

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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We thank the reviewer for insightful comments on the MS. We revised the manuscript following all the comments given by the reviewer 2. Our replies to the comments kindly given by the reviewer 2 were given below. We also uploaded annotated manuscript file as a supplement with revised supporting materials. Within the file, we showed the revised parts, where yellow and purple backgrounds show the revision related to 1st and 2nd reviewers, respectively.

Please note that the title was already changed to "Oxalate metal complexes in aerosol
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particles: implications for the hygroscopicity of oxalate-containing particles" following the suggestion given by the reviewer 1.

**** GENERAL COMMENTS ****

=== Comment 1 === The largest false assumption is, although not clearly mentioned in the text, oxalic acid exists in the form of external mixture (e.g., oxalic acid, sulfate, and nitrate NOT mixed in the aerosols). But atmospheric aerosols, in particular after experiencing atmospheric processing, are mixed with secondary chemical species (e.g., sulfate, nitrate, organics) [e.g., Furutani et al., 2009]. The authors argued that oxalic acid were formed in cloud droplets and/or at aerosol surfaces, which exactly the way of formation of secondary species. This means oxalic acid was produced in a form of "internal mixing" and mixed with other chemical species as observed by single particle mass spectrometry [Sullivan and Prather, 2007]. . . .

Reply: Our speciation results of Ca and Zn do not show that the oxalate exists in the form of external mixture, since XAFS spectra depend on the local structure around Ca and Zn atoms. Thus, we added a sentence describing the fact in the Section 3.6.

Revision (Section 3.6): One may think that speciation of Ca and Zn by XAFS assumes that oxalic acid exists in the form of external mixture of oxalic acid, sulfate, and nitrate in the aerosols. However, the speciation results do not mean that the metal-oxalate complex exists in the form of external mixture. Considering that oxalic acid is formed in cloud droplets and/or at aerosol surfaces, it is most likely that the oxalic acid is produced in a form of "internal mixture" with other chemical species such as sulfate, nitrate, and organics. XAFS results are compatible with the form of aerosol as internal mixture, since the spectra only show the local structure around Ca and Zn limited within second neighboring atoms from the center atoms (= Ca and Zn), which cannot be affected by whether the oxalate is in external or in internal mixture.

=== Comment 2 === Authors estimated impact of the metal-oxalate complexation would result in the reduction of aerosol cooling effect by 3-21% (P27114 L7-9), how-

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ever, this simple estimate is based on mass fraction of dicarboxylic acid to the total aerosol mass under the false assumption of “external mixture” of dicarboxylic acid. Such simple partitioning of indirect effect which related to CCN activation of aerosols is not valid in the atmosphere as the example of EC aerosols indicated.

Reply: We agreed with the comment and removed the discussion related to the estimation of the aerosol cooling effect.

=== Comment 3 === The chemical speciation of oxalic acid is quite valuable. But detail of multi-component fitting is not provided. Including certain chemical species seems to improve over all fitting. Although residual R is defined as a quality measure of the fitting (P27105 L22), no information about R is provided. Authors should “show” R values for different combinations of chemical species and how they concluded inclusion of certain species. This is important to justify the choice of chemical species and should be presented and discussed more in detail. Just simply showing the fitted spectra (e.g., Figures 5, 8) do not help to judge the fitting quality.

Reply: R factors of all fitting results were shown in Table S4. All speciation results based on the XANES and EXAFS fitting were determined to make the R values minimum in the fitting procedures (Section 2.3). In the procedure, the maximum number of possible species (end members) was limited to three, since it is possible that the increase of the number simply make the R value lower. In the procedure, metal-oxalate complexes, Ca and Zn oxalates were need to fit the spectra within the limitation. For example, (Section 3.3) assuming that gypsum and Ca nitrate were the main Ca species in the aerosols in the fitting, the sample spectrum could not be fitted, especially around 4047 eV (Fig. S4), where the R factor was 0.00436. On the other hand, the spectra could be fitted perfectly, even around 4047 eV, by assuming that Ca oxalate was included as possible Ca species with $R = 0.001038$ (Fig. S3).

Revision 1 (Section 2.3): All the speciation results based on the XANES and EXAFS fitting were determined when the R value was minimum in the fitting procedures. In

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the procedure, the maximum number of possible species (end members) was limited to three, since it is possible that the increase of the number simply makes the R value lower. Errors related to the least-squares analysis for the fraction of each species obtained from the XANES fitting were calculated using the Athena XAFS analysis software package (Ravel and Newville, 2005).

Revision 2 (Section 3.3): For example, assuming that gypsum and Ca nitrate were the main Ca species in the aerosols in the fitting, the sample spectrum could not be fitted, especially around 4047 eV (Fig. S4), where the R factor was 0.00436. On the other hand, the spectrum could be fitted perfectly even around 4047 eV by assuming that Ca oxalate was included as possible Ca species with $R = 0.00104$ (Fig. S3).

=== Comment 4 === Figures of size distributions are presented as separate figure (Figures 2, 3, 4), but they are frequently compared each other. I suggest to merge them into one figure like Figure 2 (a)(b)(c)(d) to facilitate easy comparison.

Reply: The figure was corrected as suggested.

=== Comment 5 === Y-axis of size distribution plots are all $dC/d\text{Log}D$. But no $d\text{Log}D$ correction seems to be made. Using values presented in supporting material (Table S1), I could re-create the all size distributions in Figures 2, 3, and 4. That means no $d\text{Log}D$ correction was made. $d\text{Log}D$ correction is to correct the different bin sizes like one obtained by MOUDI in plotting size distribution. $d\text{Log}D$ means $\text{Log}D_{\text{upper}} - \text{Log}D_{\text{lower}}$. Without this correction, shape of the size distribution will be quite different and not right. Authors should correct this.

Reply: The aerosols size in Table S1 is $d\text{log}D$, which was corrected as suggested.

=== Comment 6 === Looking at air mass back trajectories, most of the trajectories passed over metropolitan Tokyo area, which may indicate impact of mega-city emission on the chemical composition. Also Tsukuba is a middle size of city and not free from local contamination. Are there any possibilities of impact of the mega-city emission?

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Reply: We agreed with the comment. The revision needed for this comment was already made in the first revision made in response to the first review.

Revision (1st paragraph in Section 3.1): The results of backward trajectory (HYSPLIT4) analysis suggested that the air mass in winter in Tsukuba was transported through northeastern China, Korea, and Japan which was 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 areas in Japan, since the trajectory passed through Tokyo and Osaka. The seasonal trend is a typical for the air mass around Japan, and the chemical composition of the aerosols reflects the source of the air mass (Var et al., 2000).

**** SPECIFIC COMMENTS ****

=== P27100 Abstract L5-7 === Comment: “secondary organic aerosols (SOA) play a key role in the solar radiation balance in the troposphere as SOA can act as cloud condensation nuclei (CCN) and extend the lifespan of clouds” I also think SOA plays an “important” role in regulating solar radiation budget, but hard to say it plays “key” role. Could you cite suitable references which indicate SOA’s “key” roll, if you think it plays “key” role.

Reply: Corrected as suggested.

=== L11-14 === Comment: “We employed X-ray absorption fine structure spectroscopy to characterize the calcium (Ca) and zinc (Zn) in aerosols collected at Tsukuba in Japan with fractionation based on particle size using an impactor aerosol sampler.” I don’t fully understand this sentence (particularly the part highlighted by yellow).

Revision (abstract): We employed X-ray absorption fine structure spectroscopy to char-

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acterize the calcium (Ca) and zinc (Zn) in aerosols collected at Tsukuba in Japan. Size-fractionated aerosol samples were collected for this purpose using an impactor aerosol sampler.

=== L20 === Comment: “suggesting that oxalic acid does not act as CCN in the atmosphere.” Authors draw this based only on two measurements in Japan. Is this generalization/conclusion (oxalic acid is not CCN active in the atmosphere) valid? Given the limited data set, I believe that “oxalic acid may not be always CCN active” is more correct statement.

Replay: The text was corrected following the suggestion.

=== L20 === Comment: “Thus, it is possible that the cooling effect of organic aerosols assumed in various climate modeling studies is overestimated because of the lack of information on metal oxalate complexes in aerosols.” Three questions and issues: (1) Is oxalic acid major component to organic aerosols? (2) How much does oxalic acid contribute to total atmospheric aerosols? (3) Is oxalic acid really a large contributor to atmospheric CCN? In fact, oxalic acid in aerosols acts as CCN activator, not CCN. Yao et al. (2000), which authors frequently cited in this paper, showed oxalic acid is just less than 5% of sulfate component in Hong Kong. Authors also claimed dicarboxylic acids are 30% of total OC (P27114, L5). Is oxalic acid significant relative to sulfate component (aerosols) and other chemical components (aerosols)?

Reply: Although the ranges are large, it has been reported that (i) organic aerosols account for 10%–70% of the total aerosols (Saxena and Hildemann, 1996; Zappoli et al., 1999; Turpin et al., 2000), (ii) the amount of dicarboxylic acids was about 30% of the total organic aerosols (Satsumabayashi et al., 1989, 1990; Sempéré and Kawamura, 1996; Decesari et al., 2000), and (iii) oxalic acid has the highest concentration among various dicarboxylic acids (e.g., Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Kawamura et al., 2005; Hsieh et al., 2009). Thus, we can say that oxalic acid is an important component in aerosols. On the other hand, the concentra-

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tion of oxalic acid in aerosols is less than 5% that of sulfate aerosols in our study. The contribution of oxalic acid as atmospheric CCN can be lower than that of sulfate, but the metal-complexation of oxalate is important to understand the hygroscopic nature of oxalic and other dicarboxylic acids in the aerosols. In summary, we think that the last sentence in the previous version may be too strong and the sentence was revised as follows.

Revision (abstract): Thus, it is possible that the cooling effect of organic aerosols assumed in various climate modeling studies should be estimated by including the information on metal oxalate complexes and metal complexes with other dicarboxylic acids in aerosols.

==== P27101 L17==== Comment: “Among the various organic aerosols studied, water-soluble organic compounds (WSOCs) in aerosols influence the surface environment as they act as CCN” I don’t understand this sentence. Particles are CCN, but compounds are not CCN since compounds usually does not refer particles, but components in the particles. Water soluble organic compounds are CCN-active material, but not CCN.

Reply: We agree with the comment. The sentence was already corrected in the first revision, which also meets the comment by the second reviewer.

Revision (1st paragraph in Section 1): Among the various organic aerosols studied, water-soluble organic compounds (WSOCs) in aerosols influence the heat budget at earth surface as they act as CCN activator because of their hygroscopic properties.

==== L19 ==== Comment: “dicarboxylic acids have been identified as a major constituent of organic CCN (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yao et al., 2002).” All references cited here do not report that dicarboxylic acids are major constituents of organic CCN, but simply reported concentrations of dicarboxylic acids in the atmospheric aerosols. Also as far as I know, nobody clearly reported that dicarboxylic acids are the major constituent of organic CCN.

Reply: We agree with the comment. The sentence was already corrected in the first revision, which also meets the comment by the second reviewer.

Revision (1st paragraph in Section 1): We can assume that dicarboxylic acids (DCA) contribute to the CCN activity, considering that DCA, which are major constituents of WSOCs, have hygroscopic nature (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yao et al., 2002; Crahan et al., 2004; Lohmann and Leck, 2005; IPCC, 2007).

=== L21 === Comment: “Moreover, WSOCs increase the cloud Albedo effect (i.e., cloud lifetime effect) by extending the lifetime of a cloud depending on their hygroscopic properties (Grahan et al., 2004; Lohmann and Leck, 2005; IPCC, 2007).” Please cite suitable reference(s) which shows/suggests WSOCs affect lifetime of a cloud and thus increase cloud Albedo effect (cloud lifetime effect). Cloud lifetime effect by atmospheric aerosols has been well-known, but not specifically for WSOC as far as I know. Grahan et al., 2004 => Crahan et al. 2004

Reply: This sentence was already removed in the first revision in response to the comment by the reviewer 1.

=== L24 === Comment: “Oxalic acid is a major component of dicarboxylic acids or secondary organic aerosols, and is thought to act as CCN.” Please cite references (major component of SOA). I don’t think oxalic acid is a major portion of SOA, although it may be a major portion of identified SOA.

Revision (2nd paragraph in Section 1): Oxalic acid is a major component of dicarboxylic acids and also an important component of identified secondary organic aerosols (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yu, 2000).

=== L2 === Comment: “(i) aerosols contain various metal ions originating from sea salts, desert dusts, continental soils, and anthropogenic sources; (ii) oxalic acid is formed in the aqueous phase at aerosol surfaces in the atmosphere, which provides

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a reaction field for metal complexation; and (iii) polyvalent metal ions can form stable complexes with oxalate ions (Warneck, 2003; Grahan et al., 2004; Lim et al., 2005; Carlton et al., 2007).” None of the cited references (Warneck, 2003; Grahan et al., 2004; Lim et al., 2005; Carlton et al., 2007) mentioned about metal complex formation of oxalic acid. Please cite appropriate references for metal complex formation by oxalic acid.

Reply: These sentences do not try to give evidence showing directly the formation of metal-oxalate complexes. We tried to give facts from which we can expect the formation of metal-oxalate complexes in aerosols. The references were more specifically shown in each factor.

Revision (2nd paragraph in Section 1): We expect that oxalic acid can form metal oxalate complexes in aerosols by reacting with metal ions due to several reasons: (i) aerosols contain various metal ions originating from sea salts, desert dusts, continental soils, and anthropogenic sources; (ii) oxalic acid is formed in the aqueous phase at aerosol surfaces in the atmosphere or cloud droplet (Warneck, 2003; Grahan et al., 2004; Lim et al., 2005; Carlton et al., 2007), where the aqueous phase can be a reaction field for metal complexation; (iii) polyvalent metal ions can form stable complexes with oxalate ion (Table 1).

=== P27105 L7 === Comment: “The zinc (Zn) K-edge XANES and EXAFS data were measured at Beamline 12C” XANES and EXAFS were both used. Ordinary atmospheric chemistry readers are not so familiar with XAFS and do not know the difference, advantage, disadvantage, principles between XANES and EXAFS. Please provide brief description for them and cite proper reference(s).

Reply: New sentence was added after the sentence in the comment.

Revision (2nd paragraph in Section 2.3): XANES reflects valence and symmetry of the element, while EXAFS shows interatomic distance and coordination number. Applications of both XANES and EXAFS result in higher reliability of the speciation data. The

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EXAFS was not used for Ca speciation due to the poor quality of the spectra. It is usual that EXAFS quality is worse than XANES, since the latter needs measurement for longer energy range with smaller oscillations.

=== L27 === Comment: “The error for each fraction of the end members obtained from the XANES fitting was calculated using the Athena XAFS analysis software package (Ravel and Newville, 2005).” No error evaluation is provided. This is an important part of chemical speciation and should discuss more in detail.

Revision (3rd paragraph in Section 2.3): Errors related to the least-squares analysis for the fraction of each species obtained from the XANES fitting were calculated using the Athena XAFS analysis software package (Ravel and Newville, 2005).

= P27107 L8=== Comment: “The formation of oxalate in the aerosols can be deduced from the chemical composition of the WSCs of the size-fractionated samples (Fig. 1 and Table S1)”. I don’t understand what you are saying in this sentence.

Revision (1st paragraph in Section 3.2): The formation process of oxalate in the aerosols can be deduced from the concentrations of the WSCs at various particle sizes of the aerosols (Fig. 1 and Table S1; Yao et al., 2002).

=== L16 === Comment: “Similarly, ammonium in both seasons is formed in the droplet mode (Figs. 2 and 3).” Based on what could you conclude ammonium is formed droplet mode? What is droplet mode?

Reply: The discussion of ammonium here was removed, since the discussion on the size distributions of oxalate and sulfate is not directly related to that of ammonium.

=== L23 === Comment: “oxalic acid particles can be captured in preexisting aerosols, such as sulfate aerosols, after the formation of an oxalate aerosol in the gas to particle conversion process (condensation mode)” Gas to particle conversion process is “condensation of gas molecules onto pre-existing aerosols”. If particles are merged into one, this is “coagulation”. This sentence mixes up concepts of “condensation” and

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“coagulation”. Please clarify and correct.

Revision (1st paragraph in Section 3.2): Oxalate in aerosols can be formed by several mechanisms: (i) oxalic acid in aerosols are formed by gas to particle conversion (condensation), (ii) oxalic acid particles can be captured in preexisting aerosols, such as sulfate aerosols (coagulation), and (iii) oxalate can be formed in the aqueous in cloud droplet or at particle surface by chemical reaction.

=== P27108 L1 === Comment: “because the maximum surface area of the (secondary) aerosols had a particle size $< 1 \mu\text{m}$ (Seinfeld and Pandis, 2006).” This is generally true, but it varies due to variable nature of size distribution. You cannot assume $< 1 \mu\text{m}$ has the largest surface area, especially during dust event (more supermicron aerosols than usual).

Reply: We agree with this comment. Since (i) statement can be true to secondary aerosol and (ii) the size distribution during the dust event is an exception for this discussion, the revision below was made.

Revision (1st paragraph in Section 3.2): because the maximum surface area of the secondary aerosols had a particle size $< 1 \mu\text{m}$ in the period without dust events (Seinfeld and Pandis, 2006).

=== L2 === Comment: “The second and third processes can explain the shift towards a coarser particle size by: (a) evaporation of oxalic acid in the finer particle sizes, which would result in an increase in the relative amount of oxalate in the coarser particles (Yao et al., 2002); and (b) a heterogeneous reaction of oxalic acid with coarser particles, such as sea salt (Yao et al., 2002; Mochida et al., 2003). Further discussion regarding the shift in particle size will be given in Sect. 3.6.” This mechanistic discussion is based on lots of assumption. It is not amenable to elucidate formation mechanism based only on size distribution. In the present study, based only on TWO samples. You cannot speculate based on speculation.

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Reply: We added more data to this discussion in Fig. S2. We examined size-distribution of oxalic acid for aerosols collected in Okinawa island (Hedo, Okinawa, Japan) in 2008 containing sea salts from marine sources. In the samples, the shift of the peak was observed for oxalate in the aerosols. On the contrary, the peak shifts were not found for the size distributions determined for Beijing, remote region from ocean (Fig. S2). These results suggest that the aerosol samples affected by the supply from ocean can have the shift of peak of oxalate in the size distribution. Detail information of any sampling places is shown in Table S1.

Revision (1st paragraph in Section 3.2): A similar shift has also been observed by Yao et al. (2002), Mochida et al. (2003, 2007), and our observation at Okinawa island (Hedo, Okinawa, Japan) and Beijing. Details of the information of Hedo and Beijing were shown in supporting materials (Table S1 and Fig. S2). These results suggested that the aerosol samples affected by air mass from ocean can have the shift of peak of oxalate to larger particle size in the size distribution as clearly observed in Hedo (Fig. S2).

=== P27109 L0 === Comment: “Ca oxalate in the finer particles” Different people can have different size for the words of fine or coarse. Author should clarify fine or coarse at the first usage.

Reply: The text was corrected as suggested.

Revision (2nd paragraph in Section 3.3): This result confirms that Ca oxalate is the main Ca species in the finer particles (0.43–2.1 μm and 0.65–2.1 μm during the winter and the summer, respectively).

=== L5 === Comment: “Figure 5 shows the spectra of aerosol samples and Ca species used to fit the sample spectra. The fractions of Ca species obtained from the fitting are shown in Table 2, and the results of the XANES spectra of various Ca species are shown in Fig. S2. Based on these results, it is suggested that Ca oxalate was observed in the finer particles as 0.43–2.1 μm and 0.65–2.1 μm during the winter and

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the summer, respectively.” Need to show R to check the quality of multi-component fitting. This is critical to judge whether other new component(s) like metal complex should be included or not. More detailed evaluation and validation about including metal complex in the fitting.

Reply: The text was corrected as suggested.

Revision (3rd paragraph in Section 3.3): For example, assuming that gypsum and Ca nitrate were the end members of Ca in the aerosols in the fitting, the sample spectrum could not be fitted especially around 4047 eV (Fig. S4), where the R factor was 0.00436. On the other hand, the spectrum could be fitted perfectly even around 4047 eV by assuming that Ca oxalate was one of main Ca species with $R = 0.00104$.

=== L13 === Comment: “In this range, the molar concentration of Ca^{2+} ions was lower than that of the total oxalate concentration, supporting the presence of Ca oxalate in this particle size. Gypsum and Ca nitrate were also observed in the same particle size range, and the XANES spectrum of Ca oxalate was similar to that of gypsum and Ca nitrate (Fig. S2).” Author stated that Ca oxalate XANES spectrum is similar to those of gypsum and Ca nitrate. Then how Ca oxalate can be differentiated from gypsum and Ca nitrate, and isolated from XANES spectrum?

Reply: The previous sentence was not good, since it can lead to the misunderstanding of the fitting procedure. The spectra of gypsum and Ca-oxalate were different enough to distinguish them in the XANES spectra. Thus, the sentence that the spectra of gypsum and Ca nitrate are similar was removed.

=== P27110 L22 === Comment: “Based on the fitting of the XANES spectra (Table 3), $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Zn oxalate) in the aerosols was observed in the finer particles that also contained $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Zn sulfate). On the other hand, the Zn species in the coarser particles were $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ (Zn chloride), ZnCO_3 (Zn carbonate), and ZnS (Zn sulfide), the details of which, including the sources of these species in the coarser particles, will be described elsewhere.” Again without detail discussion about quality

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of the fitting by showing R (residual) values for different combinations of standards, reader cannot judge the quality.

Reply: All the R values of our fitting results are shown in Table S4.

Revision (2nd paragraph in Section 3.4): All the related R values for the fitting were shown in Table S4.

=== L27 === Comment: “In this study, the variation of Zn species from finer to coarser particle size is important, because the effect of oxalate formation should be more marked in the finer particle sizes. Zinc oxalate was not needed to fitting the spectra of the coarser particles, but was essential to fit the XANES spectra of the finer particles.” I don’t understand this sentence. XANES spectra in coarse mode could not be fitted well with considered standards?

Reply: This sentence indicates that Zn-oxalate is not included in the coarser particles based on the XANES fitting. However, to avoid misunderstanding, the following sentence was added as the next sentence with R values after the sentence in this comment.

Revision (2nd paragraph in Section 3.4): For example, when Zn K-edge XANES spectra of 11-7 μm (coarse mode) in winter was fitted by those of Zn sulfate and Zn oxalate, the R factor was 0.0475. When Zn sulfide and Zn carbonate were used by fitting in that particles range, its R factor was the lowest value (0.00228), which discounts the presence of Zn oxalate. In finer particles (< 2.1 μm in winter and 3.3 μm in summer), contribution of Zn oxalate was needed to fit the spectra with lowest R values.

=== P27111 L4 === Comment: “Figure 8 and Table 4 show the fitting of the EXAFS data in k space and the Zn speciation data, respectively. The fitting results of the EXAFS data are more reliable than that of the XANES data, because EXAFS spectra are dependent on the neighboring atoms, interatomic distances, and coordination number, which are sensitive to the Zn speciation.” Need more brief description about principles,

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difference for XANES and EXAFS, especially for ordinary atmospheric scientists who are not so familiar to X-ray absorption spectroscopy. Also why no EXAFS result for Ca if EXAFS provides better and more reliable information about chemical speciation than XANES?

Reply: The answer to this comment was already given related to the comment for “P27105 L7”.

Revision (2nd paragraph in Section 2.3): XANES reflects valence and symmetry of the element, while EXAFS shows interatomic distance and coordination number. Applications of both XANES and EXAFS result in higher reliability of the speciation data. The EXAFS was not used for Ca speciation due to the poor quality of the spectra. It is usual that EXAFS quality is worse than XANES, since EXAFS needs measurement for longer energy range with smaller oscillations.

=== L12 === Comment: “This result shows that Zn oxalate was formed in the aqueous phase at the particle surface, which is caused by the increase in [surface area]/[volume] ratio with decreasing particle size.” Why can this be derived? It can be just size dependence of oxalic acid and/or Zn.

Reply: We think that the dependence can be well explained by the reaction at the particle surfaces, though heterogeneous uptake on aerosol particles cannot be ruled out. To explain this more clearly, the next sentence was added in the revised version.

Revision (3rd paragraph in Section 3.4): For instance, Takahashi et al. (2009) suggested that the secondary gypsum fraction formed by the reaction at particles surface increased with the decrease in its particles size, which may be valid to other species formed at particles surface. In our study, the ratio of [Zn oxalate]/[Zn]_{total} increased with the decrease in the particles size (Table 4 and Fig. S7), suggesting that the reaction of particle surface was important for the formation of Zn oxalate, though heterogeneous uptake on aerosol particles cannot be ruled out.

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=== P27114 L27 === Comment: “In our XAFS study, Ca oxalate was found in the droplet mode, suggesting that Ca oxalate in this particle range formed by evaporation of cloud droplets (incloud process).” What is droplet mode? How can this be differentiated and decide? If the droplet mode is false, then this formation mechanism will fail, too. Assignment of droplet mode is safe?

Reply: This is essentially same comment for P27107 L16. Droplet mode is a mode which has a peak in the size distribution around aerodynamic diameter of $0.7 \mu\text{m}$ (Meng and Seinfeld, 1994). The explanation and the reference were added in the revised version.

=== L7 === Comment: “However, if Ca is present as small particles of minerals in the finer particle size region, then it is likely that oxalic acid can dissolve Ca^{2+} ions out of these Ca minerals to form Ca oxalate on the particle surface.” How Ca^{2+} ion can exist in the smaller size range? You mentioned in the smaller size Ca concentration is usually low and exists as gypsum and/or calcite.

Reply: This sentence was removed in the revised version.

=== L9 === Comment: “This mechanism can explain the shift in the oxalate peak in the size distribution to larger sizes in summer, because the abundance of Ca in the coarser particle size range is larger in the summer.” I don’t understand this sentence. How formation mechanism of Ca oxalate related to the change in size distribution of oxalate?

Reply: We added next sentence in the discussion.

Revision (2nd paragraph in Section 3.6): Mochida et al. (2003) suggested that the uptake of dicarboxylic acids by mineral dust particle can change the size distribution of dicarboxylic acids such as oxalate. Thus, Ca in aerosols rich in coarser particles can change the oxalate size distribution by oxalate uptakes, where it is moly likely that Ca oxalate is formed.

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=== L13 === Comment: “In our XAFS study, the [Zn oxalate]/[Zn]total ratio increased with the decreasing particle size, suggesting that Zn oxalate was rich at the particle surface.” Why increasing behavior of [Zn oxalate] / [Zn total] as size decrease is the indication of surface-bounded Zn oxalate? It could be just a size distribution.

Reply: This is the same comment to the one to P27111 L12. We think that the dependence can be well explained by the reaction at the particle surfaces, though heterogeneous uptake on aerosol particles cannot be ruled out. To explain this more clearly, the next sentence was added in the revised version.

=== L23 === Comment: “These results suggest that the oxalate formation process is different between winter and summer.” You cannot say “different formation mechanism” just because of different size distribution!

Reply: The sentence was already removed from the manuscript in the first revision in response to the comment by the reviewer 1.

=== L24 === Comment: “In winter, a gas phase reaction, such as an oxidation reaction of volatile organic compounds, can be the dominant factor in the finer particles, whereas reactions in water around the particle can be important in summer. Thus, finer particles of noncomplexed oxalic acid during winter can be higher than that in summer in particle sizes <0.43 μ m and metal oxalate complexes can be formed in particle sizes 2.1–3.3 μ m in summer.” Speculation based on faulty speculation: : :

Reply: The sentence was already removed from the manuscript in the first revision in response to the comment by the reviewer 1.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C14416/2011/acpd-10-C14416-2011-supplement.pdf>

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

C14432

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