

The authors are grateful to reviewer 2, Akinori Ito, for providing feedback to the manuscript. Our detailed point-by-point response to the comments is reported below.

Reviewer 2:

General comments

Model predictions of metal speciation and solubility in aerosols and fog are highly uncertain. The authors collected total suspended particulate (TSP) and fog water samples at Henties Bay and seawater on the seashore during the period of 3-11 September. They combined thermodynamical modelling with field measurements using X-ray absorption near edge spectroscopy (XANES), Transmission electron microscopy (TEM), Dynamic Light Scattering (DLS), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Previous study at the Henties Bay Aerosol Observatory (HBAO) showed strong link between MSA (methane sulfonic acid) and iron solubility up to 20% but not between oxalate and iron solubility. Conversely, their XANES results showed that photochemical reduction to Fe(II) was not a significant process involved in the enhanced iron solubility in the fog samples but the presence of iron-oxalate complexes that could explain its enhanced solubility in fog samples. Their TEM and DLS measurements revealed the presence of nano-sized colloidal particles containing Fe and Al in filtered fog samples that may appear as soluble in ICP-MS measurements. The modeling exercises with direct measurements performed in this paper may help us to advance our understanding of metal speciation and solubility in aerosols and fog. I have some comments and questions to improve this paper.

Specific comments

L.61: Please specify the photo-reduction processes of marine biogenic emissions and explain the role of MSA (methane sulfonic acid) and oxalate in enhanced solubility to elucidate the complement to those findings.

We have now expanded this based on the reviewer's suggestion: "Such processes can involve the formation of photoactive complexes involving Fe(III) and methanesulphinic acid which absorbs and photolyses in the visible range to produce Fe(II) and methanesulphonic acid among other species (Siefert et al., 1994). Similarly, Fe(III)-carboxylate complexes can undergo photochemical redox reactions where the Fe(III) is reduced to Fe(II) (Johansen and Key, 2006).

Johansen, A. M., & Key, J. M. (2006). Photoreductive dissolution of ferrihydrite by methanesulfinic acid: Evidence of a direct link between dimethylsulfide and iron-bioavailability. *Geophysical Research Letters*, 33(14). <https://doi.org/10.1029/2006GL026010>
Siefert, R. L., Erel, Y., & Hoffmann, M. R. (1994). Iron photochemistry of aqueous suspensions of ambient aerosol with added organic acids*. In *Pergamon Geochimica et Cosmochimica Acta* (Vol. 58, Issue 15).

L.68: What is the role of butenes in the formation of metal-ligand complexes?

There isn't a clear link between butenes and complex formation. We realised that the sentence can be misleading so we have removed the reference to butene emissions.

L.83, L.310: Please correct section 0.

We have corrected all the references to sections in the revised manuscript.

L.89: What are the differences in the leaching method from the previous study at HBAO? Please explain the leaching protocol whether nano-sized colloidal particles are measured as soluble in ICP-MS measurements.

The leaching method used here was the same as in previous studies, and described in the companion paper by Formenti et al., this issue. All samples analysed by ICP-MS were previously filtered through a 0.2 μm filter that is not able to capture all nano-sized particles as shown in our recent paper (Giorio et al., 2025, Iron Speciation in Urban Atmospheric Aerosols: Comparison between Thermodynamic Modeling and Direct Measurements. *ACS Earth and Space Chemistry*. <https://doi.org/10.1021/acsearthspacechem.4c00359>). It is therefore the dissolved fraction of metals that was analysed by ICP-MS, comprising soluble metals and nano-sized colloidal suspensions. The word “soluble” has now been replaced with “dissolved” throughout the manuscript. We have also clarified this in the methodology section at line 153 of the revised manuscript: “As for TSP samples, the dissolved fraction is defined operationally as passing through a 0.2 μm filter which may include nano-sized particles as reported in a previous study (Giorio et al., 2025).”

L.108: Please explain the differences in the operational definition of “soluble” and “dissolved” to elucidate dissolved metals in fog and soluble metals in TSP. Please specify whether dissolved or soluble trace metals in your method include nano-sized colloidal particles.

This has now been addressed as a result of the previous comment.

L.161: Why don't you include organic complexation of Fe with humic-like substances, as you mentioned in L.290?

We didn't include complexes with humic-like substances due to a lack of reference standards.

L.193: This is probably the major reason of low pH calculated in sea salt and Ca-containing aerosols under high RH and thus resulting in free form for a large fraction of the metal ions as, as you mentioned in L.322. It is highly recommended to use the model which considers the alkaline minerals.

Unfortunately, E-AIM does not consider Ca and Mg. Isorropia II could be used, but various studies have pointed out that isorropia does not perform well when run in reverse mode (with only particle phase concentrations available) and at very low or very high relative humidities (such as in this campaign) (Hull et al., 2025; Haskins et al., 2018; Peng et al., 2019). In addition, we do not have measurements of carbonates that would also contribute to the uncertainty on the calculated pH. This has now been explained in the text at lines 201 of the revised manuscript: “This can lead to an underestimation of the real pH of aerosols. The model ISORROPIA II could be used to consider these species, but a few studies have pointed out that ISORROPIA does not perform well at very high relative humidity (such as in this campaign) when run in reverse mode (i.e., when only particle phase measurements are available) (Haskins et al., 2018; Hull et al., 2025; Peng et al., 2019). In addition, the absence of carbonate measurements can contribute to the uncertainty around the real aerosol pH.”

Haskins, J. D., Jaeglé, L., Shah, V., Lee, B. H., Lopez-Hilfiker, F. D., Campuzano-Jost, P., Schroder, J. C., Day, D. A., Guo, H., Sullivan, A. P., Weber, R., Dibb, J., Campos, T., Jimenez, J. L., Brown, S. S., & Thornton, J. A. (2018). Wintertime Gas-Particle Partitioning and Speciation of Inorganic Chlorine in the Lower Troposphere Over the Northeast United States and Coastal

Ocean. *Journal of Geophysical Research: Atmospheres*, 123(22), 12,897–12,916.
<https://doi.org/10.1029/2018JD028786>

Hull, T., D'Aronco, S., Crumeyrolle, S., Hanoune, B., Giammanco, S., la Spina, A., Salerno, G., Soldà, L., Badocco, D., Pastore, P., Sellitto, P., & Giorio, C. (2025). Metal speciation of volcanic aerosols from Mt. Etna at varying aerosol water content and pH obtained by different thermodynamic models. *Environmental Science: Atmospheres*, 5(1), 8–24.
<https://doi.org/10.1039/D4EA00108G>

Peng, X., Vasilakos, P., Nenes, A., Shi, G., Qian, Y., Shi, X., Xiao, Z., Chen, K., Feng, Y., & Russell, A. G. (2019). Detailed Analysis of Estimated pH, Activity Coefficients, and Ion Concentrations between the Three Aerosol Thermodynamic Models. *Environmental Science and Technology*, 53(15), 8903–8913. <https://doi.org/10.1021/acs.est.9b00181>

L.214: How did you determine the oxidation state?

We did not determine the oxidation state. Instead, we have assumed that all metal ions are present in their thermodynamically stable oxidation state. This has now been specified at line 234 of the revised manuscript: “For all metal ions the thermodynamically stable oxidation state was considered.”.

L.248: What do you mean by scarce vegetation sources in this Namib region? Please rephrase this.

In this hyperarid region, there is hardly any vegetation, therefore, no sources of nutrient coming from vegetation.

This has now been clarified at line 269 of the revised manuscript: “...scarce vegetation sources in this hyperarid Namib region where there is hardly any vegetation.”

L.256: What are the marine phytoplanktonic emissions of NO? Do you mean photochemical production of nitrogen oxides? Please rephrase this.

In the text, we have added “by photooxidation”. It now reads : “The elevated nitrate concentrations can be attributed to the atmospheric processes affecting the important marine phytoplanktonic emissions of reactive nitrogen species (organic nitrogen and/or NO) ending, by photooxidation, in particulate nitrate formation (Altieri et al., 2021).

L.257: Please explain why weaker correlation of nitrate with MSA than oxalate supports this hypothesis.

Oxalate and MSA are tracers of secondary chemistry. Therefore, if nitrate is correlated to them, that strengthens the secondary origin of nitrate.

To avoid any confusion, we have rephrased, the sentence now reads: “The correlation of the nitrate concentrations with markers of secondary chemistry, such as oxalate and MSA ($R^2=0.89$ and 0.53 , respectively) in our coastal fog samples supports this hypothesis.

L.281: Please explain the conversion of the unit in the method.

The passage has been clarified (line 303 of the revised manuscript) and now reads : “For the comparison, fog water-dissolved metal concentrations (measured in μM) were transformed into air concentrations (in ng/m^3) using the liquid water content ($\text{g H}_2\text{O}/\text{m}^3$). This allows for comparison of fog concentrations with dissolved metal concentrations in TSP. The ratio of fog concentrations to TSP concentrations is shown in Table 3. ”

I.286 and Table 3: It is not clear whether the metal solubility is enhanced or the metal concentration is larger. How do you explain the lower values of the ratio between the mass concentration of dissolved metals in fog samples and soluble metals in the corresponding TSP samples than the unity? Please show the metal solubility in aerosol and fog samples, separately. Please also compare the solubility with the previous study at the HBAO.

In table 3 we compare dissolved metals in TSP and fog by calculating a ratio of their concentration in fog and TSP (converted in ng/m^3 of air sampled). Therefore, values above unity indicate a higher dissolved concentration in ng/m^3 in fog compared to TSP. Metal solubility in TSP samples is discussed in the companion paper by Formenti et al., this issue while only the dissolved fraction was measured in the fog samples.

I.297: How can you explain the lowest Fe solubility differences observed in the H1001 sample collected during daytime? Is this photochemical reduction consistent with the results on I.387, “photochemical reduction to Fe(II) was not a significant process involved in the enhanced iron solubility in the fog samples”? Please compare Fe solubility in fog samples and in the corresponding TSP samples quantitatively.

Solubility data for TSP are discussed in the companion paper by Formenti et al., this issue. For fog samples, only the dissolved fraction of the metals was measured. A lower solubility difference between TSP and fog for sample H1001 could be attributed to a lower MSA concentration in the fog sample (about one order of magnitude lower), partly due to dilution (higher liquid water content), compared to the other fog samples which would make the photoreduction process suggested by Desboeufs et al. 2024, less important in this case.

I.335 and Figure S6: Figure S6 did not show Fe(III) being predominantly complexed with oxalate. Please indicate the organic ligands and sampling date to compare with Figure 2.

We have now amended the sentence into: “...being complexed also with organics, in particular oxalate”. We have also added information on the organic ligand to the caption of Figure S6 as well as sampling dates. The caption now reads: “Figure S6. Speciation of soluble metals in ALW in TSP from Henties Bay (Namibia) obtained using the model Visual Minteq for (a) Al(III), (b) Ca(II), (c) Cu(II), (d) Fe(II), (e) Fe(III), (f) Mg(II), (g) Mn(II), (h) Ni(II), and (i) Zn(II). Samples shown cover the period 3-12 September 2017 (same as in Figure 2). For all metal ions, the organic ligand was oxalate.”

I.375: How can you explain the lowest Fe solubility differences observed in the H1001 sample, which showed larger amounts of iron-oxalates in fog than aerosol, as opposed to previous studies cited on I.298? Please show the results for the fog sample H1002, which indicated the largest Fe solubility differences.

The previous study by Desboeufs et al. only analysed PM10 samples but not fog samples. Unfortunately, we do not have XANES measurements for the sample H1002, however, for sample H1001 the concentration of MSA is about one order of magnitude lower than in other fog samples so this could explain the lower solubility of Fe in that fog sample.

I.411: Can you tell the differences in colloidal materials between insoluble hydroxides and humic-like substances?

Unfortunately, it is not possible to identify organic compounds, such as humic-like substances with EDS analysis.