

## **Reviewer 2**

**This manuscript represents a thorough analysis of size-resolved aerosol composition measurements from two sites in the Po Valley during a summer campaign. In the introduction, the authors mention that the two site approach was intended to be used so that the rural site could serve as the ‘background’ for the urban measurements. In fact, the authors demonstrate that the higher relative humidity during the night at the rural site leads to substantially higher ammonium nitrate (and WSOC) at this rural site. In general, I thought the paper was clearly written, but it would be useful for the others to revisit this ‘Lenschow perspective’ in the conclusions and comment on whether a rural site can really be interpreted as the background for a nearby urban site.**

We have added this paragraph to the Discussion and Conclusions to clarify the implications of this two-site experiment:

“In conclusion, the characteristics of the size-segregated aerosol compositions and its variability at a rural site and at a urban background site in the Po Valley could be explained by a limited number of factors reflecting main physico-chemical processes and/or transport patterns in the atmosphere. For accumulation mode particles in particular, our analysis points to two main processes: “(1) The *photochemical SIA and SOA* which occur at comparable concentrations between BO and SPC and are particularly evident in daytime hours when the lower atmosphere is well mixed, and indicating that a major fraction of background submicron aerosol concentrations in the Po Valley actually originates from regional-scale sources, which can extend over vast continental areas (see also Fig. S12 in Decesari et al., Atmos. Chem. Phys., 14, 12109-12132, 2014). This has implications for air quality mitigation, because this photochemical component is expected to show little sensitivity to local-scale (city-level) regulations. (2) *Nocturnal SIA and SOA* whose formation is enhanced in the shallow, cool and humid boundary layer and mediated by the presence of aerosol liquid water. Such component of the rural background aerosol appears more volatile (hence labile) and more heterogeneously distributed across the Po Valley, with the inner part (where most agricultural activity reside) acting as a source region respect to its southern periphery (more urbanized). The rural background concentration level is therefore variable, somewhat “tilted” horizontally across the Valley, at least for half of the day. These results represent an example of a limitation to the classical Lenschow model.”

**I also include some minor questions and suggestions:**

**Page 5, Line 9 – ‘which did not justify the presence of ALW on particles’ should be reworded to ‘which prevented accurate calculation of ALW on particles’**

Done

**Section 2.3 – Can the authors confirm whether inorganic carbonate salts have the ability to contribute to the WSOC reported by their measurement protocol? If not, in which category would the mineral dust carbonate be counted?**

When measuring TC on liquid samples (water aerosol extracts in this case) the instrument performs two distinct analyses on each sample: total carbon (TC) is measured by combustion at 680°C in the presence of a catalyst to become CO<sub>2</sub>, which is measured by a non-dispersive infrared gas analyser (NDIR); then inorganic carbon (IC) is measured by introducing another aliquot in a reaction vessel where, after acidification, IC is decomposed to CO<sub>2</sub>, similarly quantified by NDIR. The organic fraction (WSOC) is obtained

by subtracting IC from TC. it is worth specifying that in the water soluble fraction of aerosol the contribution of inorganic carbon was most of times under detection limit for Po Valley aerosol samples.

This information has been added in Section 2.3.

#### **Section 2.4 – Which site was used as the origin of the back trajectories?**

The used trajectories have been calculated for SPC. Based on the horizontal resolution of the GDAS meteorological data used in the calculation by the HYSPLIT model, i.e.  $1^\circ$ , which corresponds to  $\sim 100 \text{ km} \times 100 \text{ km}$ . The SPC trajectories can be considered valid for BO most of the time (as BO is only 30 km distant from SPC), but SPC, being located on a terrain with a simple orography, is probably an easier “target” for back-trajectory analysis.

**Page 11, Lines 25-30 – The moderately good correlation coefficient of 0.7 between WSOC and sulfate could be due to shared photochemical sources, but it may have other origins as well. Given that the values for each constituent range from 0.2 – 2, and there probably isn’t a factor of ten variability between photon flux between days, there’s likely at least one other factor driving the shared variability.**

This is probably due to the fact that sulfate and at least a fraction of WSOC are stable photochemical products (at least as WSOC carbon mass, not necessarily molecular composition). Their concentration will therefore depend on a multi-day air mass history and, since back-trajectories analysis shows that air masses were very diverse during the experiment (Fig. 2), this could be the reason for the order of magnitude of variation in concentrations. The regional-scale nature of photochemical SIA and SOA was better clarified in the text.

**Section 3.5 – The numbering of the rotated components doesn’t make sense to the reader. Also, the last three components that are discussed are not identified by the numbering system used in Table 2.**

In order to make the PCA results easier to read we changed the numbering of the rotated components for both sites in Tab. 2, just ordering them by decreasing values of explained variance. The numbers on the text have been changed accordingly.

**Page14, Lines35-38–Could the higher nighttime droplet mode sulfate measurements at SPC be the results of more cloud processing of SO<sub>2</sub> as a result of higher RH?**

During all the campaign the sky was generally cloud free, with the exception of the period preceding the days 5-6 July, when clouds developed west of the sites and some showers occurred in the Northern part of Italy, though only scattered clouds were present at the two sites. Cloud processing of SO<sub>2</sub> can be hypothesized only for this second stagnant period.

**I suggest adding a scale bar to Figure 1.**

Done

**Figure 7 – it doesn’t really make sense to have negative ALWC values. I would recommend using the boxes to show the interquartile range, or the 10th and 90 percentiles, rather than +/- the standard deviation.**

The ALWC plots for both sites have been changed into boxplots showing the interquartile range.

**Figure 8, panel a – it would be useful to have the y-axis of this figure on a log scale as well**

Done