Reply (in green) to REFEREE 2

Decesari et al. present a very interesting and novel analysis of Reactive Oxygen Species (ROS), including examinations of ROS in aerosol and fog and the effects of fog scavenging and chemistry on aerosol ROS. The design of the experiment, which takes advantage of differential fog scavenging of different aerosol ROS components (e.g., metals vs. WOC), is particularly clever. The manuscript is well written, concise and even spare in its style, effectively conveying a lot of information in a compact form.

Reply: we thank the Referee for her/his comments, which turn helpful in clarifying specific points of the manuscript.

I have a few, mostly minor, comments that should be addressed:

1. In performing mass balances of ROS and other components across aerosol and fog over time, the authors are assuming that there are no significant changes due to factors such as changes in boundary layer depth and fog drop deposition. Nocturnal cooling of the top of a fog layer typically leads to entrainment of air from above the boundary layer and associated growth in boundary layer depth. The entrained air is likely to have very different composition than the air originally in the boundary layer. This entrainment of air of differing composition can alter the mass balance. Likewise, significant deposition of fog water over the course of an episode can substantially cleanse the boundary layer of scavenged particles, again altering the mass balance. These factors need to be clearly outlined as sources of possible error in the mass balance analysis that is central to the paper.

Reply: The Referee is right. Nocturnal cooling at top of the fog layer makes this unstable, as documented by previous observations at the site (Wobrock et al., 1998). Occult depositions of fog were also investigated in past campaigns (Jaeschke et al., 1998). In general, the real atmosphere is not a closed system in any dimensions, even horizontally. Therefore, our interpretation of the results, assuming a “box model” where sinks and external sources of materials are ignored, can be valid only in a first approximation. Our assumption is primarily supported by the mass balance achieved between daytime PM concentrations and the lumped nighttime PM and fog components concentrations (Fig. S1): the mass balance shows that PM behaved approximately conservatively in the PBL in the days considered in this study. We acknowledge, however, that the PM mass balance can be affected by compensating fluxes of particles in and out the PBL (entrainments and depositions).

2. Lines 9-12 of abstract: this sentence should be rewritten to more clearly distinguish primary and secondary particle source contributions that the authors are referring to.

Reply: Estimates of the relative contributions of biomass burning and secondary sources to PM mass concentrations during the November 2015 fog campaign are currently not available. Nevertheless, the AMS proxies for biomass burning POA and for oxidized organic aerosols (m/z 60 and m/z 44, in Table 2) indicates that the organic composition during the November 2015 field campaign is compatible with that observed during the previous experiments at the site where quantitative source apportionment of submicron PM was carried out (Gilardoni et al., 2016). This is why we stated that “Po Valley PM, which is mainly composed of biomass burning and secondary aerosols” in the abstract, without reporting the actual shares of PM mass. The point here is that the PM composition in a rural area like the Po Valley is *qualitatively* very different from that of urban environments, much more impacted by traffic emissions and more extensively studies for ROS.

3. Section 2.2: more information should be presented concerning cleaning of the fog sampler and any contamination contained in collector blanks.

Reply: The collector and its strings were extensively cleaned at the beginning of the fog season (approximately two weeks before the samples object of this study were collected). In particular, the strings (stainless steel) were carried to a chemical laboratory where they were gently brushed to remove any stuck residues from fog sampling in the previous winter and washed with milliQ water in an ultrasonic bath. Finally, they were brought back to the field and mounted on the fog collector before first the automatic sampling system was switched on around mid-November. This information will be added to Section 2.2.

4. P3, line 12: This should be the PVM-100 not PVM-10.

Reply: correct. It is PVM-100.

5. P.3, lines 15-16: I suggest you explain to the reader that multiplying by LWC yields “air equivalent concentrations”

Reply: we will add the following sentence to the text: “Concentrations of analytes in fog samples, expressed in µg mL^{-1}, were converted into µg m^{-3} by multiplying with the fog liquid volume (mL m^{-3}). The latter was not estimated by the mass of sampled fog water multiplied by the flux of the fog collector, because the collection efficiency is typically much smaller than 1 (about 40%, according to Fuzzi et al. 1997). We used instead the liquid water content (LWC) measured by the PVM-100 and averaged over the sampling time of the fog collector to multiply by the concentrations of chemicals in fog water to get air equivalent concentrations (µg m^{-3}) of the fog components”.

6. Section 2.3: Please explain to the reader why you chose to filter the fog samples. Suspended particulate matter inside fog drops is also scavenged material that should be considered as part of the overall system ROS mass balance.

Reply: true, and in fact we performed ROS analyses on both filtered and unfiltered extracts. Since fog chemical components partition selectively between the soluble and insoluble phases, performing the analysis of ROS activity with and without filtration provides useful information on the nature of the redox-active compounds (Fig. 2).

7. P.3, line 25: change “chromatographers” to “chromatographs”

Reply: will be corrected.

8. P. 4, lines 9-10: I am confused why the authors would extract fog water with Milli-Q water. Is this statement in error?

Reply: This was mentioned in error. Please see below the corrected sentence: “In this method, samples (filters) were first extracted using an initial sonication period for 15 min with high-purity 10 Milli-Q (18 mΩ) water.”

9. P. 5, line 29: change “what observed” to “what is observed”

Reply: will be corrected.

10. P. 5, line 30: change “ammonia” to “ammonium” since you are discussing ionic species here

Reply: will be corrected.

11. P. 6, line 15: change “adsorbed” to “absorbed”

Reply: accepted.

12. P. 6, lines 35-36: The statement “fog scavenging denudes particles of WS components” is misleading. It sounds like material is being stripped off particles while what is really happening is

that the fog is selectively scavenging some particles and leaving others intact in the aerosol. Please rephrase.

Reply: Accepted. The sentence will be changed into “as fog scavenges the WS components of the particles”.

13. P. 9, lines 3-5: This sentence needs to be rewritten to improve the grammar.

Reply: the text will be rephrased as follows: “The uptake of reactive gases could explain the excess of WSOC in fog water compared to the scavenged fraction of daytime PM1 (Figure 1 c,d) as well as the higher intrinsic toxicity of fog components , as shown in Figure 1 b”.

REFERENCES:

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Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., 10 Costabile, F., Gobbi, G. P., Pietrogrande, M. C., Visentin, M., Scotto, F., Fuzzi, S., and Facchini, M. C.: Direct observation of aqueous secondary organic aerosol from biomass-burning emissions, Proceedings of the National Academy of Sciences of the United States of America, 113, 10013-10018, 10.1073/pnas.1602212113, 2016.

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