

## ***Interactive comment on “Inorganic salts interact with organic di-acids in sub-micron particles to form material with low hygroscopicity and volatility” by G. Drozd et al.***

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We thank the reviewer for his or her helpful comments and insight. We respond to the specific points below.

1. The authors only investigated the oxalic acid and its salts and the general conclusion that author stated may not apply to other dicarboxylic acid, as indicated by the other reviewer. I suggest the authors revise the conclusion carefully, unless additional information is provided.

As suggested, the title was changed to: “Inorganic salts interact with oxalic acid in

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sub-micron particles to form material with low hygroscopicity and volatility”

The conclusion section was modified to read 30670/L6: “Our results are specific to OxA, but strong binding may occur for other DCA. Highly oxidized, soluble organic species, particularly including carboxylic acid groups, can strongly decrease hygroscopicity in particles dominated by divalent salts”

2. Line 20 on P30654 and corresponding discussion on the surface enhancement of oxalate salts in the manuscript, I agree that Mg Oxalate could be enhanced on the particle surfaces, but it is not clear to me this also applies to Ca and Zn salts. Please provide additional references.

Ault et al. 2013 directly observe the surface enhancement of both Ca and Mg, suggesting this behavior is not specific to Mg and may apply to divalent salts in general. Furukawa et al. (2011) also see higher fractions of oxalate bound zinc to total zinc with decreasing particle size, suggesting that higher surface area-to-volume ratios, and hence the potential of formation of ZnOx at the surface and corresponding surface enhancement. These references are present in the text, and citations are not used in the abstract.

The text was modified at 30656/L28: “Finally, a recent study has directly shown the surface enhancement of both Ca and Mg, suggesting this behavior is not specific to Mg and may apply to divalent salts in general (Ault et al., 2013).”

3. P30656, L22, wrong citation. Laskin et al.(2005) did not investigate the surface reactions between oxalic acid and metal-chlorides.

The reactions of interest in this reference, on L22, were the solubilizing of minerals by reaction with nitric acid. The reference, on L24, does refer to reactions between oxalic acid and metal-chlorides. The reference on L22 has been changed to Laskin et al. 2012.

4. P30658, L24, Please add the purities for these chemicals.

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This information was added at 30658/L23 "Salt particles were generated from aqueous solutions of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (Sigma Aldrich 98%),  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (Fisher Scientific >= 99 %),  $\text{ZnCl}_2$  (Sigma Aldrich 98%) ,  $\text{NaCl}$  (Fisher Scientific >= 99 %),  $\text{Na}_2\text{C}_2\text{O}_4$  (Fisher Scientific > 99.5%)."

5. P30659, L10-L12, is that 10% RH higher then deliquescence RH? If yes, shouldn't all particles be aqueous?

We expect that re-humidifying does make the particles aqueous, but due to OxA deposition the exact hydration state is uncertain. To suggest this more clearly the text has been modified at 30659/L12:

"Re-humidification will hydrate particle surfaces and may create aqueous droplets; causing mixing to facilitate surface chemistry prior to measurement."

6. P30659, L20, I didn't find any data on the amount of adsorbed the oxalic acid on the particles. Please provide estimated coating or mass ratio of oxalic acid to inorganic or size distribution after coating. As it is described and showed in Fig.1, poly-dispersed particles were passing through the coating devise. Inorganic seeds with difference size would be expected to have different coating thickness which means that the reaction may produce different amount of oxalate salt. So, the composition of particles with different size can be different thus when you measure the CCN activity, you are looking at different particles at different sizes.

The measured volumetric growth factors (~20% for all salts), calculated from changes in geometric mean diameter, have been added to Table 4. The composition may indeed be different at different sizes. The linearity of sc vs. dp for the monovalent salts suggests the variation in composition with size does not seem to be significant enough to effect CCN measurements. The hygroscopicity of the monovalent salts does not approach that of oxalic acid for any of the salts, further supporting that the salts, at all sizes, are not dominated by oxalic acid. We do not expect markedly different deposition behavior between monovalent and divalent salts. The text was modified to address this

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issue: 30663/L4

"The CCN activity of the aerosol is defined by the minimum dry diameter,  $dp_{50}$ , at which 50% of the particles activate at a given sc.  $dp_{50}$  is determined by fitting a sigmoid curve to the measured ratio of CCN to CN concentrations as a function of dry particle diameter, accounting for multiply charged particles as in Moore et al. (2010)."

30667/L4: "These results, with the measured growth factors after OxA deposition, are listed in Table 4. Growth factors are calculated from particle geometric mean diameters. Some variation in composition (amount of OxA deposition) with size is expected. Three factors suggest that even small particles do not have excessive volumetric fractions of OxA: the linearity of the sc vs. dp plots for the monovalent salt particles the fact that their hygroscopicities are well below that of pure OxA, and the agreement between their calculated and measured values of  $\kappa$ . The measured values for  $dp_{50}$  will only be affected by changes in composition for particles with diameter near  $dp_{50}$  and above. Any size-dependent deposition should be biased towards smaller particles, due to larger surface area to volume ratios. "

7. P30662, L15. Please provide references.

Reference to Petters 2007 was added.

8. P30663, L17. Please provide references.

Reference to (Seinfeld and Pandis 2006) was added.

9. P30664, L13, Please include the densities in the tables.

Densities were added to Tables 2 and 3.

10. P30665, L6-7, this sentence is not clear.

The sentence was changed to read: "For the pure divalent salt particles, our experimental  $\kappa$  values agree closely with the  $\kappa_{\text{intr}}$  for the chloride hydrate salts rather than the pure salts."

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11. P30665, L13-15, the statement is not clear and should be explained in more details.

The sentence was changed to read: "For example, the  $dp_{50}$  for  $\text{CaCl}_2 + \text{OxA}$  at an  $sc$  of approx. 0.4 is roughly 30 nm below the linear trend of the  $\kappa$  values at high  $sc$ . This dependence on size, and hence surface-area:volume ratio, suggests that surface effects are at play. The process of CCN activation begins with water adsorption and is then governed by component volume fractions, so the surface-area:volume ratio of the particle, which is size-dependent, may be affecting particle hygroscopicities."

12, P30666, are these calculations referred to the data in Table 4? Why there is only one value for some systems, not a range?

These equations are used to calculate data in Table 4. The mixed salt systems were shown with a range of values because of the uncertainty of the exact amount of insoluble material formed from a mixture of divalent and monovalent salts, but for clarity, Table 4 was changed to show only the lower estimates of  $\kappa_{\text{calc}}$  for all particles. The text at 30667/L4 was changed to read: "The  $\kappa_{\text{calc}}$  data in Table 4 are calculated using Eqs. 8 and 9."

13, P30667, L4-6, I think the authors somehow misinterpreted the study by Laskin et al 2012.  $\text{Cl:Na}$  could be zero for some systems, for example, citric acid/NaCl after reaction.

$\text{Cl:Na}$  was above zero in Laskin et al. 2012 for all the di-acid particles, only citric acid, which is a tri-acid, actually showed  $\text{Cl:Na}$  ratios of zero. The text at P30667/L4 was changed to read: "The complete reaction is in fact not likely to occur, as the  $\text{Cl} : \text{Na}$  ratios for di-acid particles with initial 1 : 1 molar ratio of acid to salt observed by Laskin et al. (2012) never reached zero."

14. P30667, L11-27, the statements and conclusions are lack of supports. First, as mentioned above, you may look at particles with different compositions at different sizes, depending on the extent of the reactions and how much oxalate was formed.

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So the presented direct comparison of kappa values maybe not so straightforward. For example, the curves in Fig.3 for mixed particles. Second, the study by Sullivan et al. 2009 cited here didn't provide kappa values for M-Ox. Did you measure the CCN activity and calculate kappa values for the pure oxalate salt, e.g. Mg-Ox, Ca-Ox, and Zn-Ox? The values in Table 4 for mixed  $\text{MCl}_2 + \text{OxA}$  could be the values for fully reacted particle, i.e. only M-Ox left. This could be also the reason that the discrepancies between measured values and calculations based on Eqn. 8 and 9. Please also provide the uncertainties for all the  $\kappa$  mean in the tables.

First, while particle composition may not be perfectly uniform across particle sizes, the measured  $\kappa$  values would correspond to pure M-Ox particles, and it is certain that the particles do not reach this composition. This Sullivan 2009 reference should be Sullivan 2009a, which does include the  $\kappa$  values for M-Ox materials. We did not independently measure the pure M-Ox CCN activities. Based on the linearity of  $sc$  vs  $dp$  for the monovalent salt particles, the fact that their hygroscopicities are well below that of pure OxA, and the agreement between their calculated and measured values of  $\kappa$ , we are confident that the particles do not have enough OxA deposition to become pure M-Ox particles. Uncertainties for  $\kappa$  were added.

15. P30668, L25-28, this sentence is not clear. What do you mean "seem to behave as if made from pure CaOx"?

These sentences were changed to read: "The NaOx particles were generated by atomizing an aqueous solution of sodium oxalate. The CaOx particles, made by depositing OxA on  $\text{CaCl}_2$ , volatilize as if made from pure CaOx."

16. P30669, L1, what do you mean " clear increase in signal"? I suggest the authors use quantitative value to define the onset temperature, for example a ratio of signals of 1.1 to that at 25 degree.

This value of 1.1 is indeed useful in defining an onset temperature. The figures were changed to reflect this.

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Table 1 and Figure 5 were updated and the text was changed to read: "A quantitative estimate of the onset evaporation temperature was defined as: signal/signal25C <= 1.1. The resulting onset temperatures were: NaOx(1): 115 C, NaOx(2): 75 C, CaOx: 115 C"

17. Table 1, for the enthalpy calculations, why the last 4 or 3 data points are used? It is clear that it is not linear as shown in Fig. 5 from 75 degree.

The numbers in parentheses indicate the number of data points used. We selected data in the temperature regions where the data is linear. The caption for Fig. 5 was update to indicate this: "Onset temperatures for evaporation and  $\Delta H_{vap}$  of oxalate at different temperature ranges; The number of data points used in the linear fits are in parentheses."

18. Table 2, what is Na2Ox as compared to NaOx in Table 1? Please provide the reference for kappa for NaCl.

In fact these are these should both read Na2Ox, and all instances in the paper have been changed to Na2Ox. These were data from separate experiments, rather than presenting them separately, these values were averaged, and the tables and figures were updated. The NaCl value was from Sullivan 2009a.

19. Fig.1 Caption, this is only for CCN measurements.

The caption was changed to read: "Figure 1. A schematic diagram of the experimental setup for CCN measurements."

20. Fig.2 I suggest to separate the data and plot them in two panels for readability.

While some of the data does overlap, we feel that it is best for comparison to show all the monovalent salt data together.

21. Fig.5, why the normalized signals are different for two independent experiments? Did you have duplicated experiments for CaOx? Any experiments for the mixed parti-

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cles shown in Table 4?

The obtained data for individual NaOx experiments do have some differences – NaOx(1) was observed slightly less volatile than NaOx(2) at higher T. The probable reasons for the observed differences are 1) the signals presented in Fig. 5 are combinations of two traced signals (formic acid + oxalic acid) and 2) at higher temperatures the determination of the actual heating temperature is harder (estimated based on lower T data). Therefore we feel that it is better to present the NaOx data as an average of the two experiments (see figures above, answer to q.16). All the experiment done with the CIMS are presented in Table 1. No duplicated experiments for CaOx were performed. However, as the main goal of the CIMS analysis was to qualitatively compare the evaporation of OxA, NaOx and CaOx aerosol, further experiments were not necessary. Volatility measurements were not made for the mixed salts in Table 4.

Technical comments: 1. P30655, L22, missing “.” for the end of sentence. “.” Was added

2. P30664, L5. Delete “.” “.” was deleted.

3. P30664, L23. Should be “Fig.2” Figure reference was corrected.

4. P30668, L3, correct the reference, should be 2003? Reference was corrected to 2003.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 30653, 2013.

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