

Interactive comment on “Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implication for seasonal formation mechanism of Secondary Organic Aerosol (SOA)” by Chunlei Cheng et al.

Anonymous Referee #3

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The authors present results measurements of ambient aerosol during two periods (summer vs winter) in the Pearl River Delta. Most of the discussion focusses on oxalate loadings and its mixing state. Based on correlations with metal-containing particles, the authors conclude that iron has an important role in OH formation and therefore in oxalate formation. While generally the manuscript is well written, the discussion of the chemical mechanism is very weak and hand waving. Without running a detailed multiphase model, such conclusions cannot be drawn with certainty. Therefore, I suggest removing the discussion of the role of iron and the chemical mechanism in general. After my additional comments below are addressed, the manuscript may be suitable

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for publication.

Major comments

1) The suggested chemical mechanism is oversimplified and contains several misconceptions and/or omissions:

a) Generally, it is assumed that direct OH uptake is the main source of OH in the aqueous phase [e.g., Ervens et al., 2003; Herrmann, 2003; Tilgner et al., 2013]. Therefore higher OH(gas) concentration will lead to higher OH concentration in the aqueous phase. Higher OH(aq) concentration will also lead to more oxidation of oxalate and therefore less SOA.

b) Higher iron concentration might lead to more OH. However, more importantly is the effect of the loss of oxalate due to the photolysis of the iron-oxalato complex. While this reaction is mentioned in the manuscript, its predominating role in oxalate loss [Sorooshian et al., 2013] is not discussed in a balanced way.

c) At low pH, it can be expected that reaction rates are lower since in general the undissociated acids (glyoxylic, glycolic) react more slowly than their dissociated counterparts. Oxalate has a very low pKa (1.23) so that even at low pH a substantial fraction is still present as oxalate. Could changes in pH and therefore reaction rates explain some of the temporal trends?

d) At very low pH (< 1.23), it is expected that oxalic acid is present in undissociated form and therefore not able to make salts or complexes that ‘trap’ it in the particle phase. This fact contradicts the trend of increased oxalate concentrations at low pH. This should be discussed.

e) The proposed mechanism is by no means new or detailed (l. 360). It does not include any sinks of oxalate, nor complex formation. It is one possible formation mechanism of oxalic acid from glyoxal. The generalization to dicarbonyls and aldehydes is not correct since only small compounds (C2) will follow the suggested reaction path-

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ways.

2) The number fraction of oxalate containing particles seems very low. Is this comparable to other measurements? What was the mass fraction of oxalate (a) in the particles and (b) related to the total aerosol loading?

3) Was all iron in the particles in form of soluble iron, i.e. available for reaction?

4) Oxalate and the other DCAs usually represent only a very small fraction of the total organic aerosol mass. Therefore the title is misleading as it talks about SOA in general.

5) It seems based on Figure S5, that RH was always < 100% (except a very brief period). Therefore, the discussed aqueous chemistry will have to take place in aqueous aerosol. There are many studies that have discussed different reaction pathways in aqueous aerosol vs cloud [e.g., Tan et al., 2009; Lim et al., 2010] with less efficient oxalate formation in the former. In addition, it seems likely that iron ions might be less dissolved in the rather highly concentrated aqueous aerosol solutions. All discussion is about chemistry as it happens in cloud droplets. These two regimes should be differentiated.

6) While briefly discussed, it is not clear to what extent different air masses cause different oxalate levels. How much of the measured oxalate is background material? Did other meteorological conditions affect the concentrations such as changes in boundary layer? 7) I am not sure what Figure S6 is really showing. Does it show a correlation of organosulfur particles and oxalate or does it simply show that more particles cause higher concentrations of 'everything'? How about the mixing state of organosulfur compounds and oxalic acid particles? The fact that they are in the same particle class, does not necessarily mean that they are internally mixed and therefore their formation pathways are related.

Minor comments

I. 83: Oxalic acid does not have a low vapor pressure. Its presence in ambient particles

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is due to salt and/or complex formation (cf also comment 1d).

I. 119/120: There are several studies that have shown good agreement between predicted and measured oxalate levels [e.g., Wonaschuetz et al., 2012]

I. 121 and 122: These sentences are repetitive.

I. 240: The study by Sorooshian et al. focused mostly on the destruction of oxalate in the presence of iron.

I. 264, and other places: 'Mixing ratio' usually refers to the ratio of molecules of one type to the total number of molecules (e.g. ppb = 1 in 10^9 molecules). The authors should change their wording as I assume here 'mixing ratio' is used in the meaning of 'number of particles that are internally mixed'.

I. 289: Are all particles larger in winter than in summer or only those that contain oxalic acid?

I. 296-300: The mentioning of malonic acid is distracting here and does not lead to additional evidence or insights.

I. 316: It is true that OH (like all other radicals) has a relatively short life time in the gas phase. However, the partitioning to the aqueous phase is limited due to its even shorter lifetime in the aqueous phase. Its solubility and the quick consumption in the aqueous phase leads to the limitation.

I. 320: Fenton reaction is not a photolysis. In I. 337, it is stated correctly that Fenton reactions do not need necessarily light.

I. 344: What are the influences of pH(is) from RH and inorganic ions? Figure S5 does not include any discussion.

I. 354: Not clear why 'on the other hand' as the following sentence is just another example of oxalate degradation.

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l. 439/440: This is a very strong and vague statement. How do the results of the current study help improving climate models and air pollution mitigation strategies?

Technical comments

l. 102: replace 'suggest' by 'suggested'

l. 181: replace 'introducing' by 'introduced'

l. 240: replace 'possibly' by 'possible'

l. 273: remove 'that'

References

Ervens, B., C. George, J. E. Williams, G. V. Buxton, G. A. Salmon, M. Bydder, F. Wilkinson, F. Dentener, P. Mirabel, R. Wolke, and H. Herrmann (2003), CAPRAM2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, *J. Geophys. Res.*, 108(D14), 4426, doi: 10.1029/2002JD002202.

Herrmann, H. (2003), Kinetics of aqueous phase reactions relevant for atmospheric chemistry, *Chem. Rev.*, 103(12), 4691-4716.

Lim, Y. B., Y. Tan, M. J. Perri, S. P. Seitzinger, and B. J. Turpin (2010), Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10(21), 10521-10539.

Sorooshian, A., Z. Wang, M. M. Coggon, H. H. Jonsson, and B. Ervens (2013), Observations of Sharp Oxalate Reductions in Stratocumulus Clouds at Variable Altitudes: Organic Acid and Metal Measurements During the 2011 E-PEACE Campaign, *Environ. Sci. Technol.*, 47(14), 7747-7756, 10.1021/es4012383.

Tan, Y., M. J. Perri, S. P. Seitzinger, and B. J. Turpin (2009), Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal-OH Radical Oxidation and Implications for Secondary Organic Aerosol, *Environ. Sci. Technol.*, 43(21), 8105-8112,

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10.1021/es901742f.

Tilgner, A., P. Bräuer, R. Wolke, and H. Herrmann (2013), Modelling multiphase chemistry in deliquescent aerosols and clouds using CAPRAM3.0i, *J. Atmos. Chem.*, 70(3), 221-256, 10.1007/s10874-013-9267-4.

Wonaschuetz, A., A. Sorooshian, B. Ervens, P. Y. Chuang, G. Feingold, S. M. Murphy, J. de Gouw, C. Warneke, and H. H. Jonsson (2012), Aerosol and gas re-distribution by shallow cumulus clouds: An investigation using airborne measurements, *J. Geophys. Res. - Atmos.*, 117(D17), D17202, 10.1029/2012jd018089.

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