

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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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

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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 190, 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?

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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 379.

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

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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, 'Furthermore, 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 North Atlantic region, 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 553. 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

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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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