

Interactive comment on “Seasonal changes in Fe species and soluble Fe concentration in the atmosphere in the Northwest Pacific region based on the analysis of aerosols collected in Tsukuba, Japan” by Y. Takahashi et al.

Anonymous Referee #1

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This paper by Takahashi et al examines the speciation and mineralogy of iron phases in some aerosol particles collected in Tsukuba, Japan in 2002-2003, and attempts to relate this to the solubility of the iron and its origin, with implications for the source of iron to the ocean, where iron acts as a micronutrient. They have done a large variety of solid-phase analyses, leaching estimates, and even simple solubility simulation, and the story holds together remarkably well across the range of analyses. This is a very timely topic, and the solid-phase speciation techniques are state-of-the-art and have only recently been applied in this way. The core of this work certainly deserves publi-

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cation in ACPD with minor revision. I have some questions about some of the methods that might require some rethinking of some interpretations, as I lay out below (if I understand correctly). But all in all this is nice, timely work that deserves publication.

Among the positive attributes of the work... 1) The temporal trends in the solid-phase speciation make sense and fit the general pattern of the presumed origin of the aerosols 2) The hypothesis of high concentrations of oil-combustion-derived Fe during the summer months is consistent among the solid-phase speciation data, the V & Ni data, the measured Fe solubility and simulated Fe solubility, and even the concentrations of sulfate and oxalate (more on anion concentrations below).

Minor concerns that can be addressed prior to publication include. . .

1) I don't understand the true meaning of the anion data, nor of some of the cation data, as the explanation of the sampling approach is not adequate to discern. The authors should provide more explanation to clarify. For example, it appears (although I am not certain) that the particles are collected with a device that does not collect any rain (wet deposition), but rather it just collects solid phases on the filters. So the extremely soluble phases they observe are in the form of a salt or other species that dissolves readily in solution. Such salts could be collected by such a sampler, if the particles travel through a dry atmosphere in transit. But when it rains they'd presumably dissolve. If I am correct about their sampling method, the authors' estimates of the amount of soluble Fe(III)sulfate, as they refer to it, must be a minimum estimate, as the portion dissolved in transit is not detected by this method. I would like the authors to acknowledge this. All of this assumes that I understand their particle collection methods correctly. On this front, the authors should state in the methods that they do not sample "wet deposition". This does not negate their interpretations. Rather, it seems to imply that there could be a lot more of this soluble Fe(III)sulfate being produced and deposited, but that some of it is deposited with the rain in the aqueous phase. Along these lines, it would be helpful to report an estimate of rainfall during each of the measurement intervals. What would be useful to know is not just the amount of

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rain that fell but the amount of time during which rain was falling, which is probably not commonly reported. For example, if all of the rain during a week falls in one hour, the Fe(III)sulfate suspended on particles in the air at that time will be washed out and “lost” to the aqueous phase by this approach, but the rest of the Fe(III)sulfate emitted during that week will be collected on the filter (I think). But if the same amount of rain falls gradually over 3.5 days during that week, I can imagine that all of the Fe(III)sulfate present in the air during those 3.5 days will be “lost” to the aqueous phase, with the result that roughly half of the Fe(III)sulfate emitted as particles will NOT be collected by the method used in this paper. I’m just asking, at minimum, for the authors to point out that their estimates of Fe(III)sulfate are minimum estimates at all times, for this reason. And this assumes I understand their sampling method correctly. 2) Please explain when the chemical analyses were done. The samples were collected 10 years prior to publication. Were analyses also done 10 years prior to publication? If they were done one year prior to publication, how much did the solid-phase speciation change during sample storage?? 3) The concentration of EDTA used in their experiment is extremely high (100 μM), several orders of magnitude higher than, say, siderophores in the ocean. How does this impact their estimate of seawater-soluble Fe? I note that despite this fact, the SW-soluble Fe conc is not enormously higher than the MQ-soluble Fe, so perhaps this does not have a huge impact on their results, despite this EDTA conc being very high. 4) P. 7610, lines 15 & 17. Is the EF for Na higher or lower than for other metals? They say higher on one line and lower on another line. 5) The sampling intervals (Table 1) seem strange and incomplete. However they do span most of the year, so the data should still capture an annual cycle, unless they missed anomalous short events. This possibility should at least be acknowledged. 6) Fig 13 seems unnecessary as the ideas are more clearly conveyed already in Fig 10. 7) I am not an expert in the interpretation of raw EXAFS and XANES data, so I hope someone who is also reviews this and comments on this aspect.

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