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Atmospheric Chemistry and Physics
Discussions

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.

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We thank the referee #1 for the constructive comments. Our replies to the comments and revisions made according to the comments are listed below. All revisions made in the revised version were in red shown in the supplement file uploaded with our replies.

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Comment 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 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.

Reply to the comment 1: We acknowledge this comment. As pointed out by the reviewer 1, we did not collect wet deposition samples. Thus, this fact was written in the Materials&Methods section. In addition, (i) total precipitation, (ii) number of rain events with total precipitation above 5 mm, and (iii) number of the days with the events during the sampling period were included in Table 1 as suggested by the reviewer 1. In particular, duration time when rain was falling is important rather than total precipitation during the period. We also think that the frequency of the rain is also important, since one rain event can remove most of the water soluble components in the atmosphere whether it is heavy or light rain. For example, although the total precipitation is very large in August and October due to the heavy rain on Aug. 14-16 and Oct. 13-14, 2003, the days covered by the rain event were similar among the seasons. As suggested by the reviewer 1, the amount of Fe species washed out by the precipitation depends not on the absolute precipitation amount but the time with such precipitation events. Thus, we do not think that the precipitation itself influence greatly the amount of Fe in dry deposition in our samples, but we would like to point out that the Fe(III) sulfate amount estimated in this work can be the minimum estimates.

Revision 1 (Section 2.1): This method can collect dry deposition or total suspended particles (TSP) in the atmosphere, whereas wet deposition samples were not collected in this study.

Revision 2 (2nd paragraph in Section 3.4): There are other factors that can affect the amount of soluble Fe related to the sampling method employed in this study, such as (i) contribution of wet deposition and (ii) difference between troposphere below and above the atmospheric boundary layer (ABL). First, the amount of soluble Fe in the aerosols can be reduced by rain during the sampling period, which cannot be directly estimated in this study, since we did not collect wet deposition samples. In Table 1, (a) total precipitation, (b) number of rain events with total precipitation above 5 mm, and (c) number of rainy days during the sampling period were given. In particular, duration of rain and frequency of the rain is important rather than the total precipitation during the period, since one rain event can remove most of the water soluble components

in the atmosphere whether it is heavy or light rain. For example, although the total precipitation is very high in August and October due to the heavy rain on Aug. 14-16 and Oct. 13-14, 2003, the numbers of rainy days were similar to those in the other months. Thus, it is not likely that the precipitation itself biases any particular month to compare the amount of soluble Fe in the dry deposition. However, we would like to point out here that the amount of soluble Fe in the atmosphere estimated in this study can be a minimum estimate, since Fe in wet deposition was not measured in our method.

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Comment 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??

Reply to the comment 2: This is a very important question and also our concern regarding to this study. Most of the data were measured in December, 2006. The samples were stored in a desiccator, since the reactions that can alter the species proceed in the presence of water. Therefore, it is not likely that original Fe species is changed during the storage. To confirm the aging effect, we measured Fe K-edge XANES during the revision in 2013. The two spectra shown in Fig. S1 were almost identical, suggesting that Fe species is not subject to change during the storage. This discussion was included in the revised manuscript.

Revision (Section 2.3): Most of the XAFS data for the aerosol samples were collected in December 2006. To prevent changes of the Fe species, the samples have been stored in a desiccator, since the reactions that can alter the species proceed in the presence of water. Therefore, it is not likely that original Fe species changed during the storage. To confirm the lack of an aging effect, we measured XANES for an aerosol sample (Feb. sample) in June 2013. The two spectra shown in Fig. S1 were almost identical, suggesting that Fe species is not subject to change during the storage.

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Comment 3: The concentration of EDTA used in their experiment is extremely high (100 uM), 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.

Reply to the comment 3: EDTA was primarily added in the leaching water to keep Fe in the solution once after the dissolution of Fe into the aqueous phase. The concentration can be very high compared with that of siderophores in the seawater. On the other hand, however, amount of aerosol to water is also very high compared with that in the natural system. Thus, we think that the absolute concentration of EDTA is not very important, if we employ same procedure to obtain soluble Fe content in the aerosol samples. This discussion was included in the revised version.

Revision (4th paragraph in Section 3.4): One may think that the concentration of EDTA used in this experiment is too high. However, EDTA was primarily added in the leaching water to keep Fe in the solution and to avoid reprecipitation of Fe in the solution before measurement of the dissolved Fe. On the other hand, the amount of aerosol relative to that of water is also very high in the experiments compared with that in the natural system. Thus, we think that the absolute concentration of EDTA is not very important, but sufficient amount of EDTA is necessary to determine the amount of soluble Fe in the aerosols.

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Comment 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.

Reply to the comment 4:We acknowledge this comment. We meant that the EF of Na is relatively lower, but higher than one, which suggests that a part of Na can be provided from sea salt. The sentence was revised as follows.

Revision (2nd paragraph in Section 3.1.3): These elements are presumably suspended and transported from natural sources such as crust or soil. Sodium, which is abundant in sea-salt particles, has EF values above 1, suggesting that aerosols at Tsukuba contain some sea salt components (Furukawa and Takahashi, 2011).

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Comment 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.

Reply to the comment 5: We acknowledge this comment. It is true that the span did not cover whole year. This situation was indicated in the revised manuscript.

Revision (Final paragraph in Introduction): Although the sampling period does not cover the whole year round, the collection of the sample from Dec. 2002 to Oct. 2003 can give us an idea of variation of [FeSol] and [FeTotal] in the atmosphere.

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Comment 6: Fig 13 seems unnecessary as the ideas are more clearly conveyed already in Fig 10.

Reply to the comment 6: Fig. 13 was moved to Supporting Information as Fig. S9.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C3959/2013/acpd-13-C3959-2013-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 7599, 2013.