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Interactive comment on "Characterisation of aerosol provenance from the fractional solubility of Fe (Al, Ti, Mn, Co, Ni, Cu, Zn, Cd and Pb) in North Atlantic aerosols (GEOTRACES cruises GA01 and GA03) using a two stage leach" *by* Rachel U. Shelley et al.

Anonymous Referee #1

Received and published: 12 December 2017

This manuscript describes the results obtained from different leaching methods used to liberate soluble trace elements from aerosol samples collected over the North Atlantic Ocean. The majority of the work focuses on leaches with ultra-high purity water (UHP) and an acetic acid solution, although some results obtained from leaching with seawater are also reported. The dataset presented is of high quality and it has been subjected to a very thorough analysis. The manuscript is highly suitable for publication in Biogeosciences, although I feel that some clarifications of relatively minor points are necessary.

Although the manuscript focuses on the UHP and acetic acid leach results, Section 3.3.3 presents results obtained by leaching a subset of the aerosol samples using sea- water. Currently the manuscript contains no information about how these experiments were performed. Please add this.
Thank you for your review.
A description of this can be found starting at line 474, and Section 3.3.3. starts with, 'Seawater leaches were conducted on a subset of samples (GA03-2011), to investigate the suitability of seawater as the leach medium in the instantaneous leach.'

Non-seasalt (nss) sulfate concentrations in the aerosol samples were estimated using aerosol chloride concentrations as an indicator of seaspray content. I understand that this was the only indicator available, since major cations (e.g. sodium or magnesium ion concentrations) were not measured. However, chloride is not an inert species in marine aerosol, since it can be converted to hydrogen chloride and lost to the gas phase (Andreae and Crutzen, 1997). The extent of chloride loss is likely to be greater in polluted air types, such as those originating over Europe and North America, but all of the samples will be affected to some extent. Thus, the nss concentrations presented here will be over-estimated and it would be helpful to note this in the text.

The description of the calculation of nss-SO42- has been removed as the aerosols acidity section, which used the nss-SO42- data, is no longer included in this manuscript.

I found it difficult to compare the results presented in the main body of the manuscript with those in the Supplementary Information (and in the two earlier manuscripts in which previous work on these samples was presented) because different labels have been used for the samples in different places. If it is not possible to only use a single set of labels, please could all the different labels be added to the tables in the supplement?

Thank you for drawing attention to this. This is a good point. In Shelley et al. (2017), which only discussed samples from GA01, the label 'A' referred to aerosol samples to differentiate them from the rain samples 1(R) in the figures. A note has been added to

the caption to notify readers to this. A similar note was added to the caption for Table S1, as well as the labels being added in brackets after the GEOTRACES sample numbers. The labelling convention in Shelley et al. (2015, GA03 only), is the same as in this manuscript.

There is also a specific issue with the naming convention for sample M3-GA03. The "M" here (and the map in Shelley et al., 2015) imply that this was a Marine sample. The discussion on lines 328 -332 specifically state that it had a European air mass back trajectory. Please clarify this.

You are correct. This was an error in the manuscript. In addition, further clarification and discussion has been added from Line 381.

I assume that positive matrix factorisation analysis (lines 350 onward) was done using total trace element concentrations. Please could this (or the correct information) be specifically stated. **Correct. Added at Line 306.**

All of Figures 2 – 7 would be improved by the addition of error bars. This would greatly assist the reader in putting the relatively high variability in calculated parameters (TE ratios to Al, or percentage soluble fractions) for samples with low total concentrations into context with the low variability, high total concentration samples with North African origin.

We agree however, there are several reasons why error bars have not been added to the plots. The reason plots that include fractional solubility data on one or both axes don't have error bars is that replicate digests/leaches were not conducted for all of the samples, and with the exception of one sample, there are no replicates on the same sample for total and the soluble concentrations. Therefore, a SD for the fractional solubilities cannot be calculated. I appreciate that this is not ideal.

Error bars could have been added to Fig. 2, but by doing so it is very hard to see the different symbols.

For the elemental ratios, calculating the SD was not a problem, as it was possible to summed the SDs for the two elements being ratioed. However, the problem is that by adding error bars to the plot it makes really hard to see the different shapes and colours of the symbols. As such, the plots have not got error bars added, but the SDs have been added in brackets after the relevant samples in Table S1.

Where we are talking about a high degree of variability in the data, we are talking about within the aerosol source categories, rather than replicates of the same sample. This data has already plotted with error bars and can be found in the Supplementary Material, Figure S3. The data can be found in Tables S3 and S4.

Minor points:

Line 95: "seawater" spelling. **Corrected**

Lines 103-115. Much of this paragraph is repetition of material from previous paragraphs. It could easily be shortened. **The introduction has been rewritten to reduce the repetition, and the sections referred to here now start at line 93.**

Line 319: The eruption of Eyjafjallajökull took place in 2010, not 2011.

Corrected

Line 353: I think Fig S2b should be referenced here, not S1b. **Corrected**

Line 369: The panels of Fig. 4 are not labelled on the figure. **This has been corrected.**

Line 374: "the ranges of fraction solubility" - I think there is a misspelling here. **Corrected.**

Lines 382-387: This is a very long and cumbersome sentence. Please consider splitting it. **This has been changed to, 'The ability of models to replicate subtleties in aerosol TE solubility may prove critical in forecasting ecosystem impacts and responses. Due to the magnitude of North African dust inputs to the North Atlantic region (very high dust inputs result in a high soluble aerosol TE flux despite relatively low fractional solubility), this is a particular challenge and is compounded by additional unknowns such as how aerosol acidity will be impacted by the combined effects of increasing industrialisation/urbanisation, and changes in the magnitude of future mineral dust supply and biomass burning (Knippertz et al., 2015; Weber et al., 2016).' Starting at line 561.**

Lines 444-445: "The differences source dependence of" Please correct.

Corrected

Line 481: Panel h of Fig 6 shows data for cadmium. Lead data is on panel i.

Corrected

Lines 509-511: This statement is very speculative. Please add further explanation or consider removing. **The section on aerosol acidity has been removed.**

Line 534: I am a little confused by the opening statement of this sentence. This manuscript has been devoted to the direct measurement of TE solubility!

This sentence has been removed. The original point was that we don't measure solubility directly, but calculate it from leach data that is sensitive to differences between the various leach protocols.

Lines 536-537: "in regions of high mineral dust deposition and/or productivity fractional solubility". An odd construction. What is productivity fractional solubility? **Corrected – this was missing a comma between productivity and fractional solubility**

Lines 538-839: How is it possible to have an inverse relationship between TE fractional solubility and aerosol provenance? **Corrected – provenance has been removed**

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Interactive comment on "Characterisation of aerosol provenance from the fractional solubility of Fe (Al, Ti, Mn, Co, Ni, Cu, Zn, Cd and Pb) in North Atlantic aerosols (GEOTRACES cruises GA01 and GA03) using a two stage leach" *by* Rachel U. Shelley et al.

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General comments:

This paper reports Fe, Al and trace metals composition and solubility in aerosols particles collected in North Atlantic Ocean. Even if it exists a lot of data on the solubility of Fe and major trace metals in Atlantic area (for ex. Clivar, AMT. campaigns), new data and in particular new perspective for using this data is always interesting. In this idea, the title of this manuscript was promising but finally, it is rather disappointing after reading. Indeed, even if the title implies a discussion on the relation between solubility and aerosol origin, the paper is limited to a dataset of solubility values as a function of air mass back-trajectories. It's very frustrating because the material is present to make this study original and significant. Another purpose of paper is the investigation to different leaching protocol for solubility measurement standardization. This twofold topic (provenance and protocol) makes abstruse the main objective of the paper.

Thank you for your review.

The discussions about standardisation have been removed.

Although this experimental work has been carefully conducted and contains interesting results, it is short of new findings in this current state due to a lack of guidance in the discussion on the results and of comparison with the literature. Consequently, I strongly encourage the authors to work again on this manuscript because your data could bring appreciable and consistent results for the community.

The major highlights proposed in this paper are "trace elements from aerosols from 1) North Africa were always the least soluble, and the most homogeneous . . ., 2) aerosols from the most remote locations were generally the most soluble, but had the most spread in the values of fractional solubility and 3) primarily pollution-derived TEs (Ni, Cu, Zn, Cd and Pb) were significantly enriched above crustal values in aerosols, even in samples of North African origin."

The focus has changed: the main findings are now that (1) there are exceptions to the general trend that fractional solubility of TEs is inversely related to atmospheric loading. The fractional solubility of Mn, Zn and Cd appears to be independent to atmospheric loading, and (2) air mass back trajectories are not sufficiently discriminating to identify aerosol source.

The critical point on this paper is the signification of term "provenance". In the manuscript, the aerosol provenance is considered as the "back-trajectory". Firstly, the back-trajectories were made for an arrival height of 500m, whereas the maximum altitude of boundary layer is often between 200 and 600 m in North Atlantic (Petenko et al., 1996; Fuhlbrügge et al., 2013), and aerosol sampling was in the boundary layer, so it is not automatically consistent.

The GA01 back trajectories presented in the Supplementary Material of Shelley et al.

(2017) were simulated for arrival heights of 50, 500 and 1500 m. The back trajectories for GA03, presented in Shelley et al. (2015) have been redrawn with the same three arrival heights as the GA01 samples (50, 500 and 1500 m), to include at least one arrival height in the MBL. The four representative AMBTs from GA03 and all AMBTs from GA01 can now be found in the Supplementary Material (Fig. S1).

Moreover, the "loading" in various aerosols is not only dependent on the trajectory but also on emissions along the transport of air masses. A same air masses can be a mix between various types of aerosols. In consequent, as solubility is dependent on kind of particles, it's obvious to observe a largest variability of solubility for aerosols from most remote locations in comparison to dust samples (findings 1) and 2)). In one case, it's a same source and in the other case that includes various sources and hence kind of particles. The relevant conclusion of this work should precisely be that aerosol provenance is not sufficient to estimate composition and solubility of trace metals.

This is now a key conclusion to the paper. However, the regional groupings, as determined by AMBT, are retained as a way of grouping the data to look at regional variations in fractional solubility.

From your database and the previous conclusions of Shelley et al. (2015) on the identification of sources of TEs (not provenance) in aerosols, further investigations could enable to emphasize a relationship between TEs solubility and origin. In this purpose, the origin of aerosol is a huge question which demands a more extensive bibliography to provide convincing proof of metals sources. A part of this comparison with bibliography is provided in the session 3.1 and 3.2. Nonetheless, the structuration of the paper is to much confuse to extract the pertinent information (see specific comments). These sessions should only include a summary of appropriate results from Shelley et al. (2015) for the discussion on the link with solubility. Moreover, a relevant bibliography is often missing in the manuscript. Several field campaigns during the last decade (AMMA, DODO, DABEX or SAMUM) + specific works (e.g. Trapp et al., 2010) permitted to improve our knowledge about the African dust composition before and after transport. Even if this literature is focused on major metals as Al, Fe or Ti, this literature about Saharan dust characterisation should be used to validate/discuss your aerosol origin. Moreover, the category "high latitude dust" is very extended with Al/Fe ratio ranging from 0.1 to 1 (L322-334), suggesting a variability of aerosol sources in these samples (see specific comments). The conclusion of authors about the mixed volcanic and anthropogenic origins of GA01 samples is supported only by the back-trajectories (not shown) and a comparison with the TEs concentrations in volcanic ash from Achterberg et al. (2013), but no comparison on elemental ratios is provided. Is this variability is consistent with the typical composition of volcanic or cold environment dust? Again, several papers report Fe or metals content in high latitude volcanic regions producing dust as Iceland (e.g. Baratoux et al., 2011, Óladóttir et al., 2008 and 2011). It could be interesting to compare with these data for discriminating the origin of this high latitude dust.

Further discussion of the high latitude dust sources is now included in the text, and a table of elemental ratios from the various studies in regions that contribute aerosols to the North Atlantic is included in the Supplementary Material (Table S2).

The third conclusion of a paper is that polluted derived TEs were significantly enriched above crustal values in aerosol and notably in dust samples (A1-15), on the basis of comparison with UCC. This conclusion is already in Shelley et al. (2015) for GA03 cruises. The new information could be for GA01 for high latitude dust, but this work is not done. Furthermore, I'm not agree with your conclusion on the enrichment "even in samples of North African origin". As a matter of facts, Shelley et al. (2015) conclude that except Cd, the "pollution-derived" elements present EFs less than 10 with respect to Al in the African samples (See Shelley et al., 2015, figure 6). Moreover, your main argument is that these elements have some significant increase from the

UCC mass ratio in your dust samples (see specific comments: P11,L336). However, it’s known that the production of mineral dust is associated to a chemical fractioning due to the size partitioning between coarse rich-Si grains and the finest clay fraction during sand- blasting. It means an enrichment in Al, Fe, Ca. in dust particles in comparison to soil (Lafon et al., 2006). Thus, the authors are surprised at Al/Fe ratio around 0.76 (P9, L275). Yet, this value is fully consistent with the common knowledge on African dust (see previous comment on bibliography + e.g. Formenti et al., 2011 or 2014 and ref therein or Lazaro et al., 2008). Due to the trace metals partitioning in soil size fraction, this fractioning and hence enrichment probably happens also for trace metals in mineral dust. Your data seem to confirm this trend, previously observed by Trapp et al. (2010) after long-range transport. it’s bad that this point of view is not addressed here. . .

The original intention was to argue that the UCC ratio is not representative of North African dust inputs, but that the ratio we observed is consistent with other studies. We don’t think that the North African dust is enriched with pollution-derived elements, but that there could be a component of aerosols coming from Europe mixed in with the Saharan end-member, which is also consistent with other studies (e.g. Baker and Jickells, 2017). A new table has been included in the Supplementary Material (Table S1), which includes elemental ratios from studies in the AMBT regions. It does not include literature data from a Saharan end-member as this was discussed extensively in Shelley et al. (2015).

Finally, a part of the manuscript is focused on the standardization of methods to estimate TE solubility. The conclusion on this session is not convincing for me because the proposed “upper limit” is not supported by the “reality” of aerosol dissolution in atmospheric or sea waters. The 25% acetic acid leaching protocol includes a heating at 90˚C during 10 min. This leaching protocol is issued from Berger et al. (2008) who recommend the heating to dissolve the refractory forms of metals bound with intracellular protein or intracellular trace metals in particles collected in river plumes, i.e. organic macromolecules bound trace metals (heating enabling the degradation of these polymeric structures). Your arguments are based on the capacity of this protocol to reproduce acid digestion in gut krill. Yet, the dissolution in this condition is probably more aggressive than gut krill due to this step of heating. The risk with this protocol is to access to refractory form which is never available for phytoplankton. Besides in your data, the solubility of Al is higher than the one of Fe with this protocol, isn’t it due to leaching some aluminum from the refractory alumino-silicate minerals (see specific comments, P13, L400)? What is the relevance of this refractory forms of TEs for estimating their bioavailability? Do you have literature to support the fact of organo-metal complexs are bioavailable? In my opinion, it could be more interesting to use this 25% acetate soluble fraction as a proxy of organically bound trace metals and discuss on the link between source/instantaneous solubility and chemical form of trace metals, rather as an “upper limit” of solubility which is probably never reach in the natural conditions.

We absolutely agree that this is an upper limit, and potentially an over-estimation of the upper limit. However, we feel that the use of the heating step is justified as we wanted to use exactly the same protocol as the SPM leaches done on GA01, and some GA03 samples to allow direct comparison between the two datasets. A key goal of this work was to link the atmospheric inputs to processes occurring in the ocean. Data from the aerosol leaches and dissolved and particulate trace elements indicate that atmospheric inputs are not the dominant source of Al, Fe or Pb along the GA01 transect (Menzel-Barraqueta et al.,; Tonnard et al.,; Zurbrick et al., submitted to this special issue).-However, we have acknowledged that there could be an overestimation of the upper-limit of solubility in the text (from line 209), although the Ti fractional solubility data presented in Figs 4a and b suggests otherwise. We feel that if refractory metal is liberated it has the potential to be bioavailable to some micro-organisms, e.g. Tricho (Rubin et al, 2011). In future, it would be a good idea to conduct experiments to test the difference in fractional solubility estimates using this protocol with/without the heating step on different types of aerosols.

In answer to your question about the bioavail ability of organically-complexed TEs, the review by Shaked and Lis (2012) investigates this question, and provides examples of literature that supports this. for Fe. This paper is cited in the manuscript.

Specific comments :

The paper is a part of range of publications associated to Atlantic Geotraces campaigns. The presented data analysis is supported by numerous other works issued from these campaigns. The crucial information to understand the results is not always specified in the text and it's necessary to study the cited papers to understand the interpretation of results. For example, the back-trajectories are at the heart of the discussion in this paper, but they are not available in the text (see below). The categories of trace metals "lithogenic", "anthropogenically enriched" and "mixed source" which are issued from Shelley et al. (2015) appear P9, L336 without previous explanation. **Additional wording has been added to this text that we hope provides suitable clarification. The text starting at Line 461 now reads "Figure 5 highlights the distinction between the lithogenic elements, Al, Fe and Ti, which have uniformly low solubility in UHP water (mostly < 20 %), and extremely low solubility in North African aerosols (< 1 %), and the anthropogenic, pollution-dominated elements, Ni, Cu, Zn, Cd and Pb which have solubility up to 100 %. Manganese (Mn) and Co have both lithogenic and anthropogenic sources, so are classified as "mixed-source", and have intermediate solubilities."**

Moreover, the structuration of the paper is not linear and implies several repetitions or meandering discussions, which drow up the conclusions. This paper has no clear guidance and is hard to follow. For example: In "Introduction": a first background on the leaching protocol between L67 and 86, then a second part of this background with repetition is presented between L95 and 124. Or In "Results and Discussion", the discussion on the ratio Fe and Al begins L255 up to L265 in session 3.1, then continues in L275, then is addressed in the next session 3.2 (L 295-335). The UHP water soluble fraction starts to be discussed in the session 3.2., then be continued in the session 3.3. "Aerosol solubility". I advise to re-organise your paper, with a session: "metals origin" including a "clear" summary of Shelley et al. (2015) focused on their conclusions about origin of Fe and TEs as a function of provenance completed with a work on identification of sources from adapted bibliography then a second session presenting "solubility" not as a function of back trajectories but a function of metals source (and in consequence with adapted figures).

The problem with repetition has been addressed through restructuring and rewriting sections. There are new sections headings: 3.3.1. Identifying sources of TEs. The 'solubility' section is still structured by AMBT category because clear sources could not be identified that would have enabled reorganising the data accordingly. However, a new section has been included (Section 3.4) at the end of the manuscript that discusses sub-groups within the AMBT categories that are suggested by cluster analysis of the total TE data and the fractional solubility of TEs.

Certain experimental points need also to be specified to clarify the conclusions of this work.

P5, L148, please precise the cut-off diameter (or PM fraction: TSP, PM10.) of the aerosol sampler. **TSP has been added to text. Line 138.**

P7, L226-L228 and session 3.4: The determination of nss-SO42- is calculated from soluble Cl-. However, it's known that there is a potential depletion of Cl- during transport of sea salts due to the reactivity with anthropogenic gas in particular acid gas as HNO3. The probability of this depletion increases with the increase of acidity (e.g. Kerminen et al., 1998; Yao et al., 2003; Newberg et al., 2005; Chi et al., 2015). In consequence, the fraction of nss-sulfate could be overestimated. Moreover, your method of calculation of acidity excluded all the organic acid, such as oxalic acid, formic acid. . .which are observed in marine atmosphere (e.g. Kawamura et al., 2017). Lastly, acidity measurement based exclusively on sulfate and nitrate implies that these species are in their acid forms. However, it's known that these compounds are associated to neutralizing compounds as NH4+ (Weber et al., 2016). In general, ammonium concentrations or Cl-depletion are used to estimate the aerosol acidity (Newberg et al., 2005; Hennigan et al., 2015). You mention all this literature and these works (L512-524) and you propose that "these approaches should be considered for future studies". Only even now, without at least an estimation of neutralised fraction, I think that your method suffers too much uncertainties to provide robust conclusion. So, the session 3.4 on the link between solubility and your "acidity" should be removed or completed with cation measurements.

As suggested, this section has been removed.

P8, L238: The air masses of collected samples in the cruise GA01 are not shown. "High latitude dust" includes both dust from paraglacial regions and volcanic lands. Thus, even if the provenance is "high latitude dust", the origin could be different. For the longest distance between "high latitude" and R/V, a mixing with other sources could have occurred: the collected filters close to Europe (G1-G6) could be feed by various other sources (North of Europe, Europe, marine) in comparison to the samples G12 or G14...Please show back-trajectories for at least one of the samples close to Europe and another close to North Atlantic.

Agreed. All of the AMBTs from GA01 have been reproduced and can be found as Figure S1 in the Supplementary Material. The four representative AMBTs from GA03 have been redrawn and are also included in Figure S1.

P8, L246: replace 2015 by 2014 in reference: Conway and John. And P20, L627 add 2014 in this reference. **Done.**

P8, L258: Even if the correlation between Fe and Al in "high latitude dust" samples (= Geovide samples, please be homogeneous between text and Figure 2) is good, the ratio Fe/Al is variable (Figure 3), suggesting various mineral source: please complete this discussion. **This discussion can now be found starting at line 346.**

P8, L260 to P9L265: "no correlation between Fe and Al in the samples of N. American (r^2=0.153..) and marine (r^2=0.016..) provenance". However in the figure 2b, the plots between Fe and Al concentrations show a R^2= 0.983 for N. American aerosols, and R^2=0.758 for Marine aerosol. Why is this difference between text and figures? On the basis of a bad correlation, you argue a strong influence of anthropogenic emissions on the Fe/Al ratio in N. American samples. Yet, the ratio (0.86) is consistent with a mineral origin. The quality of correlation changes all the discussion on the origin of Fe, so please clarify that.

This was a mistake and has been corrected, starting at line 286.

P9, L273 : You propose that "other sources are responsible for residual variance" for metals as Ni or Cd. It could be useful for the discussion on solubility to distinguish correlation (and consequent residual variance) between TEs and Al for each provenance as for Fe. The figure 3 seems show that all the TEs are correlated with Al in the N. African samples, meaning probably that the anthropogenic influence is poor in these samples.

This is not done as a new Figure 4 and discussion has been added instead, which includes all TEs under discussion.

P10, L322: "the most heterogeneous group", for what?

Of the Fe/Al ratios. This wording has been deleted. It now reads, 'In contrast, samples from the most remote locations, the Marine and High Latitude aerosols, had the most spread in their fractional solubility and elemental ratios....'. Starting at line 614.

P11, L336 : Why do you consider all the metals as anthropogenically enriched what-ever the provenance whereas all these metals in dust samples (A1-A15) are probably originated from dust from the enrichment factor calculated in Shelley et al. (2015)?

We don't, we had previously argued that the samples had a relatively low concentration of Al compared to other elements.

P11, L350 : Why do you use a PMF analysis with 2 profiles whereas at least 3 are potentially present in your samples : African dust, Anthropic and High latitude dust ? Did you take only trace metals in PMF anlaysis? Nitrate or nss-Sulfate are good proxies to discriminate anthropogenic source. Moreover, PMF is a stastistical method, even if the factor 2 is richest for "anthropogenic" metals, that doesn't mean that this factor doesn't include a mineral fingerprint, for example the high latitude dust. It's clear for the A1-A15 samples, the high contribution of finger 2 is probably due to the fact that metals from mineral fingerprint is taken into account in this factor. This method with your applied conditions is not sufficiently discriminating to be useful here. The discussion on PMF analysis should be removed, because it provides no appropriate information on the provenance of TEs.

The model is not stable with more than two factors, due to the relatively small dataset. This is why only two factors were used. We have tried to remove the North African samples to look for other groups of TEs that would be diagnostic of other sources, but a crustal factor is always one of the two factors. We also tried this with excess metal (assuming the N. African ratio as the reference ratio), but the same thing happened. We also tried adding the NO3- data to the analysis, but with no new information generated.

We agree that the PMF provides limited evidence for sources other than mineral dust, but include this figure (Fig. S2) in the discussion because of its inability to identify sources, and as a reason to try another multivariate statistical approach (cluster analysis) which is presented later in the manuscript.

P12, L382-389: I don't understand why this paragraph is here? A bad cut and paste?

This sentence has been reworded, ''The ability of models to replicate subtleties in aerosol TE solubility may prove critical in forecasting ecosystem impacts and responses. Due to the magnitude of North African dust inputs to the North Atlantic region (very high dust inputs result in a high soluble aerosol TE flux despite relatively low fractional solubility), this is a particular challenge and is compounded by additional unknowns such as how aerosol acidity will be impacted by the combined effects of increasing industrialisation/urbanisation, and changes in the magnitude of future mineral dust supply and biomass burning (Knippertz et al., 2015; Weber et al., 2016)" Starting at line 561.

P13, L398: Why do you present these data? It's not new that the solubility decreases with the total Al content (e.g. Baker et al., 1996) and your results don't provide new conclusion. On the contrary, it could be interested to plot the solubility of TEs (no Fe) as a function of atmospheric loading or Al concentrations. Firstly, that enables to valid or not your assumption on the role of scattering in our data in this trend. Secondly, it could be interested to compare the behaviour of Fe (a proxy of mineral dust) with the ones of anthropogenic trace metals.

Figure 4 has been redrawn and replaced using all TEs. The main conclusion is that Mn, Zn and Cd do not follow the same trend of having an inverse relationship with atmospheric loading as Fe and Al.

P13, L400: I wonder really if the highest Al solubility in comparison to Fe is not due to the dissolution of refractory alumino-silicate minerals. Ti and Fe have the same behavior between UHP-water and 25% acetic acid dissolution in dust samples (figure 5) and both of them are in part as oxide in mineral dust, i.e. "refractory" even at high temperature. Please complete this discussion.

This is done starting at line 434. 'Although, we cannot rule out that this effect is the result of the heating step in the 25 % acetic acid leach attacking the alumino-silicate matrix, the similarity in the trend of the solubility of Ti in UHP water and 25 % acetic acid (sharp decrease in solubility with increased aerosol loading, Figs. 4a and b) suggests that matrix attack is minimal. Further experimentation with and without the heating step would help to clarify this issue.'

P13, L403-410: This paragraph is unclear: the first sentence is too long and confused and what is the link between your data and the Madcow MODEL?

This has been moved to a new section (Section 3.5) as we wanted to draw attention to how important it is to accurately parameterise fractional solubility. This section also includes a short discussion on modelling Fe and Mn.

P13, L411-420: This conclusion is interesting but without link with the results presented in this session.

This conclusion is now supported with evidence from this study and starts at line 570.

P14, L451: The discussion around these results is for me off topic. It is a pity that this paragraph be discussed only in terms of comparison between UHP water and seawater protocol, it would be interesting to discuss precisely in terms of origin of metals and solubility in the two protocols. But again, the assumption, which is that the origin of trace metals is homogeneous and anthropogenic, doesn't enable to identify a link between solubility and chemical form. For example, could you distinguish by coloring the different origin of metals in the figures 7 (as for Fe) to see if a same metal present different behaviours for solubility?

Figure 6 – the samples have been colour-coded and a table (Table 1) has been added that shows which groups of samples have slopes that do not differ significantly from 1.0. We do not think that the origin of the metals are homogeneous (although the North African sample TE composition is more homogeneous that for the other groups), for the precise reason that multiple sources contribute to the aerosols in each region, as well as mixing occurring en route. Perhaps this is why no obvious relationship is seen between the samples being leached with either UHP water or seawater. Also, perhaps primarily because of the amount of mixing before collection, so far from sources, we are having difficulty identifying sources.

Figures 5 and 6: No uncertainty is provided in your graphs for the data, could you add this information?

Error bars have not been added because of the problem with determining the SD of the fractional solubility. In Figure 5, the addition of error bars makes it impossible to distinguish the different symbols.

Regional trends in the fractional solubility of Fe and other metals North Atlantic aerosols (GEOTRACES cruises GA01 and GA03) following a two-stage leach

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Abstract. The fractional solubility of aerosol-derived trace elements deposited to the ocean surface is a key parameter of many marine biogeochemical models. Yet, it is currently poorly constrained, in part due to the complex interplay between the various processes that govern the solubilisation of aerosol trace elements. In this study, we used a sequential two-stage leach to investigate the regional variability in fractional solubility of a suite of aerosol trace elements (Al, Ti, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb) from samples collected during three GEOTRACES cruises to the North Atlantic Ocean (GA01, GA03-2010 and GA03-2011). We present aerosol trace element solubility data from two sequential leaches that provide a "solubility window", covering a conservative, lower limit to an upper limit, the maximum potentially soluble fraction, and discuss why this upper limit of solubility could be used as a proxy for the bioavailable fraction in some regions.

Regardless of the leaching solution used in this study (mild versus strong leach), the most heavily loaded samples generally had the lowest solubility. However, there were exceptions. Manganese fractional solubility was relatively uniform across the full range of atmospheric loading (32 ± 13 % and 49 ± 13 % for ultra-high purity water and 25 % acetic acid leaches, respectively). This is consistent with other marine aerosol studies. Zinc and Cd fractional solubility also appeared to be independent of atmospheric loading. Although the average fractional solubilities of Zn and Cd (Zn: 37 ± 28 % and 55 ± 30 %, Cd: 39 ± 23 % and 58 ± 26 % for ultra-high purity water and 25 % acetic acid leaches, respectively) were similar to Mn, the range was greater, with several samples being 100% soluble after the second leach. Finally, as the objective of this study was to investigate the regional variability in TE solubility, the samples were grouped according to air mass back trajectories (AMBTs). However, we conclude that AMBTs are not sufficiently discriminating to identify the aerosol sources or the potential effects of atmospheric processing on the physico-chemical composition and solubility of the aerosols.

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1. Introduction

Aerosol trace element (TE) solubility is a key parameter of many biogeochemical models, but it is poorly constrained, e.g. Fe solubility estimates range from 0.001-90 % (Aguilar-Islas et al., 2010; Baker et al., 2016). The fractional solubility (herein referred to as “solubility”) of aerosol TEs is defined in terms of the amount of a TE in solution from any given leach that passes through a filter (usually < 0.45 or 0.2 µm), expressed as a percentage of the total (Baker and Croot, 2010; Baker et al., 2016; Jickells et al., 2016). While this operational definition accounts for some of the variability in published values, it does not account for all of it. A number of factors impact aerosol TE solubility, such as: (1) the choice of leaching protocol, and (2) the aerosol source, which in turn is impacted by a combination of factors such as the mineralogy of the particles, atmospheric processing during transport, and the presence/absence of emissions from e.g. vehicles, industry and agricultural practices. Several studies have concluded that the most significant effects on aerosol Fe solubility result from the source/composition of the aerosols, rather than changes in physico-chemical parameters, such as temperature, pH and oxygen concentration of the leach medium, or the choice of batch versus flow-through techniques (e.g. Aguilar-Islas et al., 2010; Fishwick et al., 2014).

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There have been a number of studies that have focused on the role of aerosol TEs on biogeochemical cycles in the North Atlantic (e.g. Sarthou et al., 2003; Baker et al., 2013; Buck et al., 2010; Ussher et al., 2013; Powell et al., 2015). More recently, the GEOTRACES programme has produced a number of aerosol datasets, which has stimulated further discussion on the use of this data to look for trends that link TE solubility and aerosol source (e.g. Baker et al., 2016; Jickells et al., 2016). Elemental ratios, enrichment factors and air mass back trajectory simulations have long been used as a first approximation of aerosol source, and there are many studies that employ multivariate statistical analyses for aerosol source apportionment (e.g. Chueinta et al., 2000; Laing et al., 2015). In addition, more studies are making use of stable isotope ratios to investigate aerosol provenance. Some of these methods are well-established and have a relatively long history of use in this purpose, such as Pb isotopes (e.g. Maring et al., 1987), and Sr and Nd isotopes (e.g. Skonieczny et al., 2011; Scheuvens et al., 2013 and references therein), and data from investigations of novel isotope systems are increasing. For example, Fe isotopes show promise as a way to differentiate between anthropogenic and mineral dust aerosols (Conway et al., submitted). In contrast, Cd isotopes may not be a suitable tool for aerosol source apportionment (Bridgestock et al., 2017).

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As the soluble fractions of aerosol TEs are thought to be the most-readily bioavailable forms (Shaked and Lis, 2009), the leachable (soluble) fraction is used as a first approximation of the bioavailable fraction. Therefore, experimental conditions should mimic natural conditions as closely as possible, while yielding reproducible results. Ideally, the leach protocol used fits both these criteria. However, that is not always strictly possible for reasons such as access to the leach medium of choice,

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availability of analytical instrumentation, and cost. Currently, however, there is no standardised aerosol leaching protocol, but it is recognised that this should be a priority for future studies (Baker et al., 2016). Some commonly-used leach media are ultra-high purity (UHP) water (18.2 MΩ.cm), seawater, weak acids (e.g. 1% HCl, 25 % acetic acid), or ammonium acetate buffer (e.g. Buck et al., 2006, Baker et al., 2006b; Berger et al., 2008).

To investigate the regional variation in the solubility of key TEs in the North Atlantic, aerosol samples were collected during the US-GEOTRACES GA03 campaigns in 2010 and 2011, and the French GEOTRACES GA01 campaign in 2014 (www.geotraces.org). The focus of this paper is Fe and the GEOTRACES "key" trace elements, Al, Cd, Cu, Mn, Pb, Zn, plus Co, Ni, and Ti (GEOTRACES Planning Group, 2006). This suite of TEs includes bioactive elements, tracers of atmospheric deposition, and elements characteristic of anthropogenic aerosols. Some TEs fit into more than one of these categories. Here, we use the term 'trace element' in the context of open ocean water column concentrations, thus acknowledging that elements such as Al, Fe and Ti are not present in trace concentrations in aerosol source material. Aerosol concentrations for a suite of other elements (Li, Na, Mg, P, Sc, V, As, Se, Rb, Sr, Sn, Sb, Cs, Ba, La, Ce, Nd, Th, U) were also determined, but will not be discussed further here. However, these data are available at BCO-DMO (GA03; www.bco-dmo.org/) and LEFE-CYBER (GA01; (www.obsvlfr.fr/proof/php/GEOVIDE/GEOVIDE.php), and on request from the lead author.

In this study a two-stage leach protocol was followed. the first leach employed was the "instantaneous" leach described by Buck et al. (2006) which is a flow-through method where the leach medium is in contact with the aerosols for 10 - 30 s. It can be conducted using UHP water or seawater. The advantages of using UHP water are that UHP water is a reproducible medium (allowing for inter-lab comparisons) that can easily be analysed by ICP-MS for many elements simultaneously without the need for time-consuming sample handling steps such as separation techniques and drying down then re-dissolving the residue. Leaches with UHP water can be conducted at sea, or in the home laboratory. If fresh sea water is used the leaches must be undertaken at sea.

Given that UHP water and rain water have broadly similar pH (~ pH 5.6), UHP water is used as an analogue for rain/wet deposition, as wet deposition is thought to dominate the supply of many TEs, at least at some regional and local scales (Helmers and Shremms, 1995; Kim et al., 1999; Powell et al., 2015). However, the extremely low ionic strength of UHP water, and the absence of the metal binding ligands naturally present in rain water and seawater (e.g. Chieze et al., 2012; Wozniak et al., 2014), means that UHP water is not a perfect analogue for oceanic receiving waters. As such, freshly-collected, filtered (< 0.2 µm) seawater likely produces a better estimate of the fractional solubility of TEs on first contact with oceanic receiving waters. For Fe, leaches using UHP water (~ pH 5.6)

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The instantaneous leach can be conducted using UHP water or sewater as the leach medium. The advantages of conducting it usir

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typically produce higher solubility estimates than leaches conducted with natural seawater (~ pH 8.2) due to the pH sensitivity of dissolution and the higher ionic strength of sea water. On occasions where higher solubility in seawater is observed, complexation by Fe binding ligands is likely the cause. Regardless of whether UHP water or seawater is used, the instantaneous leach likely yields conservative lower limit estimates of TE solubility due to the short contact time between the aerosols and leach medium, and reports that aerosol solubility has a bi-modal behaviour for many TEs (initial fast release, followed by a slower sustained release with time; e.g. Desboeufs et al. 2005; Kocak et al., 2007; Mackey et al., 2015).

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The second, sequential leach was employed in order to estimate an upper limit of TE solubility, and provide a “solubility window”, but also as an estimate of the maximum bioavailable fraction during the residence time of aerosol particles in the euphotic zone. We used the 25 % acetic acid leach with hydroxylamine hydrochloride described by Berger et al. (2008). The pH of this leach (pH 2.1) is just below that of zooplankton or fish digestive tracts and the reducing agent mimics the low oxygen environments inside faecal pellets and marine snow aggregates. Indeed, Schmidt et al. (2016) have demonstrated that lithogenic Fe is mobilised in the gut passage of krill resulting in threefold higher Fe content in the muscle, and fivefold higher Fe content of the faecal pellets of specimens close to lithogenic source material compared to those from offshore.

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2. Methods

2.1. Aerosol sample collection

Aerosol samples (n = 57) were collected aboard the *R/V Knorr* during the *US-GEOTRACES GA03* cruises (15 Oct – 2 Nov 2010 and 6 Nov – 9 Dec 2011, and aboard the *N/O Pourquoi Pas?* during the French GEOTRACES GA01 cruise (GEOVIDE, 15 May – 30 June 2014) (Fig. 1). Both campaigns took place in the North Atlantic Ocean, with GA03-2010 and GA01 departing from Lisbon, Portugal. The cruise tracks were designed to traverse a wide variety of biogeochemical provinces (Longhurst, 2010) including; continental shelf regions, an eastern boundary current upwelling system (off West Africa), the oligotrophic North Atlantic gyre, and sub-Arctic waters, and to span a large gradient in atmospheric dust loading. The aerosol collections have been described previously (Wozniak et al., 2013; 2014; Shelley et al., 2015; 2017). Briefly, air was simultaneously pulled through twelve acid-washed 47 mm diameter Whatman 41 (W41) ashless filter discs at approximately 1.2 $m^3 min^{-1}$ (134 $cm s^{-1}$ face velocity) using a high-volume aerosol sampler (TSP model 5170V-BL, Tisch Environmental). The metadata and concentration data for the aerosol leaches can be found in the supplementary information (Table S1). All filters were stored frozen (-20°C) and double bagged prior to processing, both on the ship and upon returning to the home laboratories.

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To avoid contamination from the ship’s stack exhaust, aerosol sampling was controlled with respect to wind sector and wind speed using an anemometer interfaced with a datalogger (CR800, Campbell

Scientific). The samplers were programmed to run when the wind was ± 60° from the bow of the ship and > 0.5 m s^{-1}. When the wind failed to meet these two criteria, the motors were shut off automatically and not allowed to restart until the wind met both the speed and direction criteria for 5 continuous minutes. In addition, the samplers were deployed on the ship's flying bridge as high off the water as possible (~14 m above sea level) to minimise collection of sea spray.

2.2. Trace element determination – totals aerosol TEs

The total digestion method of Morton et al. (2013) was used for the determination of total aerosol TE loadings (Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb). The W41 filter discs were digested in tightly-capped 15 mL Teflon-PFA vials (Savillex). Firstly, 1000 µL of ultrahigh purity (UHP) 15.8 M nitric acid (Optima or Merck Ultrapur) was added to each vial, heated to 150 °C on a hotplate, and then taken to dryness. Secondly, 500 µL of 15.8 M nitric acid (13.2 M HN0$_3$) and 100 µL of 28.9 M hydrofluoric acid (5.8 M HF) (Optima or Merck Ultrapur) was added to each vial, re-heated to 150 °C on a hotplate, then taken to near dryness. After the final digestion and evaporation step, the samples were re-dissolved in 20 mL of 0.32 M nitric acid for analysis. All filter digestions were performed under Class-100 laminar flow conditions. Total aerosol TE concentrations were determined by magnetic sector field inductively coupled plasma mass spectrometry (ICP-MS; Thermo Element-2) at the National High Magnetic Field Laboratory (NHMFL) at Florida State University (FSU; GA03) or Pôle de Spectrométrie Océan (PSO) at the Institut Universitaire Européen de la Mer, France (IUEM; GA01). Samples were introduced to a PFA-ST nebuliser (Elemental Scientific Inc.) via a modified SC-Fast introduction system consisting of an SC-2 autosampler, a six-port valve and a vacuum rinsing pump. Replicate blank solutions for the acid digestions were prepared by digesting W41 discs that had been deployed in the aerosol samplers for 1 h while not in operation, and the resulting concentrations were subtracted from all acid-digested filter samples. Details of the digestion blanks and analytical figures of merit, including CRM recoveries, have previously been reported (Shelley et al., 2015; 2017).

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2.3. Trace element determination – soluble aerosol TEs

In this study, we used a two-step, sequential leach to investigate regional variation in aerosol sources, TE fractional solubility and bioavailability. We discuss the results from (1) an 'instantaneous' leach (Buck et al., 2006), that provides a lower limit estimate of the most labile TE fraction (analogous to the initial rapid release of TEs into rain drops and the surface mixed layer of the ocean), followed by (2) a more protracted leach using 25 % acetic acid (with the reducing agent, hydroxylamine hydrochloride, and heat, 10 min at 90 °C), which mimics the slower and sustained release from aerosol particles during their residence time in the euphotic zone.

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The first step, the "instantaneous" leach, was conducted under a Class-100 laminar flow hood. In this technique, 100 mL of UHP water (> 18 MΩ·cm resistivity, pH ~ 5.5, Barnstead Nanopure) is rapidly passed through an aerosol-laden W41 filter held in a polysulfone vacuum filtration assembly (Nalgene). Operationally-defined dissolved (≤ 0.45 µm) TEs are collected in the filtrate (leachate) by positioning a GN-6 Metricel backing filter (cellulose esters) below the W41 disc in the filtration assembly (Buck et al., 2006). In this study, the leachate was transferred to an acid-clean low density polyethylene (LDPE) bottle and acidified to 0.024 M (~ pH 1.7) with UHP HCl and double-bagged for storage until analysis at FSU or IUEM. As for total elemental determinations, soluble TEs in the leachate were also determined by ICP-MS. Leachate blanks were prepared by passing 100 mL of UHP water through W41 filters that had been deployed in the aerosol sampler for 1 h while not in operation. For example, leachate blanks for Fe represented an average of 1.6 ± 0.4 % and 15.5 ± 15.8 % of the Fe sample concentrations for GA03 and GA01, respectively). A subset of samples (GA03-2011) were also leached using the instantaneous leach procedure with freshly collected, filtered (0.2 µm) seawater as the leach medium. Leachate blanks were subtracted from all leachate sample concentrations, details of which can be found in Table S1 in the Supplementary Material.

The UHP water fractional solubility was calculated using Eq. (1):

$$\frac{[element]_{UHP\ water\ leach}}{[element]_{total}} * 100 = UHP\ water\ Fractional\ Solubility \qquad (1)$$

Following the instantaneous UHP water leach, the filter was transferred to a 15 mL centrifuge tube, and the second leach was undertaken, using 5 mL of 25 % (4.4 M) ultrapure acetic acid, with 0.02 M hydroxylamine hydrochloride as the reducing agent (Berger et al., 2008). After a 10 min heating step (90 °C), the leaches were left for 24 h before being centrifuged for 5 min at 3400xg. The leachate was then carefully decanted into acid-clean LDPE bottles. In order to rinse any residual acetic acid from the filter, 5 mL of UHP water was pipetted into the centrifuge tubes, which were then centrifuged again for 5 min at 3400xg. This supernatant was then added to the acetic acid leachate in the LDPE sample bottles. As this second leach aims to access a less labile fraction of the TEs of interest (including TEs absorbed to surfaces, TE oxyhydroxides and TEs complexed by aerosol organic matter), without significantly attacking TEs bound within the mineral matrix (Koçak et al., 2007; Berger et al., 2008), it may provide an upper limit estimate for the fractional solubility of these aerosol TEs as the aerosols mix down into the ocean. There is a slight risk that the heating step could begin to attack the mineral matrix, resulting in a slight over-estimation of the upper limit of solubility, but this risk was shown to be minimal (Berger et al., 2008). Despite this risk, the heating step was included because of the desire for procedural similarity with marine particle leaches from the same cruises (e.g. Planquette et al., 2016; H. Planquette and A. Gourain pers. comm.), which have been used to assess

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As all samples in this study were leached first using the UHP water instantaneous leach, followed by a sequential leach with 25 % acetic acid, the overall solubility in 25% acetic acid was calculated using Eq. (2):

$$\frac{[element]_{UHP\ water\ leach}}{[element]_{total}} + \frac{[element]_{25\,\%\ HAc\ leach}}{[element]_{total}} * 100 = HAc\ Fractional\ Solubility \qquad (2)$$

2.4. Major anion determination

Before the UHP water leachate was acidified, a 10 mL aliquot was taken from each leach sample for the determination of the soluble major anions. The aliquot was immediately frozen for storage. The anions, Cl^-, NO_3^- and SO_4^{2-}, were determined by ion chromatography using either a Dionex 4500i (at FSU for GA03 samples) or a Metrohm, IC850 system (at Laboratoire Interunivesitaire des Systèmes Atmosphériques, Paris for GA01 samples).

2.5. Air mass back trajectory simulations

Air mass back trajectory (AMBT) simulations were generated using the publicly-available NOAA Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, using the GDAS meteorology (Stein et al., 2015; Rolph, 2017). The 5-day AMBT simulations were used to describe five regional categories, based on the predominant trajectories for the air masses. The simulations and further details of these categories can be found in Wozniak et al., (2013; 2014) and Shelley et al., (2015; 2017). Briefly, for cruise GA03 air masses were characterised as European, North American, North African, or Marine (no or minimal interaction with major continental land masses within the 5-day simulation period). For cruise GA01, all the samples were classified as High Latitude dust (originating north of 50°N; Bullard et al., 2016). The classifications are shown in Table S1, and the AMBT simulations from Shelley et al. (2015; 2017) have been reproduced and can be found in the Supplementary Material (Fig. S1). The simulations use arrival heights of 50, 500 and 1500 m, so that at least one height was located in the marine boundary layer.

3. Results and Discussion

3.1. Identifying aerosol provenance

Air mass back trajectory (AMBT) simulations are frequently used to identify the origin and/or flow path of air masses, from which a first approximation of aerosol provenance (e.g. deserts, urban regions, or biomass burning) are made. While a useful tool in oceanographic studies, AMBTs used

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alone do have limitations. Perhaps the most significant of these is that they are unable to quantify the contribution of different aerosol types or the entrainment of particles along the flow path of the air mass. Indeed, within the five categories described in this study multiple sources are likely to have contributed to the composition of the bulk aerosol of each category. This study is likely to be particularly sensitive to this as the sampling site was not static (i.e. sampling occurred along three different transects), and air masses can, and do, take different pathways within a general wind direction. Consequently, AMBTs are not adequately discriminating for aerosol source apportionment. However, we have organised the data using the AMBT categories as the objective of this study was to look for trends in solubility at a regional level, and also for consistency with our earlier published work from the North Atlantic (Wozniak et al., 2013; 2014; Shelley et al., 2015; 2017).

More powerful approaches for aerosol source apportionment consider the physico-chemical composition of the aerosols, either as the bulk aerosol or individual particles. There have been a number of field campaigns (e.g. DABEX, DODO, SAMUM and AMMA) and individual studies which have provided a wealth of information about the physico-chemical composition of African dust before, during and after long-range transport (e.g. Johansen et al., 2000; Johnson et al., 2008; McConnell et al., 2008; Petzold et al., 2009; Marticorena et al., 2010; Trapp et al., 2010; Formenti et al., 2011). These studies, and satellite data have identified the key dust source regions in North Africa (Prospero et al., 2002). Chemical composition data for other aerosol end members which supply aerosols to the North Atlantic is not as extensive, but some examples of individual studies and field campaigns can be found in Table S2. In addition, campaigns in the Atlantic Ocean which have sampled marine aerosols (e.g. Atlantic Meridional Transect, CLIVAR, GEOTRACES) have identified aerosol sources from characteristic groups of elements and elemental ratios (e.g. high concentrations of lithogenic elements are characteristic of a mineral dust, K is a tracer of biomass burning, and correlations between V and Ni are diagnostic of emissions from marine shipping; Baker et al., 2006a; Sippula et al., 2014; Baker and Jickells, 2017), organic composition (e.g. Wozniak et al., 2013; 2014, 2015), and/or stable isotopic signatures (Scheuvens et al., 2013 and references therein).

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Although atmospheric inputs to the ocean are episodic and exhibit a seasonality in the tropical and subtropical North Atlantic that is largely driven by the migration of the intertropical convergence zone (Prospero et al., 1981; Adams et al., 2012; Doherty et al., 2014). North African/Saharan mineral dust dominated the aerosol composition in the GA03 study region (Conway and John, 2014; Shelley et al., 2015; Conway et al., submitted). Other aerosol sources in Europe and North America and sea salt also contributed to the bulk aerosol to varying extents. In contrast to GA03, the GA01 transect was located north of the extent of the Saharan dust plume (~ 25° N in summer, Ben-Ami et al., 2009), and was thus influenced by a mixture of high latitude dust sources (Prospero et al., 2012; Shelley et al., 2017), which also have a seasonal cycle. As a result, a large dynamic range of aerosol loading was observed

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(Fe = 0.185–5650 ng m^{-3}; Al = 0.761- 7490 ng m^{-3}) during these two campaigns, with the highest Fe and Al loadings associated with the North African samples (GA03), lower loadings with the Marine samples (GA03), and the lowest loadings observed in the samples collected in the Labrador Sea (GA01).

Total Fe and Al were strongly correlated ($r^2 = 0.999$, Pearson's ρ $P < 0.01$), demonstrating that the two metals have common lithogenic source(s) (Fig. 2). However, this correlation was largely driven by the heavily-loaded North African samples ($r^2 = 0.997$, $P < 0.01$). For each of the other source categories, simple linear regression of the data resulted in r^2 values of: 0.879 ($P < 0.01$) for High Latitude dust (GA01), 0.890 ($P = 0.057$) for European samples (GA03), 0.983 (P 0.34) for N. American samples (GA03) and 0.751 ($P = 0.70$) for Marine samples (GA03) (Fig. 2b). Further discussion of sub-regional differences in the Fe/Al ratio are addressed later in the Discussion. For the other TEs, strong correlations for the combined GA01 and GA03 datasets were found between Ti/Al ($r^2 = 0.999$, $P < 0.01$), Mn/Al ($r^2 = 0.994$, $P < 0.01$) and Co/Al ($r^2 = 0.996$, $P < 0.01$), in accord with previous observations in this region owing to the primarily lithogenic sources of these elements (e.g. Jickells et al., 2016). The correlations between Al and the primarily anthropogenic TEs, Ni, Cu, Zn, Cd, and Pb, were also significant at the 99% confidence level; Ni/Al ($r^2 = 0.884$), Cu/Al ($r^2 = 0.652$), Pb/Al ($r^2 = 0.478$), Zn/Al ($r^2 = 0.321$), Cd/Al ($r^2 = 0.303$) due the presence of the heavily-loaded North African samples, which accounted for between 88 % and 30 % of the statistical variance for Ni and Cd, respectively. Sources other than mineral dust (e.g. metal smelting emissions, fly ash, vehicle emissions, volcanic ash, proglacial till) are presumably responsible for the residual variance. Establishing the contributions from these other aerosol sources and their influence on TE solubility is a research priority.

As the aerosol source has a direct bearing on the type and composition of aerosols, determining the source could provide useful data that might be used to predict the fractional solubility of aerosol TEs. As positive matrix factorisation (PMF) can be used for source apportionment, we used the USA Environmental Protection Agency's EPA PMF model (v. 5.0) with the total TE concentration data to look for trends in the data. However, the GA01 and GA03 dataset is relatively small (n = 57) and the model was not stable with more than two factors. The two factors were a mineral dust factor (high contributions from lithogenic TEs, in particular Al, Ti, Fe and Zr) and a pollution/anthropogenic factor (with high contributions from Zn and Pb) (Fig. S2a, Supplementary Material). As anticipated, the mineral dust factor dominated where North African aerosols were sampled, and the pollution factor was relatively more important closer to the European and North American continents (Fig. S2b). This is in accord with the samples from North Africa having elemental mass ratios that are consistently the closest to the UCC elemental ratios compared to aerosols from the other source regions (Fig. 3). In the High Latitude samples, the pollution factor and the mineral dust factor were of approximately

Deleted:),… during these two campaigns, with the highest Fe and Al loadings associated with the North African samples (GA03), lower loadings with the Marine samples (GA03), and the lowest loadings observed in the samples collected in the Labrador Sea (GA01). Total aerosol TE data from the GA01 and GA03 cruises have been discussed in detail elsewhere (Shelley et al. 2015; 2017), the data are only discussed here for comparison.

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Moved down [11]: We have previously reported a mass ratio of 0.76 for Fe/Al for the North African end-member aerosols (Shelley et

Moved down [12]: (Sedwick et al., 2007; Sholkovitz et al., 2009; 2012), North African mineral dust dominates the supply of Fe

Moved down [13]: Hence the contribution of sea spray aerosols appears to have a negligible impact on the Fe/Al ratios in the bulk

Moved down [14]: 3.2. Elemental mass ratios and aerosol

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Moved down [16]: was chosen instead of Ti, another proxy for mineral dust, due to the presence of some anomalously high Ti/Al

Moved down [17]: Elemental mass ratios from the ten most heavily loaded GA03 North African aerosols were averaged to derive

Moved down [18]: , as dust supplied by proglacial till from Iceland and Greenland peaks in spring/early summer, and can be

Moved down [19]: 3c), suggesting that even though aerosol Fe is altered towards more soluble forms during atmospheric transport

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Moved down [21]: 3b and d), there is some degree of source-dependence in the elemental ratios, with some significant increases

Moved down [22]: Buck et al., 2010; Gelado-Cabellero et al., 2012; Patey et al., 2015; Shelley et al., 2015). ¶

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Deleted: 2015; Fig. 2a), which is significantly higher than the mean upper continental crustal (UCC) ratio of 0.47 (Rudnick and Gao,

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Aluminium was used to normalise the aerosol loading data (Fig.

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Deleted: The similarity to the GA03 North African aerosols, which have an Fe/Al ratio of 0.78 ± 0.03 (Fig. 3c), and the relatively sma

Deleted: 2016), although the extensive cloud cover experienced during the GA01 cruise (May/June 2014) prevented the use of

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Deleted: In addition, positive matrix factorisation analysis suggests that aerosols from this study were dominated by two factors, a

Deleted: Unsurprisingly… the mineral dust factor dominated where North African aerosols were sampled, and the pollution factor equal dominance. Interestingly, the North African aerosols also contained a relatively strong pollution component, consistent with a northeast flow into North Africa from Europe, followed by entrainment of mineral dust during passage over the Sahara (Baker and Jickells, 2017). Given that the PMF indicates that 100 % of the variability in the Cd concentrations was explained by the pollution factor, this suggests that Cd in North African aerosols is not sourced from mineral dust, which would explain why no fractionation was observed in Cd isotopes from North African and European aerosols (Bridgestock et al., 2017). Further, it also suggests that even the relatively homogeneous aerosols from North Africa do not represent a 'pure' end-member. However, the PMF analysis was not sensitive enough to identify the full complement of aerosol sources contributing to the samples collected during GA01 and GA03.

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3.2. Elemental mass ratios and aerosol source

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Elemental mass ratios from the ten most heavily loaded GA03 North African aerosols were averaged to derive a value for the 'North African' ratio depicted by the dashed horizontal line in Figures 3(a-i). Aluminium was used to normalise the data (Fig. 3; Table S2) and was chosen instead of Ti, another proxy for mineral dust, due to the presence of some anomalously high Ti/Al ratios in some of the Marine samples during GA03 (Fig. 3a; Shelley et al., 2015). We have previously reported a mass ratio of 0.76 for Fe/Al for the North African end-member aerosols (Shelley et al., 2015; Fig. 2a), which is significantly higher than the mean upper continental crustal (UCC) ratio of 0.47 (Rudnick and Gao, 2003) but entirely consistent other studies of Saharan soils and dust (e.g. Chiapello et al., 1997; Guieu et al., 2002; Lafon et al., 2006; Baker et al., 2013).

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For North African dust there does not appear to be a discernible source dependent trend in Fe/Al ratios due to a natural variability in Fe-bearing minerals in soils in dust source regions (Lafon et al., 2006; Scheuvens et al., 2013), but it might be possible to use Fe/Al ratios for some of the other aerosol groups to suggest different sources. For example, the European samples (n = 4) fall into two sub-groups: two samples have low Fe/Al ratios (Fig. 2; E3 = 0.48, E4 = 0.10 and Fig. 3c), whereas the other two samples (E1 = 0.95 and E2 = 0.78) have Fe/Al ratios within the range of the North American samples (Fe/Al 1.1 ± 0.22, range 0.86-1.42) and all but one of the Marine samples (Fe/Al, excluding M12, 0.93 ± 0.33, range 0.59-1.61; M12, collected closest to the North African samples, Fe/Al = 0.43).

Aerosols from the more northerly section, GA01, were largely outside the influence of the Saharan dust plume (Shelley et al., 2017), and are all classified as High Latitude in this study (Fig. 3). For this group of samples, there were also sub-groups of Fe/Al ratios. During the first half of the cruise (Fig. 1), there was a group of samples (G1-6, G8 and G10) with Fe/Al ratios of 0.58 ± 0.05; Fig.3c). This is intermediate between the UCC ratio (0.48 ± 0.07) and the North African mineral dust ratio (0.78 ±

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0.03; Fig. 3c). For these samples, the wind direction was predominantly from the north/north west (Shelley et al., 2017), so it is unlikely that the observed ratios reflect a mixture of North African mineral dust and European aerosols. Rather, it more likely comes from high latitude sources, as dust supplied by proglacial till from Iceland and Greenland peaks in spring/early summer, and can be deposited over the Atlantic Ocean (Prospero et al., 2012; Bullard et al., 2016). Unfortunately, the extensive cloud cover experienced during the GA01 cruise (May/June 2014) prevented the use of satellite observations (e.g. http://worldview.earthdata.nasa.gov) which would have confirmed the presence of dust from these sources. The elemental ratios calculated from TE concentrations from volcanic ash sampled during the eruption of the Eyjafjallajökull volcano in 2010 (Achterberg et al., 2013) offers some limited support for this argument, as our range of elemental ratios encompasses this end-member (Icelandic soils are almost exclusively volcanic in origin; Arnalds 2004). However, although Icelandic sands (Baratoux et al., 2011) and tephra (Oladottir et al., 2011) have Mn/Al ratios that overlap the GA01 samples, Fe/Al is generally lower in our High Latitude dust samples (Table S2).

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A second group of GA01 samples (G7, G9, G11 and G12) had Fe/Al ratios of 0.34 ± 0.01, but no obvious link in terms of the AMBTs. The Greenland shelf and Labrador Sea samples, except G15, had low Fe/Al (0.16 ± 0.04), and were distinct from those collected on the Canadian shelf (0.48 ± 0.02). These trends strongly suggest that the High Latitude dust was made up of at least four aerosol sources.

While there is evidence for anthropogenic source(s) of aerosol Fe to the North Atlantic (Conway et al., submitted), which is more soluble than Fe associated with mineral dust (Sedwick et al., 2007; Sholkovitz et al., 2009; 2012), North African mineral dust dominates the supply of Fe to much of the study region (Baker et al., 2013; Shelley et al., 2015; 2017; Conway et al., submitted). In addition to the samples classified as European and North American, elevated Fe/Al ratios were also observed in the Marine samples (Fig. 2b). In addition to aerosols derived from continental sources (meaning either mineral dust or anthropogenic emissions), sea spray aerosols could make a relatively higher contribution to the bulk aerosol in remote oceanic locations (de Leeuw et al., 2014). However, this would have the opposite effect as the ratio of Fe/Al in surface seawater (0.017 – 0.024 in the North Atlantic gyre, 0.019 European continental shelf, and 0.030 – 0.031 in the Mauritanian upwelling zone; Hatta et al., 2015) is two orders of magnitude lower than the crustal ratio. Hence the contribution of sea spray aerosols appears to have a negligible impact on the Fe/Al ratios in the bulk Marine aerosols.

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The Marine, and the High Latitude samples had the widest range in Fe/Al ratios and were also collected in the most remote locations. These groups also had the greatest difference in the Fe/Al ratios between the total and soluble fractions, and also contained the samples with the lowest ratios of Fe/Al in the soluble fraction (minimum Fe/Al = 0.15, samples G9-GA01 and M3-GA03; Fig. 3c), suggesting that even though aerosol Fe is altered towards more soluble forms during atmospheric

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transport (Longo et al., 2016), atmospheric processing renders Al even more soluble relative to Fe. However, although the soluble ratio of Fe/Al was the same for samples G9-GA01 and M3-GA03, the fractional solubility for Fe differed from 20 % for G9-GA01 to 0.8 % for M3-GA03. We suggest that North African mineral dust was contributing to the composition of M3-GA03, resulting in the low solubility of Fe compared to G9-GA01. This suggestion is supported by isotopic evidence (Conway et al., submitted).

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For the anthropogenically-derived TEs, Ni, Cu, Zn, Cd and Pb (Figs. 3e-i) and for at least some of samples of the mixed-source TEs (i.e. having crustal and pollution sources; e.g. Mn and Co in Figs. 3b and d), there is some degree of source-dependence in the elemental ratios, with some significant increases from the UCC mass ratios in the total (Shelley et al., 2015) and UHP water soluble fractions (Fig. 3). The higher ratios of the UHP water soluble fraction compared to the total indicates that these TEs are more labile than Al. In addition, studies that have investigated the size distribution of aerosols have found that anthropogenically-derived TEs tend to be associated with fine mode aerosols (< 1 µm diameter), which are more soluble than coarse mode aerosols due to the larger surface area to volume ratio (Duce et al., 1991; Baker and Jickells 2006; Baker and Jickells, 2017). Size fractionated samples were collected during the GA03 cruise, and the smaller size fractions were indeed more soluble than the larger ones for Al, Fe and Co (Landing and Shelley, 2013). Enrichment of TEs with predominantly anthropogenic sources accords with other studies in the North Atlantic, and is most striking for aerosols that did not originate from the sparsely-populated, arid regions of North Africa (e.g. Buck et al., 2010; Gelado-Cabellero et al., 2012; Patey et al., 2015; Shelley et al., 2015).

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3.3. Aerosol solubility

3.3.1. Solubility of aerosol TEs as a function of total concentration: UHP water (instantaneous) compared to 25 % acetic acid leaches

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The UHP water soluble fraction of aerosol Fe and Al determined for all the North Atlantic GA01 and GA03 samples varied by two orders of magnitude (Fig. 4a: Fe = 0.14 - 21 %, median 2.2 %; Al = 0.34 - 28 %, median 2.7%). Although a broader range of Fe and Al solubility was observed in this study, both these results and those reported by Buck et al. (2010) using the same approach (Fe = 2.9 - 47%, median = 14%, and Al = 3.7 - 50%, median = 9.5%) broadly agree that the median UHP water soluble fractions of Fe compared to Al in the North Atlantic are similar. While there was considerable overlap in the ranges of fractional solubility of TEs in aerosols from the different regions (e.g. Fe: European 1.9 – 21 %; N. American 0.84 – 8.8 %; Marine 1.7 –18 %; High Latitude dust 1.9 – 20 %), the North African samples, identified by their orange colour, high Fe and Al loadings, and definitive AMBTs) formed a distinct cluster of very poorly soluble Fe, or Al (< 1%; Fig. 4a). However, the solubility of the North African (‘Saharan’) aerosol Fe was 1 – 2 orders of magnitude lower in this study (0.14 –

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0.57 %) than during the Buck et al. (2010) study (2.9 – 19 %). This supports the hypothesis that TEs from North African aerosols sampled closer to the source (as in this study) are less soluble due to a lesser degree of atmospheric processing and/or larger particle sizes (Baker and Jickells, 2006; Longo et al., 2016).

The inverse relationship between total aerosol loading and fractional solubility has previously been reported for Fe (Sholkovitz et al., 2009; 2012; Jickells et al., 2016) and Al (Jickells et al., 2016). Jickells et al. (2016) compiled solubility data from the North Atlantic and found that the general trend between Fe and Al solubility and atmospheric loading was robust over the range of atmospheric loadings found in the North Atlantic, regardless of the leach protocol employed. In this study, both the UHP soluble, and 25 % acetic acid soluble fractions of Fe and Al (Figs 4a and b) were related to atmospheric loading, i.e. the highest loaded North African samples had the lowest solubility. The possible exception to this trend is the fraction of Al that dissolved from North African aerosols following the 25 % acetic acid leach (Fig. 4b). However, it could simply be that we are observing scatter in our data, which is smoothed out in the larger dataset (n > 2000) examined by Jickells et al. (2016). Although, we cannot rule out that this effect is the result of the heating step in the 25 % acetic acid leach attacking the alumino-silicate matrix, the similarity in the trend of the solubility of Ti in UHP water and 25 % acetic acid (sharp decrease in solubility with increased aerosol loading, Figs. 4a and b) suggests that matrix attack is minimal. Further experimentation with and without the heating step would help to clarify this issue.

Aluminium, Ti, and Fe show very similar behaviour in Figure 4a (sharply decreasing solubility as loading increases). Cobalt, Ni, Cu, Zn and Pb solubilities decrease less strongly as loading increases, whereas Mn and Cd show no clear trend. For the acetic acid leaches (Fig. 4b), Ti follows the same trend as the UHP water leach (Fig. 4a), while Al and Fe plateau at 8-10 % solubility. The other TEs (Mn, Co, Ni, Cu, Zn, Cd and Pb) all show almost no trend with loading. The absence of an inverse trend between solubility and loading has previously been noted for Mn (Jickells et al., 2016). For Co the inverse relationship between UHP water solubility and loading was not observed when using the 25 % acetic acid leach, most likely because Co may be associated with the Mn and Fe oxides that are easily reduced using this leach. For Zn and Cd, although their average fractional solubilities (Zn: 37 ± 28 % and 55 ± 30 %, Cd: 39 ± 23 % and 58 ± 26 % for ultra-high purity water and 25 % acetic acid leaches, respectively) were similar to Mn (32 ± 13 % and 49 ± 13 % for ultra-high purity water and 25 % acetic acid leaches, respectively), the range was greater, with several samples from different regions (although not North Africa) being 100% soluble after the second leach.

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Deleted: 2016). Furthermore, given that the Sahara Desert is the largest source of mineral dust to the atmosphere globally (the North Atlantic Ocean receives ~ 40 % of the mineral dust inputs to the global ocean, Jickells et al., 2005), the effects of increasing industrialisation/urbanisation of African countries, coupled with large unknowns in the magnitude of future mineral dust supply, and biomass burning, the ability of models to replicate subtleties in aerosol TE solubility may prove critical in forecasting ecosystem impacts and responses.

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3.3.2. Solubility of TEs: UHP water (instantaneous) compared to 25 % acetic acid leaches

All ten TEs from the five different provenances were less soluble in UHP water than 25 % acetic acid (Fig. 5). This is not a surprising finding given the lower pH of acetic acid compared with UHP water, acetate being a bidentate ligand, the longer contact time of the aerosols with the leach solution, the addition of the hydroxylamine reducing agent and that the fractional solubility of TEs in 25 % acetic acid was calculated using Equation 2 (which sums the UHP water and 25 % acetic acid leach concentrations). In addition, there is some degree of source-dependent variability in the relative proportions of each TE that is released by the two leaches. In general, as with the leaches with UHP water, the North African aerosols were distinctly less soluble in 25% HAc compared with aerosols from the other source regions (Fig. 5). Figure 5 highlights the distinction between the lithogenic elements, Al, Fe and Ti, which have uniformly low solubility in UHP water (mostly < 20 %), and extremely low solubility in North African aerosols (< 1 %), and the anthropogenic, pollution-dominated elements, Ni, Cu, Zn, Cd and Pb which have solubility up to 100 %. Manganese (Mn) and Co have both lithogenic and anthropogenic sources, so are classified as "mixed-source", and have intermediate solubilities. Like all the TEs reported here, Mn solubility in UHP water was significantly less ($p < 0.01$, two-tailed, homoscedastic t-test) in North African aerosols (median solubility = 19 %) than in the non-North African samples (median = 38%), which seems to contrast somewhat with the findings of Baker et al. (2006b) and Jickells et al. (2016) which found that aerosol source had little impact on Mn solubility. However, in common with these earlier studies (Baker et al., 2006b; Jickells et al., 2016), there was no significant source-dependent difference in Mn solubility in 25 % acetic acid (non-North African samples: 49 ± 15%, North African samples: 49 ± 6.4%).

3.3.3. Soluble TEs: UHP water compared to seawater instantaneous leaches

Seawater leaches were conducted on a subset of samples (GA03-2011), to investigate the suitability of seawater as the leach medium in the instantaneous leach (Fig. 6). During this study, Fe solubility in seawater was lower than in UHP water (Fig. 6c). This phenomenon has previously been observed in atmospheric aerosols from the North Atlantic Ocean (Buck et al., 2010). For Fe, only a few samples of North American and Marine provenance conformed to the relationship described by the equation proposed by Buck et al. (2010), with most of our data plotting above the regression line of the Buck et al. (2010) study (Fig. 6c), indicating that our data was relatively more soluble in UHP water compared to seawater than in this earlier study. One possibility is that the higher aerosol Fe loadings we observed during GA03-2011 (this study, maximum = 5650 ng Fe m^{-3}), compared to the A16N-2003 transect (Buck et al. 2010; maximum =1330 ng Fe m^{-3}), resulted in a particle concentration effect (Baker and Jickells, 2006), whereby the relationship between aerosol Fe loading and fractional solubility breaks down because dust on the filter can be a source of soluble Fe but can also scavenge dissolved Fe from the sea water leach solution as it passes through the filter. Given that the link between Fe solubility in seawater and Fe-binding ligand availability is well established (e.g. Rue and

Moved down [24]: It is noted, however, that the median values from this study fall within the range used by the MADCOW model (2.7 % and 3.3 % for UHP water and 25 % acetic acid, respectively).

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Furthermore, the fractional solubility of bioactive TEs from aerosols is taken as a rough approximation of bioavailability. Yet, clearly the choice of leach media impacts the estimated value. For elements with generally low solubility, such as Fe, the difference between 1 % and 2 % solubility is an increase of 100 %, meaning that only half the amount of dust is needed to yield the same amount of dissolved Fe, the most-readily bioavailable form of Fe (Shaked and Lis, 2009).

Moved down [25]: To complicate matters further, recent research has demonstrated that some diazotrophs are able to directly access particulate Fe (Rubin et al., 2011).

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Furthermore, in productive regions where Fe (and perhaps other TEs) associated with lithogenic particles is directly available to micro-organisms (Rubin et al., 2011) or in regions where particulate Fe is processed by zooplankton (Schmidt et al., 2016), we are likely underestimating bioavailable Fe using the instantaneous approach (Buck et al., 2006). Therefore, the different leaching approaches can be used to probe specific questions related to the response of the microbial community to changes in aerosol type and/or supply by providing a "window of solubility". This is an important consideration as the true solubility of aerosol TEs in the upper ocean cannot be directly measured. ¶

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Deleted: The differences source dependence of Mn solubility in these aerosols between the two leach types is just one example of how challenging it is to model Mn bioavailability in the North Atlantic. Nevertheless, with the exception of soluble Mn from the acetic acid leach, this TE solubility data supports the general assertion that aerosol TE solubility varies as a function of provenance and/or atmospheric loading (e.g. Baker and Jickells, 2006; Sedwic ...

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Bruland, 1995; Gledhill and Buck, 2012), an alternative explanation for the difference in Fe solubility is that the organic composition of the seawater used as the leach mediums differed between the two studies.

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Manganese is the only TE that had a slope close to unity (0.98; Fig. 6b), suggesting that solubility estimates were not impacted by the choice of leach medium used. This is consistent with other studies that have found that Mn solubility is less sensitive to the choice of leach media, or to aerosol provenance than other TEs (Baker et al., 2006b; Jickells et al., 2016). Due to the large variability in the data set, there was no significant difference between Mn solubility in UHP water or seawater (32 ± 13 % and 24 ± 17 %, respectively; Fig. S3 and Tables S3 and S4, Supplementary Material). Table S5 shows which regions had slopes for UHP water versus seawater fractional solubility that did not differ significantly from 1.0 at the 95 % confidence level (t-statistic).

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Lead was the only TE with all slopes differing significantly from 1.0, and the only TE where the solubility in seawater was higher than in UHP water for virtually every sample (Fig. 6i). As for Pb, most of the Co data falls below the 1:1 line (Fig. 6d), indicating that Co was also generally more soluble in seawater than UHP water. In contrast, the opposite trend was observed for Fe and Ni (Figs 6c and e), perhaps due to differences in the availability of metal binding ligands in the seawater used. A challenge of using seawater as the leach medium is that it is difficult to control for natural variability in the types and concentrations of organic ligands. Consequently, it is not possible to determine conclusively why contrasting trends in the fractional solubility of TEs were observed. For this reason, we advocate for the use of UHP water as a common leach medium to facilitate comparisons of solubility resulting from differences in aerosol composition. An additional benefit is the ease of analysis of UHP water compared to seawater.

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Numerous laboratory studies have demonstrated a link between atmospheric acid species and Fe solubility (e.g. Spokes and Jickells, 1995; Desboeufs et al., 1999; Meskhidze et al., 2003), and in field studies some degree of correlation between nss-SO_4^{2-} and soluble Fe has been observed for samples collected over the Pacific (e.g. Hand et al, 2004; Buck et al., 2013) and Atlantic Oceans (

3.4. Visualising marine aerosol sources using multivariate statistical approaches

As the PMF analysis was only able to identify two significant factors accounting for the total aerosol TE concentrations, another multivariate approach was taken. Heirachical cluster analysis (Ward's method, Euclidian distance) was performed using the R statistical package (v. 3.3.0; R Core Team, 2016) to look for trends in the data that might reveal the various aerosol sources. Heirachical cluster analysis was performed on (1) log transformed total aerosol TE plus NO_3^- concentration data (Fig. 7a), and (2) log transformed TE fractional solubility plus NO_3^- concentration data (Fig. 7b). The NO_3^- concentrations appear in both runs as we wanted to include TEs plus an indicator of anthropogenic pollution.

Figure 7a shows two main branches to the dendrogram of the total TE concentration data. One branch groups all the North African and European samples and two North American samples (N2 and N4) together, and the other branch groups all other samples together. Samples closest to each other are the most similar to each other, and those joined in the same groups share similar characteristics. Therefore, in this analysis, the North African samples are grouped together, as are the High Latitude samples. All but three North African samples form a distinct sub-group. The three remaining North African samples (A8, A9 and A11) share more characteristics with the European samples, lending support for mixing of aerosols from the two regions. Counterintuitively, the two European samples with the lowest Fe/Al ratios (E3 and E4) are the ones that are most similar to the two North American samples, which have relatively high Fe/Al ratios of 0.90 and 0.87. The GA01 samples (with the exception of one sample, G15) form a distinct cluster, but with three sub-groups: one is the Greenland/Labrador Sea samples (without G15), and the other two are related to each other but distinct from the Greenland/Labrador Sea samples and are a mixture geographically of the other samples. However, there is a trend, the 'middle' group is the group of samples collected closest to land, the group to the right is the group of samples collected furthest from land. The other groupings are made up of a mixture of North American and Marine samples. This could suggest that the Marine samples are comprised predominantly of North American aerosols from more than one source. The only anomaly is the two North American samples that 'look European'.

Although there are differences between Figures 7a (total TEs) and 7b (25 % acetic acid fractional solubility; Eq. 2), the general trend of an inverse relationship between TE atmospheric loading and fractional solubility holds, as the North African samples with the highest concentrations and lowest fractional solubilities appear on the left in Figure 7a, and on the right in Figure 7b. In terms of fractional solubility, the N. African samples form a distinct cluster, but this cluster is made up of two sub-groups: one collected during GA03-2010 and one during GA03-2011. The samples from near Greenland and the Labrador Sea are also distinct from the other GA01 samples (again with the exception of G15), and also distinct from all other samples. The European samples, all other GA01 samples, and three North American samples form a loose cluster. The remaining North American samples and all the Marine samples form another loose cluster.

Plotting the data this way still does not allow us to identify the aerosol sources definitively, but it does allow us to visualise which samples have the most similar physico-chemical characteristics and confirms the general trend of a relationship between aerosol loading and fractional solubility and, by extension, bioavailability, even though we have demonstrated that this relationship is not present for all TEs. This knowledge is then useful as a general rule of thumb in biogeochemical models, although clearly other factors also exert controls on aerosol TE solubility. For example, during their investigations of the GA03 aerosols, Wozniak et al., (2013; 2014; 2015) proposed a role for water

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During their investigations of the GA03 aerosols, Wozniak et al., (2013

soluble organic carbon (WSOC) in controlling the solubility of Fe. Desboeufs et al. (2005) also found evidence for a link between total carbon and TE solubility in regions impacted by anthropogenic activity. Thus, the carbon content of aerosols is also implicated as a control on aerosol Fe solubility, but the relationship is frequently not linear.

Deleted: Thus, both aerosol acidity and organic carbon content are implicated as controls on aerosol Fe solubility, but the relationship is frequently not linear. One explanation for this lack of linearity was proposed recently by Hennigan et al. (2015). They concluded that molar (or mass) ratio techniques are not suitable for predicting aerosol pH (or acidity), and cautioned against drawing conclusions based on proxy methods (e.g. nss-SO$_4^{2-}$ or NO$_3^-$). Instead, they recommend that either a thermodynamic modelling approach (constrained by gas and aerosol measurements), or the phase partitioning of NH$_3$, should be used for predicting aerosol pH. Weber et al. (2016) take this further and argue that the best approach for predicting aerosol pH is the phase partitioning of NH$_3$. These approaches are beyond the scope of the present study, but should be a consideration for future studies due to the pH-dependency of aerosol TE dissolution, especially given the neutralising influence of NH$_3$, carbonate mineral phases, and sea salt

3.5. Choice of leach and modelling TE solubility

The ability of models to replicate subtleties in aerosol TE solubility may prove critical in forecasting ecosystem impacts and responses. Due to the magnitude of North African dust inputs to the North Atlantic region (very high dust inputs result in a high soluble aerosol TE flux despite relatively low fractional solubility), this is a particular challenge and is compounded by additional unknowns such as how aerosol acidity will be impacted by the combined effects of increasing industrialisation/urbanisation, and changes in the magnitude of future mineral dust supply and biomass burning (Knippertz et al., 2015; Weber et al., 2016). In other words, it is important to accurately constrain aerosol trace element solubility with high quality data in order to improve the predictive capacity of models. Clearly the choice of leach media and protocol impacts the measured fractional solubility. This is shown in both Figures 4 and 5 and has a number of implications with regard to modelling the impact of atmospheric deposition on marine biogeochemistry. For example, for elements with generally low solubility, such as Fe, the difference between 1 % and 2 % solubility is an increase of 100 %, meaning that only half the amount of dust is needed to yield the same amount of dissolved Fe. To complicate matters further, recent research has demonstrated that some diazotrophs are able to directly access particulate Fe (Rubin et al., 2011). The significance of this is that *Trichodesmium* are common in the North Atlantic gyre under the influence of the Saharan plume, and the North African dust samples have higher fractional solubility for Fe using the acetic acid leach. If *Trichosdesmium* are able to access the acetic acid soluble fraction of the aerosol Fe, as the study indicates (Rubin et al., 2011), our data suggests that twentyfold more aerosol Fe is available for uptake than is suggested from the instantaneous UHP water leach. This suggests that in regions where *Trichodesmium* proliferate, we are likely to underestimate bioavailable Fe using the instantaneous UHP water leaching method.

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There are implications for modelling the impact of atmospheric deposition for other TEs. Although, the lack of source dependent differences in Mn solubility in these aerosols makes modelling Mn solubility simpler, there was still a difference in the fractional solubility calculated from the two leaches (UHP water: 32 ± 13 % and 25 % acetic acid: 49 ± 13 %). However, for Al, there was a large range in solubility:0.3 – 28 % using UHP water and 4.1 – 100 % using 25 % acetic acid. Both ranges far exceed the relatively narrow range used in the MADCOW model (1.5 – 5 %), which has been used to estimate atmospheric inputs based on dissolved Al concentrations in the mixed layer (Measures and Brown, 1996). It is noted, however, that the median values from this study fall within the range used by the MADCOW model (2.7 % and 3.3 % for UHP water and 25 % acetic acid, respectively). We highlight this issue to draw attention to some of the problems inherent in modelling TE solubility and its impact on the chemistry and biogeochemistry of the upper ocean.

Given that the different leaching approaches access different fractions of aerosol TEs that can dissolve from aerosols at different rates (e.g. TEs loosely bound to surfaces and TEs that are associated with less reactive phases) (e.g. Kocak et al., 2007; Mackey et al., 2015), we need to conduct experiments that elucidate the relationship between the soluble and bioavailable fractions. In the meantime, we suggest that the 25 % acetic acid leach might be better to estimate the bioavailable fraction given that Fe (and perhaps other TEs) associated with lithogenic particles are directly available to micro-organisms in productive regions and regions with high dust inputs (Rubin et al., 2011) and that aerosol particles can be processed by zooplankton (Schmidt et al., 2016).

4. Conclusions

Aerosol TE solubility is usually determined using operationally-defined methods, while biogeochemical models require robust relationships between two or more parameters that can be used to predict TE solubility in order to constrain the bioavailable fraction of aerosol TEs. In this study, we used a two-stage leach (UHP water followed by 25 % acetic acid with hydroxylamine hydrochloride) to investigate the fractional solubility of a suite of trace elements (Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) from aerosols collected in the North Atlantic during three GEOTRACES campaigns (GA03-2010, GA03-2011 and GA01). Five regions were identified based on air mass back trajectory (AMBT) simulations; i) North Africa, ii) Europe, iii) North America, iv) High Latitude, and v) Marine. However, the AMBTs were not able to sufficiently discriminate aerosol sources within these regions. Of these five categories, the North African aerosols were the most homogeneous in terms of their fractional solubility and elemental ratios. In contrast, samples from the most remote locations, the Marine and High Latitude aerosols, had the most spread in their fractional solubility and elemental ratios. Elemental ratios were discussed rather than enrichment factors normalised to UCC composition since earlier work highlighted that the UCC ratios are not representative of the North African mineral dust end-member, which dominates aerosol supply in much of the study area.

We observed an inverse relationship between the fractional solubility of Al, Ti, Fe, Ni, Cu and Pb and aerosol loading for all leach media (UHP water, filtered seawater, and 25 % acetic acid with hydroxylamine hydrochloride). However, Mn, Zn and Cd fractional solubility appears to be independent of atmospheric loading. For Co, the inverse relationship between UHP water solubility

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Data availability

Data is available at BCO-DMO (GA03; www.bco-dmo.org) and LEFE-CYBER (GA01; (www.obsvlfr.fr/proof/php/GEOVIDE/GEOVIDE.php), and on request from the lead author.

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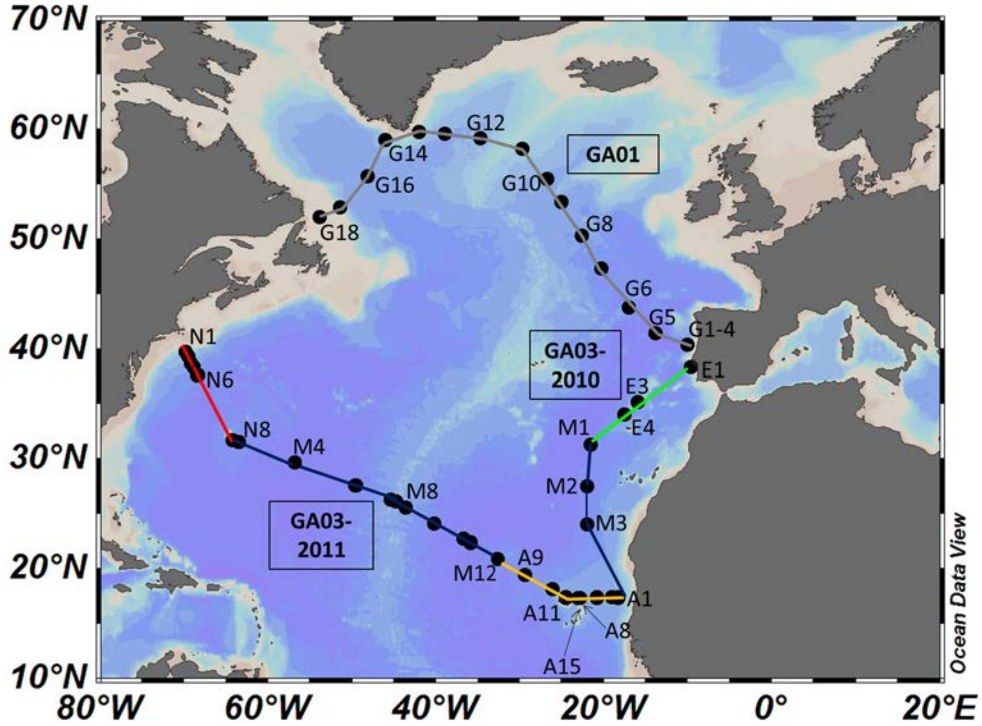

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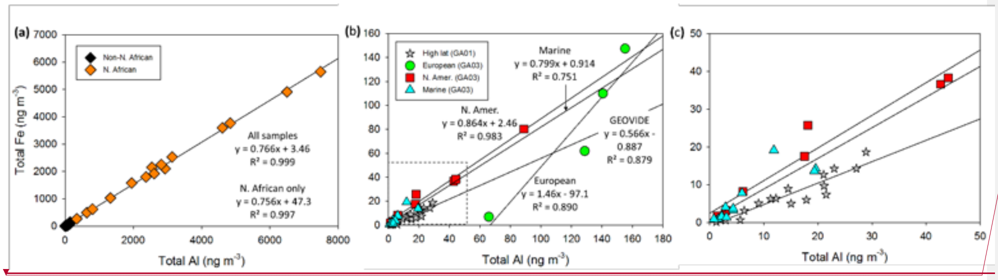

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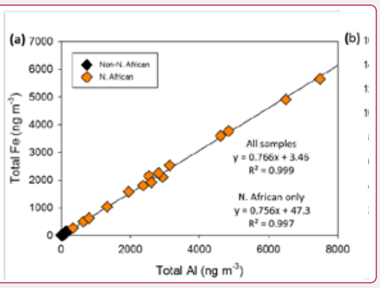

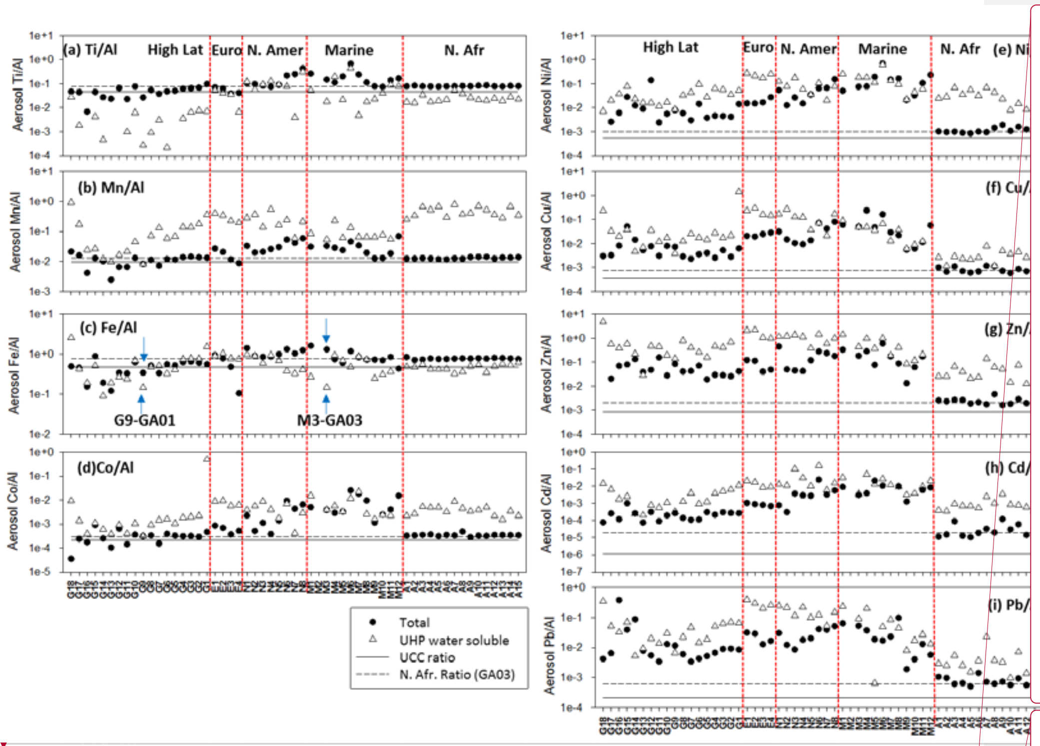

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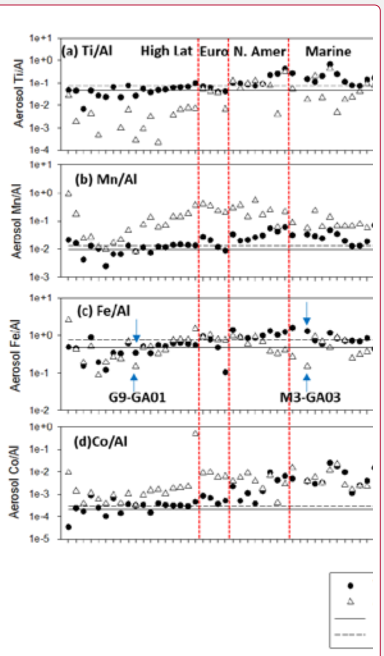

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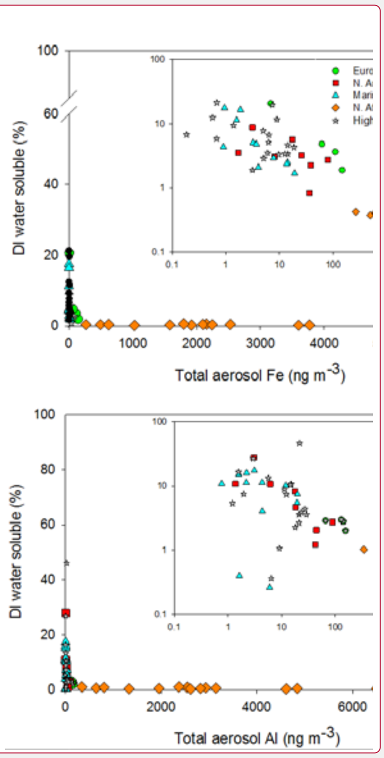

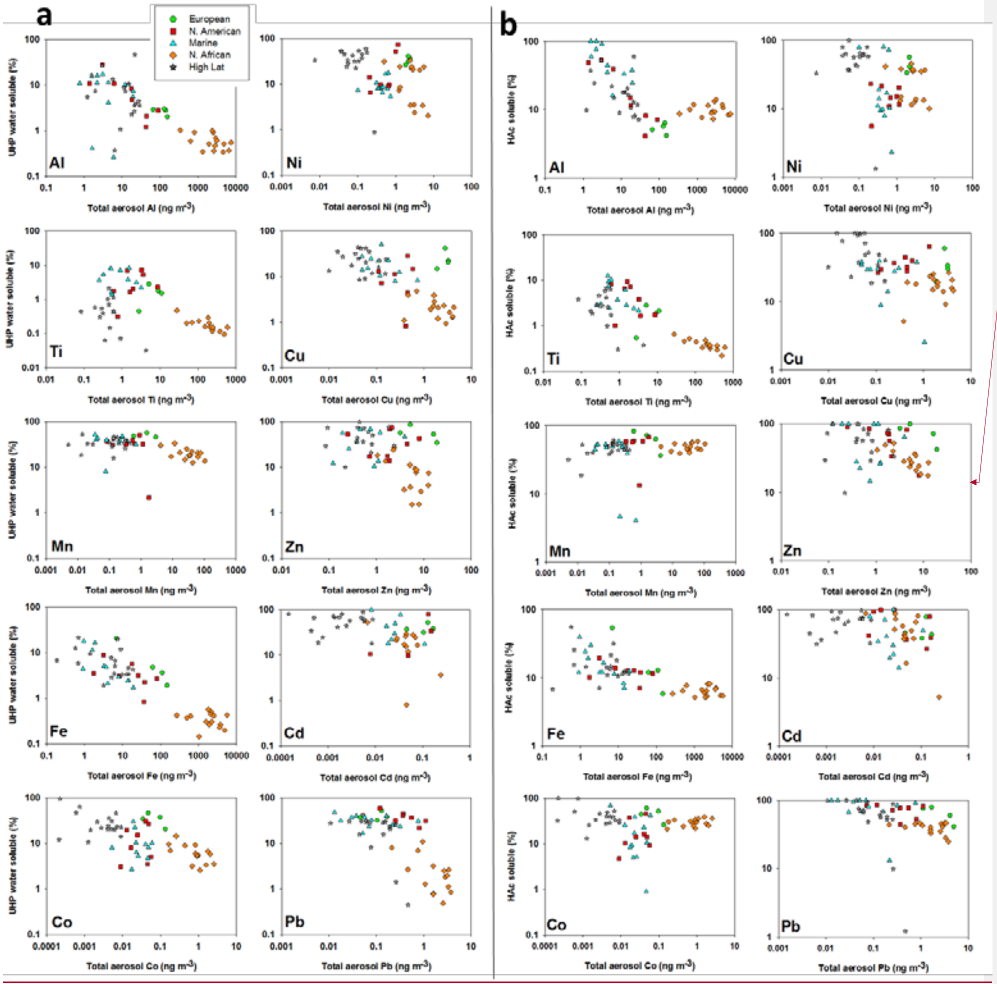

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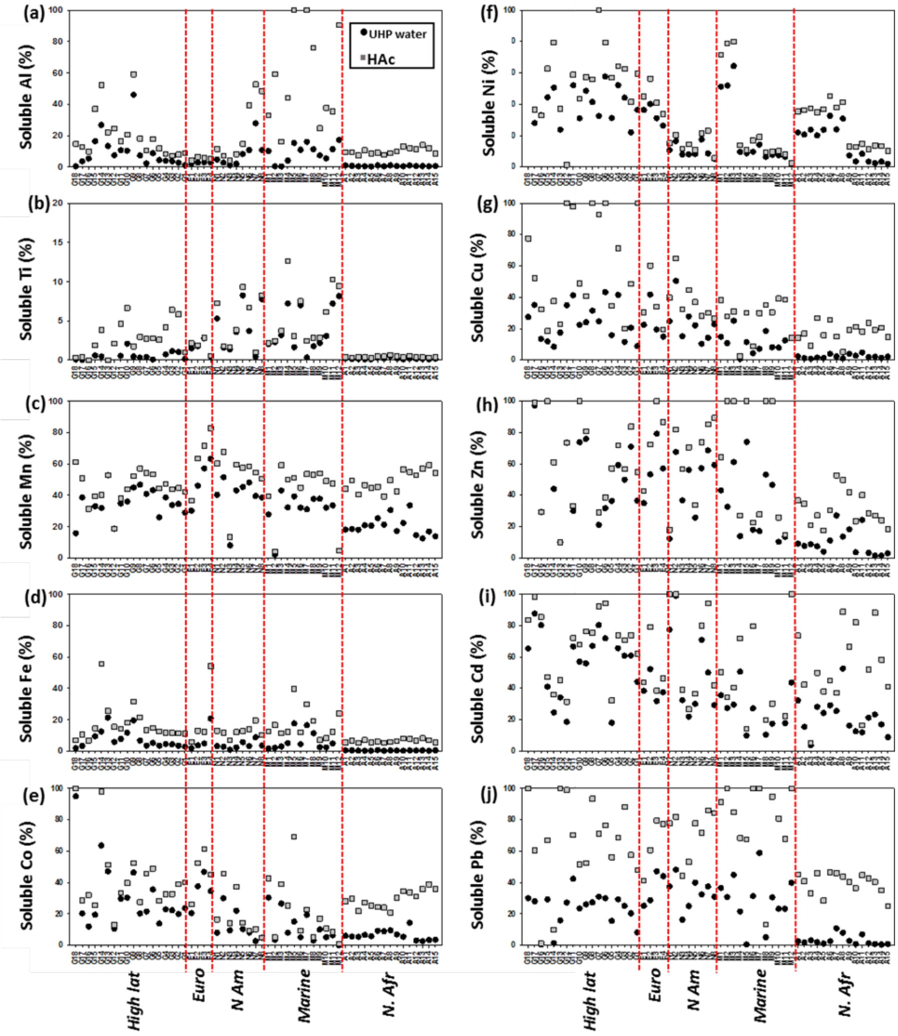

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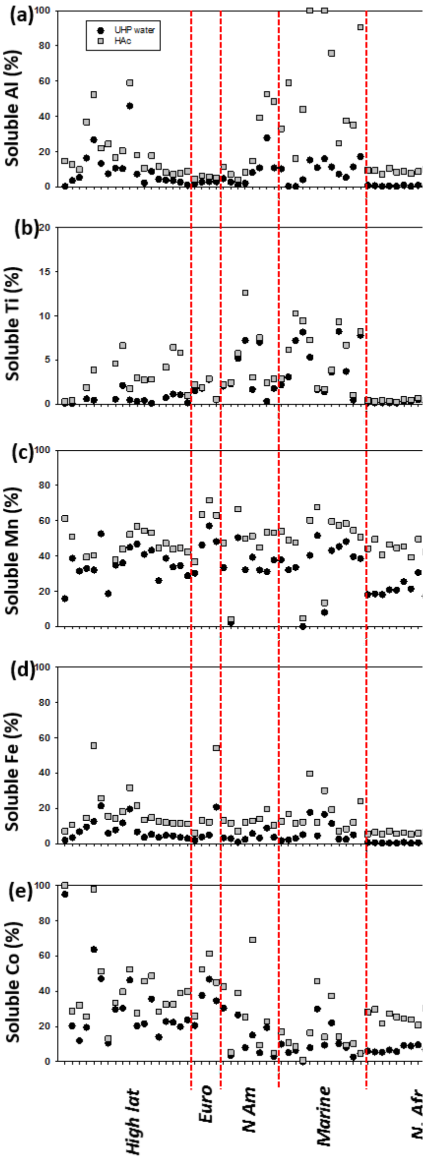

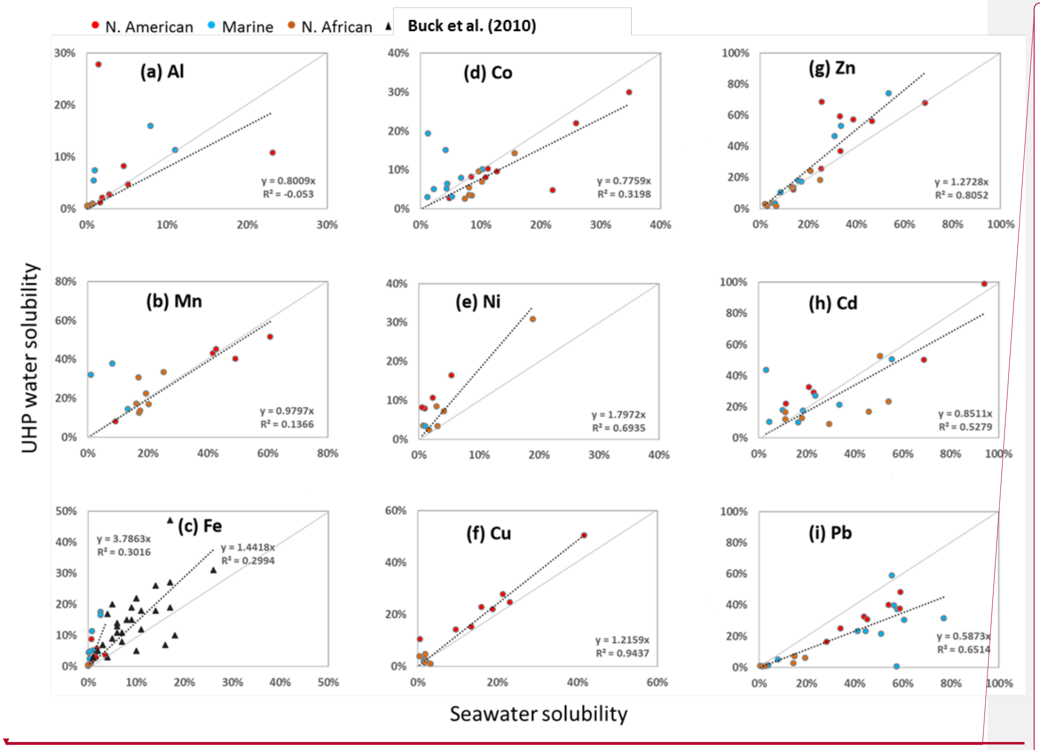

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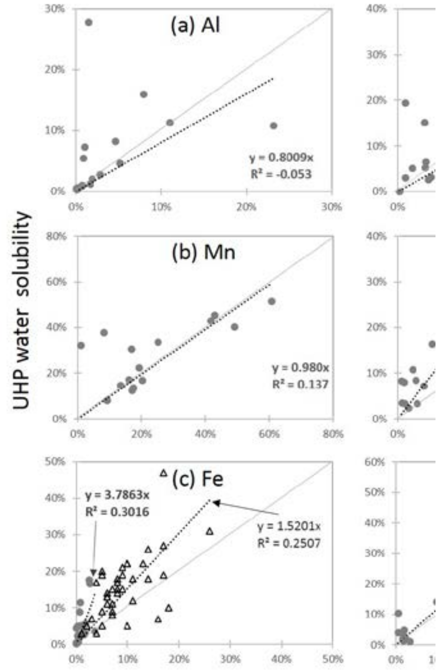

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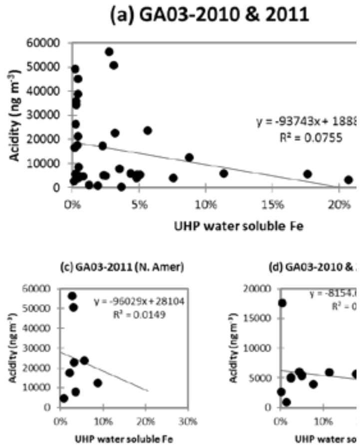

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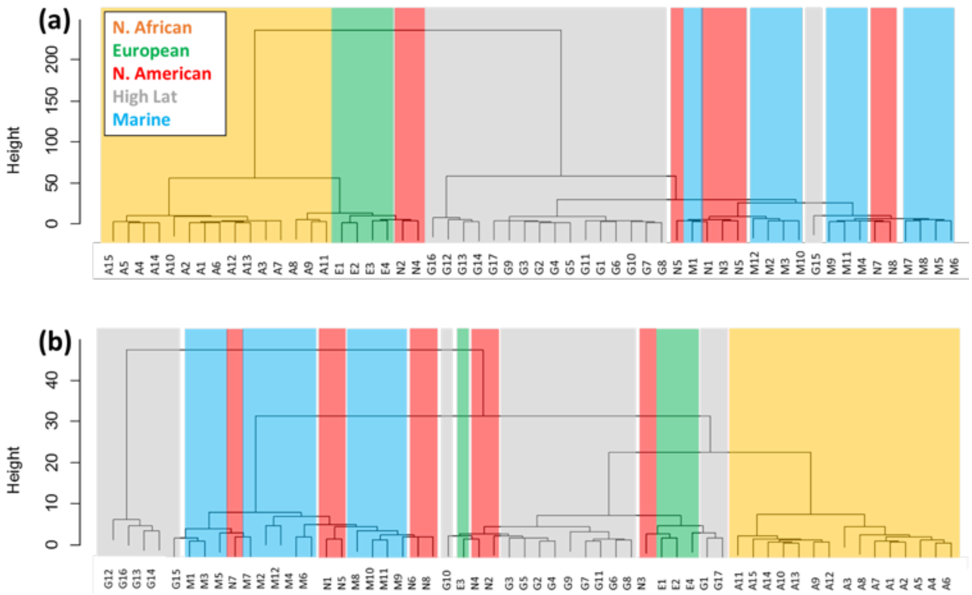

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Figure 1. The GEOTRACES GA01 and GA03 cruise tracks (GA01, GA03-2010 and GA03-2011). In total, 57 aerosol samples (GA01 n = 18, GA03 n = 39; black dots) were collected. The samples are grouped by aerosol source region (green = European (E1-4), blue = Marine (M1-12), yellow = North African (A1-15), red = North American (N1-8), and grey = High Latitude (G1-18)), identified from air mass back trajectory simulations using the NOAA ARL model, HYSPLIT (Stein et al., 2015; Rolph, 2017). Note that a different labelling convention was used in Shelley et al. (2017) to refer to the GA01 samples. Here we use G1-18 to refer to the samples collected during GA01 (A1-18 in Shelley et al., 2017), and A1-15 to refer to the North African samples from GA03.

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Figure 2. Total aerosol Fe and Al (ng m^{-3}) for: (a) all aerosol samples from cruises GA01 and GA03, (b) samples from sources other than North Africa (i.e. the black diamonds in Fig. 2a), and (c) the samples inside the dashed box in Fig. 2b. For High Latitude dust n = 18, European samples n = 4, North American samples n = 8, Marine samples n = 12, and Saharan samples n = 15. Note error bars (standard deviations shown in Table S1) are not included so as not to obscure the symbols.

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Figure 3. Elemental mass ratios (normalised to Al) of total (black circles) and UHP water soluble (white triangles) TEs. The UCC elemental ratio (Rudnick and Gao, 2003) is indicated by the solid horizontal line, and the elemental ratio in North African sourced aerosols (Shelley et al., 2015) is indicated by the dashed horizontal

line on each plot. The red vertical lines separate the aerosol source regions, which are labelled in panel (a). Samples G9-GA01 and M3-GA03 are indicated by blue arrows in panel c (see text for details).

Figure 4. (a) Percentage of UHP water soluble TE (calculated from Eq. 1) versus total aerosol TE (ng m^{-3}), (b) percentage of 25 % acetic acid soluble TE (calculated from Eq. 2) versus total aerosol TE (ng m^{-3}). Data is plotted on log-log scales.

Figure 5. Solubility of Al, Ti, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb following a UHP water leach (UHP water, black circles, calculated using Eq. 1), and a sequential leach of 25 % acetic acid (HAc, grey squares, calculated using Eq. 2). The red vertical dashed lines represent the different aerosol source categories, as labelled in panel (b). Note that Ti (panel b) is highly insoluble and has a maximum value of <13%. The data for this figure is also presented in Fig. S4 as biplots of UHP water fractional solubility versus 25 % acetic acid fractional solubility.

Figure 6. Comparison of TE solubility following instantaneous leaches using UHP water or locally-collected, filtered seawater. The solid line is the 1:1 line. Where fewer data are observed, concentrations were below detection for one or both of the two leaches. The data for soluble aerosol Fe from within our study region from Buck et al. (2010) are plotted as black triangles in panel (c).

Figure 7. Heirachical cluster analysis of (a) log transformed total TE concentration data plus NO$_3^-$, and (b) log transformed fractional solubility following the two-step sequential leach (fractional solubility calculated using Eq. 2). The coloured blocks correspond with the aerosol source regions shown in the legend.

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Figure 7. Aerosol acidity versus UHP water soluble Fe (%) for (a) GA03-2010 and 2011, (b) GA01 – High Latitude dust, (c) GA03 – N. American, (d) GA03 – Marine, (e) GA03 – North African, and (f) GA03 – European samples. ¶

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