

## ***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 #1**

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Furukawa and Takahashi report measurements of the chemical form of oxalate in aerosol particles collected in Japan measured using x-ray analysis. They also present a small set of measurements of the hygroscopicity of oxalic acid versus calcium oxalate, and then make some overstated conclusions regarding the effects of the observed chemical form of oxalate on aerosol indirect climate effects. The methods used to determine the form of oxalate are sound and produce a unique and valuable dataset that can be used to infer the solubility and thus effective hygroscopicity of oxalate in the sampled atmospheric aerosol particles. However, there are some major issues regarding how the research is discussed and the conclusions that are derived from this dataset. All discussion of aerosol indirect effects must be severely curtailed and toned-

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down; too many steps lie between the solubility of oxalate in particles and its effects on cloud properties to draw any reasonable conclusions. What is stated in this paper regarding indirect effects is pure speculation and should be clearly presented as such. There are also some issues regarding the hygroscopicity data presented that need to be addressed. The subject of this manuscript is appropriate for ACP, and should be acceptable for publication provided the issues raised here are addressed following revision.

### General comments

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 particles: implications for the hygroscopicity of oxalate-containing particles” would be more appropriate.

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 are 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.

I am unaware of a vapour 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.

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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.

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.

#### Specific comments

Abstract, line 3: “It has been estimated that the degree of cooling is large enough to cancel the warming effect of carbon dioxide.” The word “cancel” is an inappropriate description. Even if aerosol radiative forcing perfectly balanced that of greenhouse gases at the top of the atmosphere, the distribution of energy through the atmosphere would still be altered compared to the pre-industrial state.

Abstract, line 16, and numerous other instances: “Oxalic acid can act as CCN. . .”. This is an indirect description. Oxalic acid is one of many aerosol components. Particles act as CCN, individual chemicals are not CCN. Reword to “Oxalic acid is hygroscopic and can thus facilitate the CCN activation of aerosol particles at lower cloud supersaturations.”, for example.

Abstract, line 17: “while metal complexes are not hygroscopic”. Not true. As you state later in the paper, monovalent cations form soluble oxalate complexes, while polyvalent cations typically form insoluble complexes.

Page 27101, line 18: what do you mean by “surface environment”?

Page 27101, line 20: “dicarboxylic acids have been identified as a major constituent

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of organic CCN (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yao et al., 2002).” None of these papers demonstrated that DCAs are a constituent of CCN. They measured DCAs in aerosols, and you can assume that DCAs will contribute to CCN activity due to the hygroscopicity of oxalic acid and other DCAs, but this was not directly measured.

Page 27101, line 22: “Moreover, WSOCs increase the cloud albedo effect. . .”. Again, this conclusion is too strong and unfounded. The cited papers do not directly demonstrate this effect! This is all speculation.

Page 27101, line 24: “Oxalic acid is a major component. . .”. Please provide some references for this.

Page 27102, 1st paragraph: The recent paper by Evrens and Volkamer (2010) would be appropriate to cite here.

Page 27102, line 14: Mochida et al. (2007) also reported dicarboxylic acids likely mixed with mineral dust.

Page 27105, line 1: Different modes were used to measure the X-Ray spectrum of aerosol samples versus standards. This is somewhat concerning. The authors should demonstrate that the two modes give similar results, justifying the comparison of spectra taken from samples versus standards, acquired using different modes.

Page 27106, line 20: Please be more specific regarding the areas that the back-trajectories passed over. China is a huge country. It would be good to know if the trajectory passed over desert regions, large cities, etc.

Page 27101, last paragraph: What about photochemically-induced production of oxalic acid, as suggested by (Satsumabayashi et al., 1990; Sullivan and Prather, 2007)?

Page 27108, line 6: Oxalic acid can also react heterogeneously with mineral dust, particularly if it is alkaline (Mochida et al., 2007; Russell et al., 2002; Sullivan and Prather, 2007).

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Page 27108, 2nd paragraph: This discussion would be much clearer if it was presented in terms of the likely sources of the measured aerosol particles (e.g. marine, desert, anthropogenic, biomass. . .). The authors can infer some information regarding the sources by combining the size-segregated chemical composition with the back-trajectory information. See Bates et al. (2004) for an example.

Page 27108, 3rd paragraph: By calculating the ratios of e.g. Ca/Na, Mg/Na, you should be able to infer if these components were mostly from sea salt or mineral dust (Bates et al., 2004).

Page 27108, last paragraph: It would be good to briefly discuss the concentrations of Zn measured here, so the reader understands why you are focusing on Zn. Currently this is discussed later in the paper (Section 3.4). Zn can also be emitted from incineration (Moffet et al., 2008).

Page 27109, line 18, and elsewhere: Use “fit” instead of “fitted”.

Page 27109, line 20: Please explain the meaning of “end member”.

Page 27109, line 23: Be consistent about giving the chemical name and formula when discussing different chemicals, especially for the first time. I.e. gypsum, anhydrite.

Page 27111, line 13: “This result shows that Zn oxalate was formed in the aqueous phase. . .”. While the results certainly support aqueous production, other pathways such as heterogeneous uptake cannot be ruled out as the data is currently presented. The x-ray analysis would likely need to be performed on individual particles so that the chemical composition of the oxalate-containing particle was known, before a production mechanism could be proposed with any certainty. Russell et al. (2002) also detected carboxylic acids as particle coatings.

Page 27111, last paragraph: The last two sentences are confusing. This is better explained on Page 27115, line 10.

Page 27112, line 18: 0.035 mg is hardly “much larger” than 0.025 mg. These argu-

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ments don't convince me that all the oxalate compounds would have dissolved prior to analysis.

Page 27112, line 24: Again, it is inappropriate to discuss "whether or not oxalate species have a cooling effect" as that was not explicitly investigated here. Restrict your discussion to the effects of oxalate compounds on particle hygroscopicity.

Page 27113, line 15: Why weren't complexes of oxalate with Mg, Pb, Cu, and other metals (Fe?) measured here? Can they not be determined using these x-ray techniques? This should be discussed earlier in the paper so it is clear why Ca and Zn are the only metals investigated.

Page 27115, line 5: Sea salt is also a significant source of Ca, as you mention later in the paper.

Page 27155, line 20: "Zn oxalate was not observed...". I do not understand this sentence. I find this entire paragraph confusing. Line 25: Sullivan & Prather (2007) suggested uptake of gas-phase oxalic acid and precursors as a source of oxalate in mineral dust and sea salt particles.

Conclusions, line 15: "the concentration of free oxalic acid acting as CCN...", again, these types of statements must be removed, too speculative.

Table 1: What does the " $I = 0.10 M$ " notation mean?

Figs. 2 & 3: Please list the units for the oxalate concentration.

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and Prather, K. A.: Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles, *Atmos. Chem. Phys.*, 9, 3303-3316, 2009.

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