

## ***Interactive comment on “Metal complexation inhibits the effect of oxalic acid in aerosols as cloud condensation nuclei (CCN)” by T. Furukawa and Y. Takahashi***

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Received and published: 1 February 2011

We would like to thank Reviewer 1 for a very thoughtful and detailed review of our manuscript that helped to improve the paper. In the following we address all the points raised in the review. We basically followed all the comments and revised manuscript accordingly. Revised manuscript with revised part indited in yellow background was also uploaded as a supplement.

=== General comments ===

Comment 1: The title of the manuscript is misleading since no measurements of CCN activity were made. Something along the lines of “Oxalate metal complexes in aerosol  
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particles: implications for the hygroscopicity of oxalate-containing particles” would be more appropriate.

Reply: We changed the title as suggested.

=== Comment 2: The entire first paragraph on Page 27114 discussing the possible effects of oxalate complexes on indirect effects and radiative forcing should be removed. It is complete speculation and the calculations performed and extremely simplistic, and incorrect. Any change in the estimates of indirect effects as a result of these findings would have to be evaluated through proper global modeling exercises.

Reply: We removed the whole paragraph.

=== Comment 3: I am unaware of a vapor sorption analyzer previously being used to determine the hygroscopicity of aerosol particles. A potential issue is that the behavior of bulk solutions often differs from that of small particles. This might explain why the deliquescence curve in Fig. 6 is so broad; deliquescence occurs over a large range of 30% RH. However, the hygroscopicity of oxalic acid and calcium oxalate particles has already been measured using a more appropriate CCN method (Sullivan et al., 2009), and those results are in line with what is presented here: oxalic acid is hygroscopic, calcium oxalate is not. This is expected based on solubility arguments. The text should be amended to make these issues clear, and the previously reported hygroscopicity data should be discussed in more detail. The role of solubility on particle hygroscopicity is muddled in the paper. Calcium oxalate and zinc oxalate are not hygroscopic because they have low water solubilities. This results in a low effective or apparent hygroscopicity (Chan et al., 2008; Sullivan et al., 2009). Please revise the discussion of hygroscopicity throughout the paper to make these issues clear.

Reply: We removed our results on the vapour sorption analyzer and its experimental section. Instead, Sullivan et al. (2009) and Chan et al. (2008) were cited to indicate that metal-oxalate complexes with low water solubilities are not hygroscopic and do not increase the hygroscopicity of aerosol particles.

Revision (new paragraph added in the revised version; final part of Sect. 3.3): Sullivan et al. (2009) suggested that the hygroscopicity and CCN activation property of oxalic acid can be reduced by reacting with Ca<sup>2+</sup> in aerosols. Generally speaking, chemical species with low water solubilities are not hygroscopic, which results in the low CCN activity. Thus, Ca oxalate has low hygroscopicity and CCN activity due to the low solubility (0.617 mg/100g; Table 1). Similar characteristics can be extended to other metal oxalate complexes such as Zn and Pb oxalate due to their low water solubilities (Table 1). Formation of Zn and Pb complexes can be important considering their high abundances in anthropogenic aerosol particles (Espinosa et al., 2001; Manoli et al., 2002; Hao et al., 2007). To quantify the role of oxalic acid on the CCN activity of aerosol particles, the ratio of oxalic acid and total metal oxalate complexes such as Ca oxalate is important, which will be determined in Sect. 3.5 in this study.

=== Comment 4: The discussion of the aerosol samples and their composition and possible sources is too brief and lacking in detail. More effort should be used to infer the possible sources of the aerosol particles by combining the size-segregated particle composition with the back-trajectory analysis. It is important to understand what types of particles the oxalate complexes, and oxalic acid, were detected in.

Reply: Possible sources of the aerosol particles were discussed based on size-segregated particle composition and back-trajectory analysis in Sect. 3.1.

Revision 1 (the discussion in the back-trajectory analysis in first paragraph in Sect. 3.1 was revised): The results of backward trajectory (HYSPLIT4) analysis suggested that the air mass in winter in Tsukuba was transported through northeastern China, Korea, and Japan possibly subject to the influences of (i) anthropogenic aerosols from the mega cities in the three countries, (ii) mineral aerosols from arid area in northeast part of China (Mikami et al., 2006), and (iii) sea salts from Japan Sea (Fig. S1). In summer, the air mass mainly came from Pacific Ocean, but can also be affected by anthropogenic aerosols from industrial area in Japan, since the trajectory passed through Tokyo and Osaka.

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Revision 2 (new paragraph was added in Sect. 3.1): The size-segregated chemical compositions also reflect the sources. Briefly, relative composition of sulfate to Na<sup>+</sup> showed that more than 95% of sulfate is of non-sea salt origin (nss-sulfate; Table S1), most of which should be anthropogenic. The concentration of nss-sulfate was calculated as (e.g., Uematsu et al., 2010)  $[nss-SO_4^{2-}] = [total\ SO_4^{2-}]_{aerosol} - ([SO_4^{2-}]/[Na^+]_{seawater} \times [Na^+]_{aerosol})$  where molar ratio of  $([SO_4^{2-}]/[Na^+]_{seawater})$  was 0.051 (Bruland and Lohan, 2003). Thus, the aerosols samples in the both periods are affected largely by anthropogenic activities. The concentration of Na<sup>+</sup> in summer was approximately three times larger than that in winter, suggesting that aerosol samples in summer was affected by Pacific Ocean to a larger degree than in winter. These results agreed well to the back trajectory analysis (Fig. S1).

=== Specific comments ===

1. (abstract line 3): It has been estimated that the degree of cooling is large enough to weaken the warming effect of carbon dioxide.
2. (abstract lines 16 and 20): The sentences were reworded as suggested.
3. (abstract line 17): Revision: "while complexes with various polyvalent metal ions such as Ca and Zn are not hygroscopic, which cannot contribute to the increase of the CCN activity of aerosols."
4. (P27101, L18, 20): Revision: "In addition, we can assume that other dicarboxylic acids (DCA) also contribute to the CCN activity, considering that other DCA, which are also major constituents of WSOCs, similarly have hygroscopic nature (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yao et al., 2002; Graham et al., 2004; Lohmann and Leck, 2005; IPCC, 2007)."
5. (P27101, L18, 22): The sentence was removed as suggested.
6. (P27102, 1st paragraph): The paper was cited as suggested by the reviewer.
7. (P27102, L14): The paper was cited as suggested by the reviewer.

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8. (P27105, L1): We added next sentence: "We confirmed that the two modes gave identical spectra when samples were prepared appropriately to each mode (Takahashi et al., 2008, 2009)."
9. (P27106, L20): Corrected.
10. (P27107, last paragraph): We added next sentence: "In these processes, photooxidation is also important that can produce oxalate from its precursors such as unsaturated hydrocarbons and volatile organic compounds (VOCs) with OH radical or O<sub>3</sub> (e.g., Satsumabayashi et al., 1990; Sullivan and Prather, 2007)."
11. (P27108, L6): We revised the sentence: "heterogeneous reactions of oxalic acid with coarser particles such as sea salt and mineral dusts (Yao et al., 2002; Mochida et al., 2003, 2007, Russell et al., 2002; Sullivan and Prather, 2007)."
12. (P27108, 2nd paragraph): More discussion was given in this part as shown below: The size distribution of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> was similar in each period (Figs. 2 and 3), and the correlation coefficient between Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> for various particles in each period was high (Table S3). Moreover, the size distribution of these ions was different between winter and summer. The peak in Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> was found in the finer particle size in winter, but larger size in summer. Thus, Cl<sup>-</sup> in the coarser mode in summer reflects the composition of sea salts (NaCl), while NO<sub>3</sub><sup>-</sup> resulted from the uptake of HNO<sub>3</sub> gas by NaCl particle with water shell (Zhuang, 1999). Consequently, their correlation coefficient (R<sup>2</sup>) was very high (> 0.9). This result is also consistent with the backward trajectory analysis (Fig. S1). On the other hand, distribution of these ions into finer particles resulted from the gas to particle conversion of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub>, respectively (Seinfeld and Pandis 2006), NH<sub>3</sub> (gas) + HCl (gas) → NH<sub>4</sub>Cl (particle) NH<sub>3</sub> (gas) + HNO<sub>3</sub> (gas) → NH<sub>4</sub>NO<sub>3</sub> (particle) These chemical reactions depend on the surrounding environment, because Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions in the aerosols are likely to be affected by the ambient conditions, such as the RH (%), temperature, and photochemical factor (Oum et al., 1998; Zhuang et al., 1999; Yao et al., 2003; Seinfeld and Pandis, 2006;

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Thornton et al., 2010). Moreover, the origins of HCl (gas) and HNO<sub>3</sub> (gas) are mainly anthropogenic (Kaneyasu et al., 1999; Seinfeld and Pandis, 2006), showing that anthropogenic air masses affected the composition of aerosols in Tsukuba during winter in our samples.

13. (P27108, 3rd paragraph): More discussion was given in this part as shown below: "A peak in the size distribution of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions was observed in the coarser particle size in each period (Figs. 2 and 3), suggesting that the source of these ions was mainly natural, such as mineral dust from soil and arid areas and sea salt particles (Seinfeld and Pandis, 2006). The correlation coefficient of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions with Na<sup>+</sup> was relatively high (Table S2). However, enrichment factor of sea salt (EF<sub>ss</sub>) of Ca<sup>2+</sup> suggested that its source was not only sea salt but also from other sources such as soil particles. In contrast, EF<sub>ss</sub> of Mg<sup>2+</sup> is around or under 1, which is lower than that of Ca<sup>2+</sup>, suggesting that sources of Mg<sup>2+</sup> was mainly sea salt (Fig.S2)."
14. (P27108, last paragraph): 14-1: We added next sentence: "Among various heavy metals (Co, Ni, Zn, Mo, and Cd), concentration of Zn was larger than the other metals by more than an order of magnitude in the aerosols collected in Tsukuba (Ohta et al., 2003)."
- 14-2: Moffet et al. (2008) was added regarding to the incineration as Zn source.
15. (Page 27109, L18): Corrected as suggested.
16. (Page 27109, L20): Reworded as "one of main Ca species"
17. (Page 27109, L23): Corrected as suggested.
18. (Page 27111, L13): We added a phrase "though heterogeneous uptake on aerosol particles cannot be ruled out".
19. (Page 27111, last paragraph): The discussion was removed, since similar discussion is written in Sect. 3.6.

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20. (Page 27112, L18): Reworded as “larger”. In addition, the estimation was done based on the conservative value for Ca as 5wt%, which is larger than actual values.
21. (Page 27112, L24): Corrected with restricting our discussion to the effects of oxalate compounds on particle hygroscopicity. Revision: “contribute to the increase of hygroscopicity of aerosols.”
22. (Page 27113, L15): The reason why Ca and Zn are the only metals investigated was indicated in Sect. 3.4, where we wrote “In addition, (a) for other cations such as Pb and Cu, it was not possible to obtain good quality spectra for the speciation analysis due to their low concentrations and (b) our system using hard X-ray cannot be applied to Mg. Thus, we confined our XAFS measurements to Ca and Zn.”
23. (Page 27115, L5): Corrected as suggested.
24. (Page 27155, L20): Since the discussion was confusing, we removed the entire paragraph, which does not affect the main discussion of this manuscript.
25. (Conclusions, L15): Revised sentences in the conclusion are as follows “Therefore, the contribution of oxalic acid to hygroscopicity of aerosol particles must have been overestimated. Thus, the present study may claim reevaluation of the potential of oxalic acid to increase the CCN activity of aerosols, because most of the oxalic acid in the aerosols can exist as metal oxalate complexes. Similar to oxalic acid, other WSOCs, such as malonic and succinic acids, can transform to metal complexes in aerosols. Therefore, in discussing the hygroscopicity and related effects of organic aerosols, it is necessary to evaluate the contribution of the complexation of dicarboxylic acids with metal ions.”
26. (Table 1): “I” is ionic strength, which was added into Table 1 in the revised version.
27. (Figs. 2&3): unit of oxalate was corrected.

Please also note the supplement to this comment:

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<http://www.atmos-chem-phys-discuss.net/10/C13129/2011/acpd-10-C13129-2011-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27099, 2010.

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