

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

Anonymous Referee #2

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Furukawa and Takahashi collected size-segregated atmospheric aerosol samples at Tsukuba, a rural area of metropolitan Tokyo, Japan and carried out series of chemical analysis including X-ray fine structure absorption (XAFS) spectroscopy, which allows detailed chemical speciation of metal ions such as Ca^{2+} and Zn^{2+} . Based on the observed size-resolved chemical composition/speciation, they discussed formation of oxalic acid and metal-oxalate complex in the atmospheric aerosols, and concluded that most of the aerosol-phase oxalic acid exists in the form of metal-complex, which found water insoluble. They further speculated that the formation of water-insoluble metal oxalate would lead oxalic acid aerosols CCN-inactive and reduce global cooling effect of atmospheric aerosols by 3–21%, and thus contribution of the metal-complex

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formation of dicarboxylic acids requires re-evaluation of global cooling effect by atmospheric organic aerosols. The research group is an expert in XAFS spectroscopy and has successfully applied the technique for environmental samples. In the present study, the quality of their XAFS measurement / data analysis sound good and they presented unique information about chemical speciation of oxalic acid in the atmospheric aerosols (although details of XAFS data analysis (multi-componential fitting) is not provided). However, further discussions about atmospheric formation mechanism of oxalic acid and the potential global impact of the metal-oxalate complex are quite hard to be justified since many erroneous/false assumptions are made. The assessment of the global impact of metal-oxalate complexation lacks important views of atmospheric aerosols: external mixture of atmospheric aerosols and competitive CCN-activation in the aerosols mixed with other abundant CCN-active matter like sulfate. There are also many logical leaps in the discussion section (in particular in the mechanistic discussion about oxalic acid formation and global effect of metal-oxalate formation). Also more proper English expression is required to describe possibility or probability more precisely in many places. The formation of metal-complexation of oxalic acid itself is quite valuable new information for atmospheric community. I would encourage authors to focus mainly metal-complexation of oxalic acid and shave erroneous speculative discussions.

General Comments

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 spectrom-

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etry [Sullivan and Prather, 2007]. This should be also the case for the present rather aged air masses, which is further supported by the similar size distributions of sulfate and oxalic acid (Figures 2 and 3). Then, CCN activation of the aerosols will be competition between chemical species on the aerosols. On such internally-mixed aerosols, comparative quantitative assessment is required. In the present study, concentration of sulfate was always ~ 10 times higher than oxalic acid (Figures 2 and 3, Table S1). CCN activity of aerosols with such high sulfate content is close to pure sulfate aerosols and highly CCN active [e.g., Bilde and Svenningsson, 2004; Roberts et al., 2002; Prenni et al., 2003]. Mochida et al. also showed that CCN activity of Asian outflow aerosols were close to ammonium sulfate in Okinawa Island where air masses with aging time of 1–3 days were observed [Mochida et al., 2010]. If you consider elemental carbon (EC) as a proxy of oxalic acid, it would be also much easier to think about this situation. EC aerosols are quite less CCN-active when they are emitted, but after being aged, it will be CCN-active and won't suppress CCN activity of organic aerosols. It should be also pointed out that in the internal mixing condition, insoluble core like metal-oxalate will "enhance" the CCN-activity by enhancing solute effect (Raoult effect). Authors estimated impact of the metal-oxalate complexation would result in the reduction of aerosol cooling effect by 3–21% (P27114 L7–9), however, 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.

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

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not help to judge the fitting quality.

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.

Y-axis of size distribution plots are all $dC/d\log D$. But no $d\log D$ 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 $d\log D$ correction was made. $d\log D$ correction is to correct the different bin sizes like one obtained by MOUDI in plotting size distribution. $d\log D$ means $\log D_{upper} - \log D_{lower}$. Without this correction, shape of the size distribution will be quite different and not right. Authors should correct this.

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?

References

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Specific Comments Line by Line

P27100 Abstract L5-7 “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” role, if you think it plays “key” role.

L11-14 “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).

L20 “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.

L20 “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?

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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)?

P27101 L17 “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.

L19 “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.

L21 “Moreover, WSOCs increase the cloud Albedo effect (i.e., cloud lifetime effect) by extending the lifetime of a cloud depending on their hygroscopic properties (Graham 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. Graham et al., 2004 => Crahan et al. 2004

L24 “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.

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L2 "(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 a reaction field for metal complexation; and (iii) polyvalent metal ions can form stable complexes with 5 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.

P27105 L7 "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).

L27 "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.

P27107 L8 "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.

L16 "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?

L23 "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

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"coagulation". This sentence mixes up concepts of "condensation" and "coagulation". Please clarify and correct.

P27108 L1 "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).

L2 "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. P27109 L0 "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.

L5 "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 $0.43\text{--}2.1\ \mu\text{m}$ and $0.65\text{--}2.1\ \mu\text{m}$ during the winter and the summer, respectively." Need to show R to check the quality of multi-component fitting. This is very 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.

L13 "In this range, the molar concentration of Ca^{2+} ions was lower than that of the

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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 15 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?

P27110 L22 “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 of the fitting by showing R (residual) values for different combinations of standards, reader cannot judge the quality.

L27 “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 fit 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?

P27111 L4 “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, 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?

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L12 “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.

P27114 L27 “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 (in-cloud 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?

L7 “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.

L9 “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?

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

L23 “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!

L24 “In winter, a gas phase reaction, such as an oxidation reaction of volatile organic

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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 $<0.43\ \mu\text{m}$ and metal oxalate complexes can be formed in particle sizes $2.1\text{--}3.3\ \mu\text{m}$ in summer." Speculation based on faulty speculation. . .

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