT21. As noted in the caption, the aerosol size distributions of sZn, sV, sCu and sNi are very similar to that of sV while the aerosol size distribution of sTi and sAl are similar to that of sFe. The somewhat different size distributions of sFe and sV reflect the predominantly anthropogenic origin of the sZn, sV, sCu and sNi formed by condensation from the gas phase onto fine mode aerosol after high temperature combustion, a process responsible for the relatively high solubility of these elements as well. The sAl, sFe and sTi size distributions reflects their association

with dust sources yielding coarser mode aerosol material and relatively low solubility. This effect is even more marked when the total rather than soluble distributions of these elements are considered (Fomba et al., 2013). As noted elsewhere (Chance et al., 2015), sMn has a predominantly coarse mode distribution which is different to that of sFe, although in the concentrations of both elements are dominated by mineral dust (Fig. 2). Mn also has a very different solubility behaviour to the other crustal elements and both of these factors may be related to soil processing (Jickells et al., 2016).

It is also possible to distinguish between species with predominantly mineral dust or anthropogenic origins using enrichment factors (EF) which ratio the concentration of the metal to a crustal tracer such as aluminium and compare this ratio to the average crustal abundance ratios. If a metal has a crustal source it should have no enrichment, while high enrichments require a source in addition to crustal material, and this is usually anthropogenic, although this simplistic classification is complicated by natural variability in the crustal concentrations (Shelley et al., 2015;

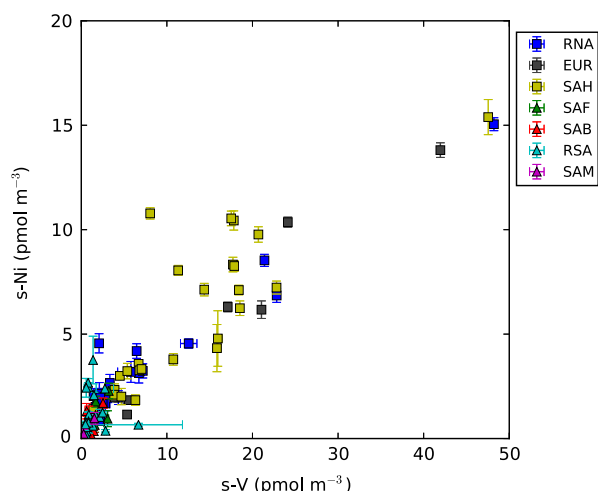


Fig. 5. The relationship between the concentrations of fine mode s-V and s-Ni in the AMT18–21 aerosol samples. Data are colour-coded according to air transport type. Codes are explained in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Reimann and De Caritat, 2000). The natural variability of average crustal source material means that enrichment factors are usually only considered to show unambiguous enrichment when $EF > 10$ (Shelley et al., 2015). We cannot use this enrichment factor approach for our data set since we do not have total metal concentration data. However, Fomba et al. (2013) have calculated enrichment factors for air masses arriving at Cape Verde from various sectors, excluding the Saharan air masses, and divided metals into three groups: essentially no enrichment (e.g. Fe, Mn), small (2–20-fold) enrichments (e.g. V) and larger enrichment factors (e.g. Ni, Cu, Zn). These enrichments are therefore broadly consistent with our interpretations above, with Fe and Mn associated with crustal sources and the other metals dominated by anthropogenic sources.

The results in Fig. 2 for the variations with air mass origin of the concentrations of the soluble aerosol trace metals associated with crustal sources (sFe, sAl, sMn and sTi) along AMT are similar to each other but very different to the other group of trace metals, which are again similar to each other - sV, sZn, sCu and sNi. These latter metals all have their maximum concentrations in the European air masses, although as with other anthropogenic components of the aerosol such as nitrate and sulphate, they also have relatively high concentrations in the Saharan air mass. The high

concentrations in the Saharan air mass mainly reflect anthropogenic contributions of these metals from European air masses that are transported southward and across the Sahara desert and then across the Atlantic, as previously described for sulphate and nitrate (Savoie et al., 1989). There is an additional potential contribution to the soluble metal concentrations from Saharan dust itself, Sahel biomass burning and emissions from urban centres in north-west Africa.

The broad geographic pattern evident in Fig. 2 for soluble aerosol concentrations for different elements reflects the relative strength of both the emissions and the elemental solubility associated with that emission source. Hence for V with a relatively low enrichment factor (Fomba et al., 2013) both European and Saharan air masses have similar concentrations, while for the more enriched metals Cu, Zn and Ni, the European air mass has higher concentrations than the Saharan. Zn concentrations are rather variable in the remote North Atlantic air mass perhaps reflecting the impact of Northern Hemisphere emissions into the remote atmosphere.

Although aerosol concentrations are lower over the South Atlantic than the North Atlantic, there are still significant differences in metal concentrations between air masses there. The African biomass burning air mass (SAB) has relatively high concentrations of nitrate and nss-potassium, and Fig. 2 suggests that biomass burning may also be a source of other trace metals (e.g. sZn, sCu), although the difference between SAB and SAF air masses is small. This difference could reflect specific metal emissions from plant burning or increased mobilisation of soil material (Jickells et al., 2016).

There is also evidence of some higher concentrations in air masses sampled in the remote South Atlantic, for example sZn, relative to the very low background values in this region. Chance et al. (2015) observed similar higher values in this region and ascribed these to transport from South America from both desert and anthropogenic sources.

3.2. Impacts on surface water biogeochemistry

As noted above, the concentrations of all the metals in the aerosols fall dramatically moving into the Southern Atlantic. The effect of this spatial gradient in atmospheric supply on the water column cycling of Fe, N and P and on nitrogen fixation and primary productivity has been discussed previously (Baker et al., 2003; Moore et al., 2009; Ussher et al., 2013). We note here that Zn, Mn and Cu are also essential elements which may influence ocean primary

Table 3
Median fractions of soluble trace metals and major ions contained in fine mode aerosol for each of the air transport types encountered during the AMT18–21 cruise.

	RNA	EUR	SAH	SAF	SAB	RSA	SAM
<i>Metal</i>							
sFe	0.50	0.38	0.54	0.52	0.34	0.43	0.44
sAl	0.50	0.58	0.55	0.47	0.38	0.46	0.24
sMn	0.55	0.58	0.55	0.47	0.38	0.46	0.24
sTi	0.35	0.50	0.40	0.37	0.37	0.42	0.46
sZn	0.70	0.70	0.60	0.61	0.64	0.61	0.62
sV	0.76	0.76	0.87	0.78	0.66	0.62	0.51
sNi	0.65	0.39	0.85	0.63	0.39	0.40	0.34
sCu	0.62	0.48	0.54	0.37	0.53	0.39	0.39
<i>Ion</i>							
NO ₃ ⁻	0.11	0.09	0.10	0.08	0.07	0.11	0.09
NH ₄ ⁺	0.75	0.71	0.88	0.65	0.79	0.58	0.65
Na ⁺	0.03	0.03	0.07	0.10	0.03	0.04	0.05
Br ⁻	0.25	0.36	0.21	0.37	0.25	0.19	0.07
Oxalate	0.31	0.52	0.42	0.43	0.33	0.46	0.36
nss K ⁺	0.06	0.06	0.38	0.20	0.13	0.02	-
nss Ca ²⁺	0.22	0.40	0.15	0.11	0.02	0.09	-
nss SO ₄ ²⁻	0.76	0.73	0.68	0.81	0.81	0.72	-

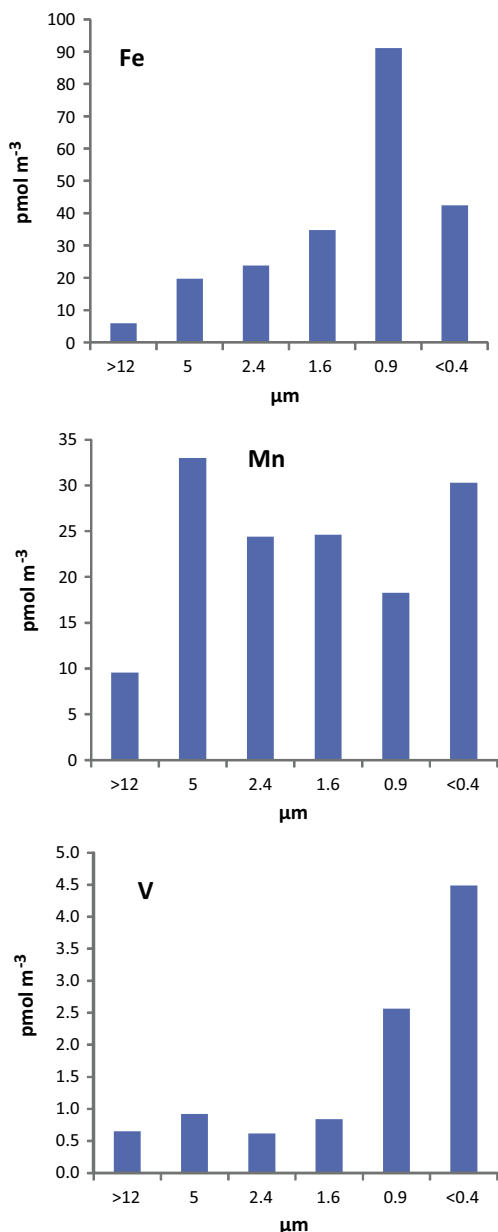


Fig. 6. Soluble TM distributions with aerosol particle modal aerodynamic diameter for sample #15 of the AMT21 cruise ($\sim 21^{\circ}\text{N}$, 39°W). Distributions are shown for Fe, Mn and V. The distributions of sAl and sTi are similar to that of sFe, while those of sZn, sNi and sCu are similar to sV.

productivity. High concentrations of Cu may also be toxic to phytoplankton (Paytan et al., 2009), although this is probably mitigated by organic complexation (Bruland and Lohan, 2003). A full understanding of the role of atmospheric deposition in modifying water column primary production should consider the interacting effect of all of these nutrients although this is greatly complicated by the ability of phytoplankton to substitute metals for one another (Moore et al., 2013; Browning et al., 2014). The results in Fig. 2 illustrate that not only does the flux (F , the product of the dry deposition velocity, v_d , and the aerosol concentration, C^a , see below) of metals vary systematically geographically along AMT, but the ratios of the different metals one to another will vary. As an example the ratios of sZn to sFe will be higher in European air masses than Saharan ones (Fig. 2).

In a previous study, we estimated dry deposition fluxes of Fe, Al and Mn to a series of sub-regions of the Atlantic Ocean, based on

observations of aerosol concentrations made between 2000 and 2005 (Baker et al., 2013). Here we use similar methods to make a first-order estimate of the dry deposition flux of the soluble metals studied here. Fig. 7 shows the distribution of the sub-regions relevant to the AMT18–21 cruises. We use the wind speed-dependent dry deposition velocity values (Table 4) and air mass weightings (the fractional occurrence of arrivals from the different air mass source regions) for September to November from (Baker et al., 2013) to estimate fluxes of each metal to allow for the different relative contributions of different air flows to each region. For the purposes of this rather simple calculation we have assumed that metals primarily associated with mineral dust aerosol (sFe, sAl, sMn and sTi) are present in particles with a mean diameter of $>5 \mu\text{m}$, while anthropogenic metals (sZn, sV, sCu and sNi) are associated with smaller particles ($0.6 \mu\text{m}$ diameter). These assumptions have an impact on the absolute magnitude of the calculated dry deposition fluxes for these metals (Table 4), but do not alter the general conclusions below about the impacts on the water column biogeochemistry. We note that dry deposition velocities are highly uncertain (possibly by a factor of 2–3 (Duce et al., 1991)) and that wet deposition is an important and often dominant deposition mechanism to the Atlantic Ocean (Baker et al., 2010, 2013). We are not able to estimate this wet deposition flux directly using our data.

Atmospheric deposition of all the metals is higher to the North Atlantic than the South Atlantic (Table 4). This can be illustrated by comparing boxes 2c and 4a. These boxes cover ocean gyre regions for which there is net downwelling of water and hence the impact of supply of these metals from below by vertical mixing can be ignored in the first instance (Ussher et al., 2013). This simplifies the assessments below of the impacts of atmospheric deposition on the water column. In the case of the crustally dominated soluble metals Fe, Al and Mn, dry deposition fluxes to box 2c are approximately two times those to box 4a and for the more anthropogenically-sourced soluble metals the differences between these boxes are slightly larger at a factor of 3.

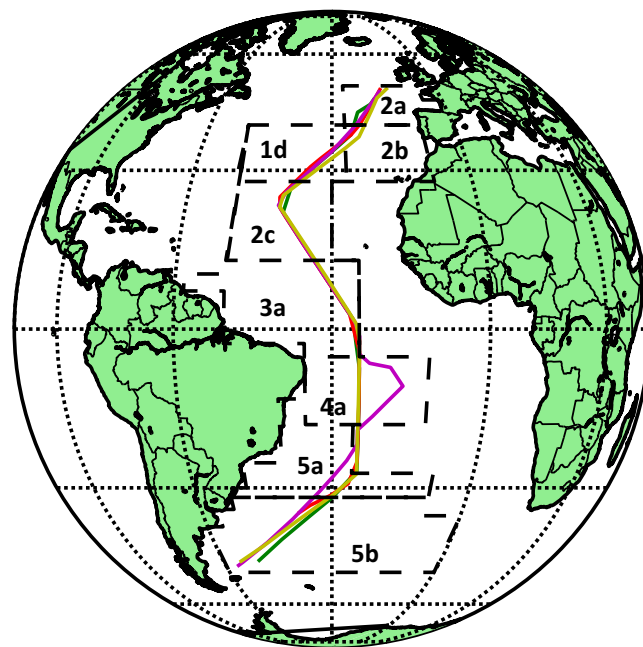


Fig. 7. AMT18–21 cruise tracks and regions used in the calculation of dry deposition fluxes for soluble trace metals. Region labels are taken from Baker et al. (2013).

Table 4
Mean climatological surface wind speed (u : m s^{-1}), dry deposition velocities (v_d : cm s^{-1}) for particles of diameter 0.6 μm and 5 μm (v_d 0.6 and v_d 5 respectively) and dry aerosol deposition fluxes sX ($\text{nmol m}^{-2} \text{d}^{-1}$) for soluble trace metals to the regions along the AMT18–21 cruise tracks shown in Fig. 7.

Box	u	v_d 0.6	v_d 5	$s\text{Fe}$	$s\text{Al}$	$s\text{Mn}$	$s\text{Ti}$	$s\text{Zn}$	$s\text{V}$	$s\text{Ni}$	$s\text{Cu}$
1d	6.63	0.021	0.63	8.3	43.1	1.86	0.12	1.66	0.11	0.08	0.22
2a	7.97	0.023	0.84	11.9	68.8	2.77	0.18	1.99	0.16	0.10	0.27
2b	6.03	0.021	0.51	11.0	75.7	4.13	0.12	1.71	0.14	0.09	0.23
2c	6.03	0.021	0.51	11.6	77.1	4.66	0.10	1.41	0.09	0.08	0.18
3a	5.83	0.021	0.47	14.6	115.0	7.97	0.08	0.83	0.08	0.06	0.11
4a	7.26	0.022	0.72	5.3	40.9	2.81	0.07	0.40	0.03	0.02	0.06
5a	6.55	0.021	0.59	4.3	46.9	1.86	0.07	0.82	0.03	0.03	0.10
5b	8.66	0.025	0.96	7.5	100.9	3.60	0.10	1.07	0.03	0.04	0.11

The impact of atmospheric deposition on surface water concentrations depends on both the input and removal processes. The removal may be by direct biological uptake where a trace metal has a biological role, or via scavenging, although scavenging is also related to productivity because it is controlled by particle concentrations which are themselves biologically controlled (Bruland and Lohan, 2003). Ussher et al. (2013) showed that atmospheric deposition creates a strong north–south surface water iron concentration gradient in the Atlantic, and that this is not simply related to atmospheric deposition because of more efficient iron recycling in the waters of the South Atlantic gyre compared to the North Atlantic gyre. Dissolved aluminium in surface waters, for which dust inputs are also an important source, also show a strong inter-hemispheric gradient with average concentrations in the North Atlantic approximately twice those in the South Atlantic although there are systematic spatial gradients in these surface water column concentrations (Ussher et al., 2013; Han et al., 2008; Middag et al., 2015).

It is then interesting to compare our estimates of TM dry deposition fluxes (Table 4) to the surface water dissolved concentrations of these metals, again focussing on boxes 2c and 4a. Since we have not determined wet deposition, we underestimate the total atmospheric flux, however the gradients between the two hemispheres can be expected to be similar for total and dry deposition. Boxes 2c and 4a are regions with low average rainfall, and hence relatively high proportions of dry to total deposition (Baker et al., 2013), so the magnitude of the flux underestimation will be lowest in these boxes.

The new GEOTRACES data sets of water column dissolved metal concentrations include some relevant Atlantic sections (Mawji et al., 2015; Middag et al., 2015). These show only a rather small inter-hemispheric surface water dissolved Mn gradient along the GEOTRACES western Atlantic section GA02 and comparison of surface water concentrations on the GA03 and GAc01 sections (Mawji et al., 2015) in the North and South Atlantic suggests little inter-hemispheric difference. A similar situation is evident for zinc with little inter-hemispheric gradient in surface water concentrations despite a 2–3 difference in atmospheric deposition fluxes. Pinedo-Gonzalez et al. (2015) have recently reported the surface distribution of several trace metals including sections across the North and South Atlantic gyres. Vanadium and nickel concentrations in the north and south Atlantic gyres are approximately 25 nM (V- north and south gyres) and 1.3 and 1.75 (Ni - north and south Atlantic gyres respectively), again suggesting little north–south difference in surface water concentrations despite 2–3 differences in dry deposition fluxes. This data suggests that for these metals (Mn, V and Ni) internal recycling processes in the surface waters act to eliminate evidence of the gradient in atmospheric inputs, in contrast with the situation for iron and aluminium. Ni is classed as a nutrient-like element and V shows slight nutrient-like surface depletion (Bruland and Lohan, 2003) suggesting a character between nutrient and conservative behaviour. Both metals have long whole-ocean, and surface water, residence times

and this probably explains the lack of response to atmospheric inputs with internal biogeochemical cycles as the dominant control. The same is likely to be the case for other metals with long residence times such as Cu and Zn (Bruland and Lohan, 2003) In the case of Mn, the vertical profiles suggest scavenged type behaviour (Bruland and Lohan, 2003) and a shorter surface water residence time, and hence behaviour similar to Al and Fe might be expected. However, photochemical processes promote recycling of Mn in surface waters and this process may be sufficient to eliminate a strong interhemispheric concentration gradient (e.g. Jickells et al., 1994).

4. Conclusions

There are strong interhemispheric gradients for a wide range of trace metals including those with crustal and anthropogenic sources, reflecting the spatial distribution of sources. We suggest shipping emissions may now contribute significantly to the anthropogenic emissions of V and Ni at least. The impact of these differences in atmospheric deposition between the northern and southern Atlantic gyres is seen in surface water concentrations of Al and Fe, and result in clear surface ocean biological responses, but not for other trace metals for which upper ocean biogeochemical processes appear to predominate.

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