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Comment

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

S. Gilardoni et al.

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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 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

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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 (Dva) 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).

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 though oxidation of SO₂ in the aque-

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ous 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 (Kaul et al., 2011, Sun et al., 2013), 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"

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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

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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 (Fig. 2 here attached) and the following paragraph is added:

"Figure 5S 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 vari-

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ables, 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

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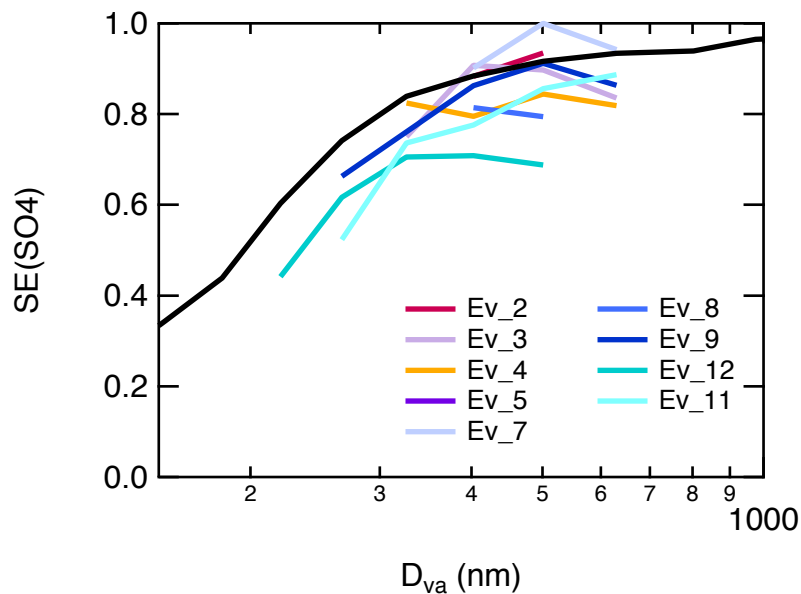
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Fig. 1. Mass scavenging efficiency size distribution of sulfate for each fog event. D_{va} is vacuum aerodynamic diameter.

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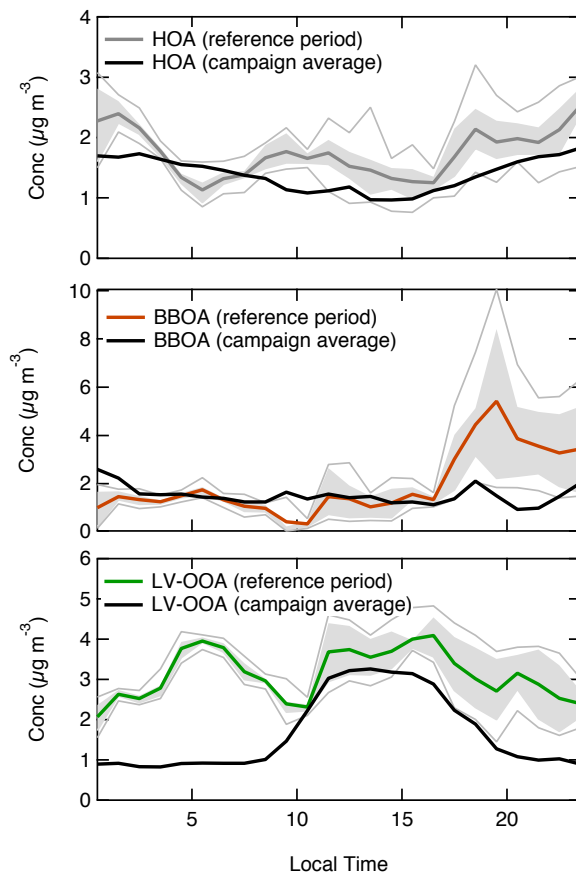


Fig. 2. Figure 5S. Comparison between diurnal time trend of HOA, BBOA, and LV-OOA during reference period characterized by the absence of fog events (22 and 23 of November) and over the entire campaign.

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