

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. For clarity, comments from the referees are reported in blue and answers from the authors are in black.

Answers to referee #1

The manuscript by Gilardoni et al. presented a detailed characterization of the scavenging efficiencies of aerosol species by fogs in the Po Valley. While the bulk scavenging efficiencies have been extensively studied previously, the size-resolved scavenging efficiencies for nitrate and organics are unique for this work. Also, the scavenging efficiencies were successfully related to hygroscopicity (k) and those of organic aerosols to their oxidation states. The results are very clear to me and the manuscript is well written. I recommend for publication for ACP.

Major comments

1. Aqueous-phase chemistry has been found to play important roles in the formation of sulfate and also some secondary organic aerosols. How important of aqueous-phase production compared to fog scavenging during the fog periods with high liquid water content? For example, is this the reason leading to the lower scavenging efficiency of sulfate (61%) than nitrate (70%)? Is the author able to show the size-resolved scavenging efficiency for sulfate although it contributed a small fraction of the total PM1 mass?

The authors agree with the referee that aqueous phase chemistry plays a major role in the formation of sulfate, and this formation mechanisms could explain the lower scavenging efficiency found for sulfate compared to nitrate during 7 out of 14 fog events. To verify the relative importance of aqueous-phase production versus scavenging, we analyzed the size segregated scavenging efficiency of sulfate. If aqueous-phase production of sulfate was relevant, we could expect a decrease in scavenging efficiency towards larger particles (cloud processing mode). If scavenging was more important, scavenging efficiency would increase in larger particles and tend asymptotically to the unity. Unfortunately, the small concentration of sulfate observed during the experiment makes it difficult to verify this hypothesis, since sulfate concentration above 500-600 nm (D_{va}) was below the AMS size distribution detection limit both before and after fog formation for all the events. The attached figure shows sulfate size segregated scavenging efficiency when detectable (fig. 1).

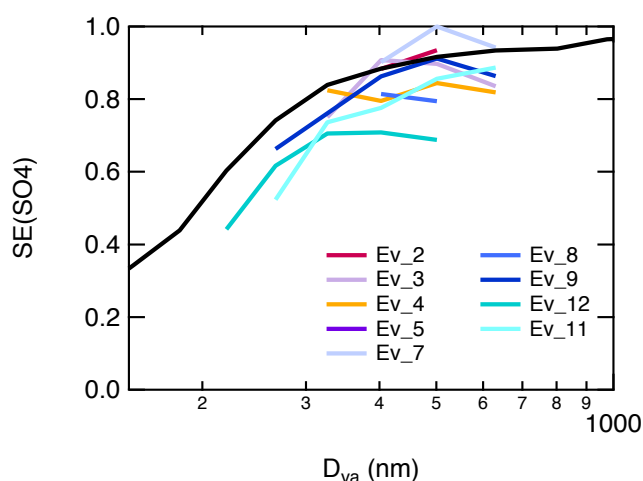


Fig 1. Mass scavenging efficiency size distribution of sulfate for each fog event. D_{va} is vacuum aerodynamic diameter.

The following sentence is added at page 14 line 26:

"The scavenging efficiency of sulfate was slightly lower than the one of nitrate (61%). The difference between sulfate and nitrate scavenging observed during events 5,7,9,10,11,12,and 13 could be explained by fog processing, i.e., in situ formation of sulfate through oxidation of SO_2 in the aqueous phase. Fog processing would contribute to sulfate formation, compensating in part the removal associated with scavenging. Fog processing plays a major role in secondary organic and inorganic aerosol formation, and its effects on aerosol composition and properties need further investigation."

2. How did the meteorological conditions and local sources affect the uncertainties of scavenging efficiencies? For example, were there any changes of planetary boundary layer height, wind direction, and also local source emissions during the formation of fog?

We acknowledge that the variability of fog scavenging observed among the 14 fog events is not discussed with respect to meteorological conditions. For this reason, the following sentence is added at page 16 line 24:

"Fog events characterized by intrusion were also characterized by lower scavenging efficiencies. During these events, the prevailing wind direction was from north, north-west, and west, where major traffic roads and urban areas are located. It is likely that transport of pollutants to the measurement site was responsible for the apparent lower scavenging efficiency. Removing these intrusion events from the list of investigated fog events reduces the variability of observed scavenging. The standard deviation of the average scavenging efficiency of nitrate, for example, goes from 18% when all events are taken into account, to 6% when only radiation fog events are considered. The standard deviation of organic average scavenging efficiency is halved (from 22% to 11%)".

Sentence at page 16 line 24 was modified as follow:

"To study the effect of chemical composition and particle size on scavenging, we investigated scavenging efficiency size distribution for the main submicron chemical components (nitrate, as representative of inorganic aerosol, and organics) only during radiation fog events"

The diurnal time trend of mixing layer height was modeled by Calmet (Deserti et al., International Journal of Environment and pollution, 571-582. 2001) based on radiosonde measurements performed by ARPA Emilia Romagna. All the events classified as radiation fog events begin around 18:00 LT, when the nocturnal boundary layer develops, and the concentration of aerosol and gas species is expected to increase. As a consequence, the variation of boundary layer height could lead to an underestimation of scavenging efficiency. Nevertheless, the almost complete scavenging of particles larger than 700 nm (Dm) and the size segregated curves of nitrate that tend asymptotically to the unity exclude a significant effect of boundary layer dynamics on scavenging efficiency. The almost complete scavenging of nitrate in larger particles also suggests that, if local nitrate sources are present, they are not leading to an underestimation of nitrate scavenging.

In order to estimate the effect of local sources of organic aerosol on its scavenging efficiency, we added the following paragraph at the end of the result section (page 16):

"Local emissions that add to or subtract from the pre-existing aerosol in concomitance with the beginning of a fog formation event could lead to the underestimation or overestimation of fog scavenging, respectively. For the OA, sources include a regional component (LV-OOA), a local component (BBOA), and a third component (HOA) that has both a local and a regional source. The concentration of HOA and BBOA factors is expected to increase during the evening hours, as confirmed by diurnal time trend observed when fog was not present (22 and 23 of November) and consistent with results reported by Saarikoski et al. (2012) for the same season. These local sources might lead to an underestimation of organic scavenging efficiency during evening fogs. Assuming that the 22 and 23 of November could be used as reference period to identify the diurnal behavior of HOA and BBOA, we can use these days to obtain a rough estimate of the scavenging underestimation. The diurnal trend of HOA and BBOA factors for the reference period is reported in Fig 5S. The trend of HOA between 16:00 and 19:00 LT in days with no fog shows an increase of about $0.4 \mu\text{g m}^{-3} \text{h}^{-1}$, while during days with fog the increase is about $0.1 \mu\text{g m}^{-3} \text{h}^{-1}$. The difference is due to fog scavenging, which corresponds to a removal rate of $0.3 \mu\text{g m}^{-3} \text{h}^{-1}$. Similarly, the average diurnal trend suggests that the removal rate of BBOA factor is about $1 \mu\text{g m}^{-3} \text{h}^{-1}$. Considering that the average organic concentration after fog formation in the evening events is about $7 \mu\text{g m}^{-3}$ and that the integration time used to calculate scavenging efficiency is 2 hours, the uncertainty on organic concentration associated with neglecting HOA and BBOA local sources would range between 8% (during the first period when BBOA contribution was negligible) and 36% (during the second period when BBOA mass fraction was more significant). Taking into account this uncertainty, the average scavenging efficiency of organics would increase from 50% to 58%,

which is within the variability of the data".

Supplement material was modified accordingly. The diurnal time trend of the three factors during the reference period is reported in Figure S5 and the following paragraph is added:

"Figure S5 shows the diurnal trend of the three factors averaged over the entire campaign and over the two days that were not characterized by fog events, here taken as reference period. The presence of fog contributes to the decrease of absolute maxima of BBOA and HOA concentrations in the evenings and the nights".

The sentence on page 16 line 7 was modified as follow:

".the intrusion of fresh air masses and the contribution of aerosol local sources would change the composition of the aerosol, making nucleation scavenging calculation inaccurate".

Technical corrections:

1. The Pearson r and correlation coefficient (r^2) were both used in the text, better use one parameter.

The coefficients r and r^2 are used in the manuscript with two different meanings. The Pearson coefficient r is used to indicate the goodness of the correlations between variables, while the coefficient r^2 is used to quantify the fraction of variability explained by a specific variable.

2. Low volatility oxygenated OA is generally abbreviated as LV-OOA rather than LVOOA.

3. P 4798, line 15, LVOAA to LV-OOA.

LVOOA was replaced by LV-OOA throughout the manuscript. LV-OAA was corrected.

4. P 4799, line 7, consistently to consistent

Consistently was replaced by consistent

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 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.

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 (Dva)".

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 Dva). 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.

"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:

$$\eta\text{-NO}_3^-_{\text{mod}} = (\sum_i [\text{NO}_3^-]_i \eta_i \Delta \log D p_i / \text{lens}_i) / (\sum_i [\text{NO}_3^-]_i \Delta \log D p_i / \text{lens}_i)$$

where $[\text{NO}_3^-]_i$ 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 was the scavenging efficiency of nitrate in size bin i and calculated based on κ , estimated from particle chemical composition according to equation 3. The dependency of η_i on κ varies with particle size (D_{va}). The following equations were used:

if $D_{va} < 166$ nm	$\eta = 0$
if $166 \text{ nm} \leq D_{va} < 240$ nm	$\eta = 3.3 * \kappa - 0.7$
if $240 \text{ nm} \leq D_{va} < 360$ nm	$\eta = 2.1 * \kappa - 0.2$
if $360 \text{ nm} \leq D_{va} < 750$ nm	$\eta = 0.6 * \kappa + 0.6$
if $D_{va} \geq 700$ nm	$\eta = 1$

On average the model overestimates the observations by 3%; 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.

$$\eta\text{-Org}_{\text{mod}} = (\sum_i [\text{Org}]_i \eta_i \text{ Mix } \Delta \log D p_i / \text{lens}_i) / (\sum_i [\text{Org}]_i \Delta \log D p_i / \text{lens}_i)$$

$[\text{Org}]_i$ is the concentration of organic in size bin i before fog begins, η_i is the reconstructed scavenging efficiency of nitrate, lens_i is the transmission efficiency of the 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 efficiencies. 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 ignores the effect of OA chemical 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."

Notes to the Editor

1. In the abstract, ARPA_ER has been replaced by ARPA-Emilia Romagna.
2. Figure 6 reports the time trend SSA calculated from absorption and total extinction. Since the trend shows some gaps corresponding to the periods when absorption data were not available, the SSA from scattering and total extinction has been added to the figure. Text has been modified as follow

Page 10 line 4

$(bx)_{573} = (bx)_\lambda (\lambda/573)^\alpha$ where bx is the extinction or the scattering coefficient measured at wavelength λ . α

is the angstrom exponent...

Page 10 line 8

$$\text{SSA} = (b_{\text{ext}} - b_{\text{abs}}) / b_{\text{ext}} \text{ or } \text{SSA} = b_{\text{sc}} / b_{\text{ext}}$$

Page 15 line 24

Figure 6 shows the trend of the single scattering albedo (SSA) obtained from combining CAPS extinction with PSAP absorption coefficients, and CAPS extinction with nephelometer scattering coefficients, according to equation 1. A good agreement between the two SSA trends is observed, with an average error below 2%. The discrepancy observed between 21 and 23 of November is likely due to the uncertainty of b_{abs} , that during these days was often below 0.05 Mm^{-1} .

Caption of Figure 6 is modified as follow:

Time trend of SSA calculated from absorption and total extinction coefficients (black) and from scattering and total extinction coefficients (red). Light blue shadowed areas indicate fog periods.

3. The unit of LWC reported in figure 2 has been corrected as g m^{-3} instead of g l^{-1} . Text is modified accordingly.

4. Although the discussion of the data in table 3 is based on carbon oxidation state (OS), Table 3 reports only the oxidation level, or oxygen-to-carbon ratio (O/C). For this reason discussion at page 21 line 18 is modified as follow:

“The scavenging efficiency of organic aerosol was slightly correlated with the average O/C ratio obtained from the FTIR data. Samples characterized by the highest O/C ratio were also associated with the highest OA scavenging (18 and 28 November). The higher scavenging of more oxygenated aerosol is also confirmed by higher scavenging efficiency of the organic oxygen compared to the total OA (Table 2)”.