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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 #2 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: Asian dust can be transported above the atmospheric boundary layer to the Northwest Pacific region. Thus surface concentrations of aerosols collected in Japan are not representative of the total dust column. Indeed, Ooki et al. (2009) measured much lower iron solubility of snow samples collected in Japan (< 1%). My concern is that the extrapolation of surface concentrations in Tsukuba would lead to an underestimate of the soluble Fe from Asian dust in the North Pacific region.

Reply to the comment 1: We acknowledge this comment. However, I guess that "underestimate" may be wrong, but the reviewer's concern is "overestimate" of the soluble Fe based on the present study. If it is, our reply is as below. We completely agree with this comment and include the discussion was included in the revised version.

Revision (Final paragraph in Section 3.4): Second, the aerosol sample collected at the ground base below the atmospheric boundary layer (ABL) in this study can be different from that above ABL that is more important for the long-range transport to the open ocean (Uematsu et al., 2003). In addition, the solubility of Fe in the sample from free troposphere can be different from that in the lower troposphere. Thus, solubility and speciation of Fe in the aerosol in the free troposphere can be important to quantify the supply of soluble Fe to the open ocean.

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Comment 2 (Section 3.4 Atmospheric concentrations of soluble Fe and fraction of soluble Fe): The positive correlation with the anthropogenic components such as sulfate or oxalate also suggests the possibility of the proton-promoted Fe dissolution, the oxalate promoted Fe dissolution, and the photoreductive dissolution.

Reply to the comment 2: We acknowledge this comment. This discussion was included in the revised version.

Revision (5th and 6th paragraph in Section 3.4): Oxalate leached from aerosol to MQ water can also contribute to the increase in [FeMQ] such as by photoreductive dissolution and complexation of oxalate with Fe (Paris et al., 2011). The effect of photoreductive dissolution cannot be discussed here, since we did not control this factor in our leaching experiments. If oxalate complexation can contribute to the increase in [FeMQ], the molar ratio of oxalate to FeMQ should be constant, considering that the mole concentrations of total Fe in aerosol were higher than that of oxalate in all months except for August (Fig. S6). More importantly, the molar ratios of oxalate to FeMQ in the leaching solution were systematically larger than 3.2 (Fig. S7). If oxalate complexation is a dominant factor for the dissolution of Fe, the molar ratio should be less than three, since the ratio of Fe-oxalate in water (=[oxalate]:[Fe]) can be from 1:1 to 3:1 based on the stability constants of Fe(II)- and Fe(III)- oxalate complexes (Martel and Smith, 1977). Thus, oxalate complexation cannot be a primarily important factor of [FeMQ], but the correlation between [oxalate] and [FeMQ] in leaching solution suggests that the oxalate complexation can enhance the dissolution of Fe to the aqueous phase. It is also suggested that pH of the solution can be also important for the dissolution of Fe into water (e.g., Desboeufs et al., 1999). It was clear that pH values were low for the three samples in this study (May, June, and July), which also showed high [FeMQ], possibly due to the large amount of acidic species such as sulfate and nitrate. The presence of a large amount of sulfate may be related to the presence of Fe(III) sulfate during the period. Thus, we can conclude that the speciation of Fe, which is also linked to acidity of the samples, can be an important controlling factor of the [FeMQ].

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Comment 3: Wet deposition is a significant fraction of the input of soluble aerosol iron to the ocean.

Reply to the comment 3: This is a question similar to comment 1 of the reviewer #1. We also think that the amount of Fe(III) sulfate, or soluble Fe content, in the atmosphere estimated in this study can be the minimum estimates, since that of Fe in wet deposition was not measured in our method. It is necessary to determine Fe in the wet deposition to estimate total amount of soluble Fe provided into ocean.

Revision (Final 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, the amount of time during which rain was falling, or even the 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 the rainy days were similar to the other months. Thus, it is not likely that the precipitation itself bias 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 the minimum estimates, since Fe in wet deposition was not measured in our method.

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Comment 4: According to Takahashi et al. (2011), the iron solubility of ferrihydrite in rainwater is 40%. Please discuss why ferrihydrite does not contribute to the total soluble Fe significantly. For example, please present the results with soluble Fe fraction simulated in rainwater as in Fig. 10 and Fig. 14.

Reply to the comment 4: We acknowledge this comment. However, the method to determine FeMQ in this study does not add oxalate in the leaching solution, which is different from that in Takahashi et al. (2011). Thus, we cannot compare the results with those in Takahashi et al. (2011).

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Comment 5: The molar ratio of oxalate to FeMQ is not necessarily constant, even if oxalate can contribute to the increase in the iron solubility, because the solubility also depends on pH and the value of pH in MQ solution is different from that in aerosol water.

Reply to the comment 5: We acknowledge this comment. However, the method to determine FeMQ in this study does not add oxalate in the leaching solution, which is different from that in Takahashi et al. (2011). Thus, we cannot compare the results with those in Takahashi et al. (2011). Revision (6th paragraph in Section 3.4): It is also suggested that pH of the solution can be also important for the dissolution of Fe into water (e.g., Desboeufs et al., 1999). It was clear that pH values were low for the three samples in this study (May, June, and July), which also showed high [FeMQ], possibly due to the large amount of acidic species such as sulfate and nitrate. The presence of a large amount of sulfate may be related to the presence of Fe(III) sulfate during the period. Thus, we can conclude that the speciation of Fe, which is also linked to acidity of the samples, can be an important controlling factor of the [FeMQ].

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Comment 6: Please present the results for FeSW in Fig. 13 to discuss the importance of Fe(III) sulfate as a source of soluble Fe in seawater.

Reply: As suggested in the next question about Fig. 14, original Fig. 13 was also for FeSW. However, as pointed out by the reviewer 1, similar figure was shown in Fig. 10a. Thus, original Fig. 13 was moved to Supporting Information as Fig. S9.

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Technical corrections Comment 7 (Fig. 14): The soluble Fe fraction was simulated in seawater. Please correct FeMQ to FeSW in Fig. 14b. Reply to the comment 7: I acknowledge this comment. The text was corrected as indicated. The Fig. 14 was

renamed as Fig. 13 in the revised version, since original Fig. 13 was moved to Supporting Information.

====== Comment 7 (References): Please provide the reference of Xie et al. (2005). Reply to the comment 7: Reply: Xie et al. (2005) was added in the reference list.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C3965/2013/acpd-13-C3965-2013-supplement.pdf

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