

Interactive comment on “Fog scavenging of organic and inorganic aerosol in the Po Valley” by S. Gilardoni et al.

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Received and published: 27 May 2014

The authors would like to thank the referees and the editor for their useful and valuable comments. We have addressed all the comments as exhaustively as we could, and modified the paper accordingly.

Answers to referee 2

This is a solid piece of work that is appropriate for publication in ACP. I only have a few minor questions/comments for the consideration of the authors.

1) The discussion of the dependence of scavenging efficiency of compositions starts with their solubilities and then later drifts to kappa values. It may be just more consistent

C2781

to work with kappa values throughout in the discussions of nucleation scavenging.

Paragraph at page 14 line 16 is modified as follow.

"The variability of scavenging efficiency among the different chemical species can be explained by their hygroscopicity (κ). Nitrate and ammonium showed the highest mass scavenging efficiencies, on average 71% and 68 %, respectively. Black carbon, the most hydrophobic component, was the species least efficiently scavenged (39% on average). OA showed the largest variability, with η ranging between 20% and 60%, in agreement with previous observations (Collett et al., 2008)".

Water solubility at page 15 line 14 is replaced by hygroscopicity.

Paragraph at page 17 line 11 is modified as follow:

"While ammonium nitrate particles are hydrophylic, organic particulate matter is expected to be more hydrophobic (Petters and Kreidenweis, 2008)".

The term solubility at page 19 line 24 and line 28 is replaced by hygroscopicity.

The term soluble at page 19 line 25 is replaced by hygroscopic.

Sentence at page 20 line 4 is modified as follow:

"more likely efficiency of mixing with highly hygroscopic species, such as ammonium nitrate"

2) Page 15: "The results of the present study confirm those observations and the similarity of nitrate and organic oxygen scavenging suggests that oxygenated organic aerosol could be a proxy for water soluble OA." This statement is a bit strong. It needs a stronger quantitative correlation to say this. In fact, it is not consistent with the tone of the FTIR results on the role of different functional groups on hygroscopicity later.

We agree with the referee about the strength of the sentence and the inconsistency with the tone of the following discussions. The sentence is removed from the manuscript.

C2782

3) In section 4.2, is the percentage of mixing estimated from the size distribution curves? If so, this can be made more explicit.

The mixing ratio was estimated based on the comparison of size segregated scavenging efficiency curves. Sentence at page 18 line 19 is modified as follow:

"Based on this conclusion, and assuming that all the scavenged organic aerosol was internally mixed with the scavenged nitrate, we can estimate the organic mass fraction internally mixed with nitrate to be equal to the organic scavenging efficiency normalized over nitrate scavenging efficiency in each size bin. According to this, 50 to 90% of organic mass resulted internally mixed with nitrate in the range 150–700 nm (D_{va})".

4) The discussion of internal mixing of nitrate and organic and similar scavenging efficiency is interesting. It is said that 90% of organics are internally mixed with nitrate. What it suggests is that it does not matter what chemistry the organics have, as long as they are internally mixed with inorganics, they will be scavenged, even at very low SS. The composition really does not make any difference. On the other hand, the discussion of FTIR results seems to give an opposite argument that functional group is related to OA scavenging efficiency. Some clarifications are needed.

We agree with the referee that a clarification is needed to introduce the discussion at the end of paragraph 4.2. The following paragraph is added at page 18 line 24.

"The correlation of size segregated scavenging efficiency of nitrate and organics suggests that OA scavenging is controlled mainly by mixing with more hydrophobic species, at least for larger particles (about 350 nm D_{va}). This result does not exclude that OA scavenging variability could be affected by OA properties. With this in mind, the OA composition was further investigated by FTIR spectroscopy"

5) Can closure analysis of scavenging efficiency be done by size segregated composition measurements and kappa estimates?

The following subsection is added before conclusions.

C2783

"Scavenging closure.

We verified the closure of nitrate and organic scavenging efficiency during radiation fog using a simple model based on size segregated chemical composition. For each fog event the efficiency of nitrate scavenging was modeled according to the following equation:

$$\eta_{NO_3 mod} = \frac{\sum_i [NO_3]_i \eta_i \Delta \log D_{va_i} / lens_i}{\sum_i [NO_3]_i \Delta \log D_{va_i} / lens_i}$$

where $[NO_3]_i$ is the concentration of nitrate before fog formation in size bin i and $lens_i$ is the transmission efficiency of the aerodynamic lens of the HR-TOF-AMS for size bin i . Values of nitrate concentration below detection limit were replaced by half of the detection limit. η_i is the scavenging efficiency of nitrate in size bin i and it is calculated based on kappa, estimated from particle chemical composition according to Eq. (3). The dependency of η_i on kappa varies with particle size (D_{va}). The following equations were used:

$$\begin{aligned} \eta_i &= 0, \text{ if } D_{va} < 166 \text{ nm} \\ \eta_i &= 3.3 * k - 0.7, \text{ if } 166 \text{ nm} \leq D_{va} < 240 \text{ nm} \\ \eta_i &= 2.1 * k - 0.2, \text{ if } 240 \text{ nm} \leq D_{va} < 360 \text{ nm} \\ \eta_i &= 0.6 * k + 0.6, \text{ if } 360 \text{ nm} \leq D_{va} < 700 \text{ nm} \\ \eta_i &= 1, \text{ if } D_{va} \geq 700 \text{ nm} \end{aligned}$$

On average the model overestimates the observations by 3% (absolute value). Only in one case the model underpredicts the measured scavenging by 5% (absolute value).

Then, we modeled organic scavenging based on the simulated nitrate size segregated scavenging efficiency and the average mixing with nitrate.

$$\eta_{Org mod} = \frac{\sum_i [Org]_i \eta_i Mix \Delta \log D_{va_i} / lens_i}{\sum_i [Org]_i \Delta \log D_{va_i} / lens_i}$$

$[Org]_i$ is the concentration of organic in size bin i before fog begins, η_i is the scavenging efficiency of nitrate calculated with Eq. (5), $lens_i$ is the transmission efficiency of the

C2784

aerodynamic lens of the HR-TOF-AMS, and Mix is the fraction of organic internally mixed with nitrate. For each fog event, Mix was estimated as the average ratio between organic and nitrate size segregated scavenging efficiency. The difference between model and observation varies between -11% and +8% (absolute values). The slightly larger discrepancy of OA scavenging is likely due to the simplified description of mixing with nitrate and the fact that the model does not include the effect of OA properties on its scavenging, such as hygroscopicity."

6) Page 20: I am not sure if these functional group analyses of oxygenated carbon are sufficient to reflect hygroscopicity. For example, the length of carbon chain was not addressed at all. It can change hygroscopicity of the alcohols or acids. Hence, by focusing the oxygenated functional groups alone, it is not surprising to find that they do not necessarily explain the variability of the organic oxygen scavenging.

Paragraph at page 20 line 5 was modified in order to clarify the limit of the discussion on oxygenated functional groups.

"This conclusion is further supported by the analysis of the main oxygenated organic functional groups. Table 3 reports the molar ratio of the carboxylic (COOH) to the hydroxyl (OH) group. For a molecule with a defined number of carbon atoms, the COOH and OH groups are expected to affect its solubility in different ways. In fact, the COOH group has a dipole moment larger than the one of an OH group, thus the COOH group would increase its solubility more than a OH group. The fog events of 28, 29, and 30 November showed a very similar COOH to OH ratio, indicating that the relative contribution of oxygenated functional groups was similar. Nevertheless, organic oxygen scavenging efficiency varied from 57% to 75%. The limited number of available measurements and the lack of information on the average OA molecular weight do not allow us to understand the effect of the chemical nature of organic oxygen on the variability of organic scavenging during the Po Valley experiment."

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 4787, 2014.

C2785