

Atmos. Chem. Phys. Discuss., referee comment RC1  
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## Comment on acp-2022-134

Anonymous Referee #1

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Referee comment on "Iron (Fe) speciation in size-fractionated aerosol particles in the Pacific Ocean: The role of organic complexation of Fe with humic-like substances in controlling Fe solubility" by Kohei Sakata et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-134-RC1>, 2022

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The processes which influence changing aerosol iron fractional solubility during atmospheric transport remain a crucial gap in our understanding. Additionally, ship-based collections of size-fractionated aerosols over the open ocean are rare. This work reports results from a field study which captures these sorts of samples and attempts to use a combination of spectroscopic and microscopic analytical methods to examine aerosol iron speciation along with chemical modeling to explore these processes. The authors find that most of the total aerosol iron was found on coarse particles of  $>1\ \mu\text{m}$  but that iron solubility was higher on smaller particles. This observation is attributed to atmospheric processes which expose the smaller particles to environmental acidity levels beyond the inherent buffering capacity of the aerosol. Further, the authors suggest that Fe(III) complexes with humic-like substances (Fe(III)-HULIS) stabilize solubilized iron during transport prior to deposition on the ocean.

This study is fundamentally sound and uses methods that are well established in the field. The novelty lies in the application of these methods on samples collected across a meridional section of the Pacific Ocean between the temperate north and south. This paper lies firmly within the scope of ACP and will be of interest to the aerosol and ocean communities following revision.

The study finds that most of the total aerosol Fe is found in the coarse fraction defined as  $>1.3\ \mu\text{m}$  but that more labile Fe was in the fine fraction. Statistical tests show correlation aerosol Fe solubility and the abundance of Fe(III)-HULIS. Using models, they suggest that aerosol Fe is solubilized at  $\text{pH} < 3$  and these complexes keep the Fe stable as pH increases as ferrihydrite precipitation is suppressed. These results are all interesting and will contribute to our collective understanding of the processing of aerosols in the atmosphere.

The text is not without weaknesses which can be improved by careful revision in some

cases but perhaps not in others. Generally, the text requires careful editing for clarity and grammar. A fundamental concern of mine is that few samples were collected for this study. In total, only five marine samples and one land-based sample encompass all measurements. My concern is that results might be overinterpreted if the samples are not wholly representative. For instance, the SPO sample covers approximately 17 degrees of latitude over four days. Are there caveats to any of the conclusions because of this? Are the SPO and CPO truly different?

Some of the conclusions hinge on inferences from the SXTM single particle analysis. More generally on this point, the comparisons of the five different samples was given far less emphasis than the geochemical modeling which I think is the reverse of the proper strategy.

The authors rely heavily on references to the supplemental material. For example, on page 11 the authors make eight references to figures and tables in the supplement. This is too much. I encourage a careful consideration of what data and figures are required and these materials be included in the main paper. As an example, I am surprised that Table S1 which includes crucial information about the aerosol size fractionation scheme, filter type, and sample description scheme is relegated to the supplement. Indeed, Equation 3 in the Supplement defines the term  $[H^+]_{\text{mineral}}$  which is used throughout the paper. This equation needs to be in the primary article.

Specific Comments:

Line 76: "...decreases a saturation index of Fe..." Revise for clarity

Line 114-115: I don't understand why the label  $PM_{1.3-10.2}$  is used for coarse particles but  $PM_{1.3}$  is used for fine. Both represent a range of size classes but only the former indicates as such.  $PM_{\text{coarse}}$  and  $PM_{\text{fine}}$  would be appropriate or, if the desire is to maintain the current form, perhaps  $PM_{1.3-10.2}$  and  $PM_{<1.3}$ .

Line 117: How were blank concentrations in ng/cm<sup>2</sup> converted to pg/m<sup>3</sup>?

Line 136: How long were the aerosol samples stored prior to labile metal extraction? Were the samples frozen?

Line 148: More details are needed on the ion analysis. What were the levels of detection? Were there issues with the stability of ammonium and/or oxalate?

Line 156:  $[H^+]_{\text{mineral}}$  must be defined in the main article.

Line 171: What is LCF?

Equations 8 and 9: What do the constants 1.76 and 0.76 represent?

Line 219: What is pH (optional)?

Line 299:  $WPO1 < WPO2 < WPO3 < SPO \approx CPO$  Does this ranking indicated aerosol abundance, particle diameter, distance, something else?

Line 349: What is  $OD_{c\text{-pre}}$ ?

Line 402: The text states that the pH of cloud water decreases by 0.03 units but the next sentence states that there is an increase in aerosol pH by cloud processes. Please clarify.

Line 435: I do not think that changing  $PM_{1.3-2.3}$  to  $PM_{1.0-2.5}$  is simplifying.

Figure 1: Suggest removing the gray arrows as these do not represent samples included in this paper.

Figure 2: Air mass back trajectories could be moved to the supplement.

Figure 6: I am not sure that the panes b, c, and e are necessary for the main paper and could be moved to the supplement as many of these images already are. 6(e) is not described in the caption.

Figure 7: Much more detail is required in the caption. Clarify that  $S(n)$  refers to specific size classes. What are the significance of Particle 1, Particle 2, and Particle 3? What is SRFA?

Figure 8 is not necessary.

