Comments from Anonymous Referee #2

General comments:

The researchers performed online measurements of fog residuals and ambient aerosols, as well as offline analysis of fog water in the Po Valley, with a focus on the organic nitrogen components. It was found that both the fog droplet residuals and fog water had enhancements of amino compounds and imidazoles. The manuscript is well written and informs an interesting topic area. I only have a few comments:

Reply: We thank the reviewer for the positive assessment of our manuscript. In the following we reply to each comment individually directly below the copied text from the reviewer. Only references exclusively used in this document and not part of the main manuscript are added in a separate bibliography at the end.

Specific comments:

Comment 35: Do the authors have any comments on the primary sources of ON and relevant formation pathways of imidizoles in the Po Valley? Line 52 mentions vehicle exhaust, biomass burning and agriculture as possible sources, and at line 312 the authors seem to dismiss local traffic sources as a source due to differences from Saarikoski et al (2012). A sentence or two in the conclusions will help showcase the relevance to other geographic regions.

Reply: We thank the reviewer for the question about sources and formation of ON and imidazoles in the Po Valley. The $C_xH_yN_1^+$ ions comprise the largest part of the ON we observe during this study, and from those ions we were able to identify a few specific aliphatic amines. These amines have a variety of potential sources, such as animal husbandry, biomass burning, industry, traffic, and even pesticides. Since we did not observe a typical daily pattern of traffic, we exclude local vehicle exhaust as a major source of the ON. We know from previous studies from the Po Valley that biomass burning is a major source of both primary and secondary OA in the winter, while agriculture and animal husbandry are major sources of VOCs and ammonia (Gilardoni et al., 2016, Saarikoski et al., 2012, Paglione et al., 2020). ON species, such as amines, have been found to contribute to aerosol mass both through gas-phase reactions (oxidation reactions with OH, NO_x, or O_3), as well as acid-base reactions (Ge et al., 2011). We believe that the ON observed in this study likely originates from various sources, where biomass burning, agriculture, and animal husbandry are the main sources. For imidazoles, it is possible that a major formation pathway is the uptake of either amines or glyoxal by ammonium in the fog droplets / deliquesced particles (see also our replies to comment 11 and comment 13 from reviewer 1). At the same time, we cannot exclude the possibility that the enhanced imidazole mass in the fog droplets could arise from dissolution of the gaseous fraction into the fog droplets / fog water. However, the strong correlations with glyoxal and NH_4^+ during the second period, where the mass concentration is much higher in the ambient aerosol and the fog residuals, indicate that it forms from this reaction in the aqueous phase. For future work, performing a positive matrix factorization analysis to investigate the potential sources, would certainly be useful in order to investigate the potential sources of ON compounds. We have added the following to the revised manuscript at line. 416 : *“These ON compounds are likely products from biomass burning, agriculture, and animal husbandry emissions.”*

Comment 36: Line 46: “Inorganic aerosol species also contribute to aqSOA. Nitrate (NO−3) is becoming more important as an aerosol component in many areas, due the reduction of other air pollutants (e.g. SO2), or where high levels of excess NH3 exist in the atmosphere (Bauer et al., 2007).” Is this sentence stating that high levels of nitrate can enhance aqSOA formation, or that inorganic nitrate is an important

PM component formed in the aqueous phase. If the latter, the first sentence should be revised as nitrate is not aqSOA.

Reply: We agree with the reviewer that this sentence was incorrect. We thus decided to remove that sentence, and the sentence after, at line 46 because they did not fit with the rest of the paragraph: *"Inorganic aerosol species also contribute to aqSOA. Nitrate (NO_3^-) is becoming more important as an aerosol component in many areas, due to the reduction of other air pollutants (e.g. SO_2), or where high levels of excess NH_3 exist in the atmosphere (Bauer et al., 2007)."*

Comment 37: Line 191: Were these ions measured using the AMS or the offline IC that was briefly mentioned previously. If it was the AMS: how were K+, Ca+, Mg2+ and Na+ treated

Reply: We understand this was not stated in the manuscript and thank the reviewer for the comment. The ions K^+, Ca^{2+}, Mg^{2+}, and Na^+ were measured using offline ion-chromatography on PM1 filter samples. Sentence at lines 198-201 now reads: "*In addition, the aerosol liquid water content (ALWC) was predicted using the aerosol inorganic species; NO_3^- , SO_4^{2-} , NH_4^+, and Cl^- measured by HR-ToF-AMS, as well as K^+, Ca^{2+}, Mg^{2+}, and Na^+ from offline ion-chromatography on PM_1 filter samples, as inputs in ISORROPIA-II model (Fountoukis and Nenes, 2007).*"

Comment 38: Line 215: Does the NMR method differentiate between different substituted imidazoles?

Reply: With the NMR method we only analyzed 1H-imidazole. Other substituted imidazoles, such as 2-Methylimidazole, could have singlets in the spectral region between 7 and 7.5ppm (actually visible in most of the fog spectra in Fig. S4) but for the moment they are not unambiguously identifiable. The inclusion of more N-heterocyclic compounds would be very interesting for future work.

Comment 39: Figure 6: I find this figure hard to interpret. Is there another way to present these results such that it is clearer which bars correspond to which axis? I also find the simultaneous use of the box plot and bars distracting.

Reply: We thank the reviewer for this comment. We refer to our reply to comment 13 from reviewer 1 for the exact changes made to Fig. 6.

References

Ge, X., Wexler, A. S., & Clegg, S. L. (2011). Atmospheric amines–Part I. A review. *Atmospheric Environment*, *45*(3), 524-546.

Gilardoni, S., Massoli, P., Paglione, M., Giulianelli, L., Carbone, C., Rinaldi, M., Decesari, S., Sandrini, S., Costabile, F., Gobbi, G. P., Pietrogrande, M. C., Visentin, M., Scotto, F., Fuzzi, S., & Facchini, M. C. (2016). Direct observation of aqueous secondary organic aerosol from biomass-burning emissions. *Proceedings of the National Academy of Sciences*, *113*(36), 10013-10018.

Paglione, M., Gilardoni, S., Rinaldi, M., Decesari, S., Zanca, N., Sandrini, S., Giulianelli, L., Bacco, D., Ferrari, S., Poluzzi, V., Scotto, F., Trentini, A., Poulain, L., Herrmann, H., Wiedensohler, A., Canonaco, F., Prévôt, A. S. H., Massoli, P., Carbone, C., Facchini, M. C., & Fuzzi, S. (2020). The impact of biomass burning and aqueous-phase processing on air quality: a multi-year source apportionment study in the Po Valley, Italy. *Atmospheric Chemistry and Physics*, *20*(3), 1233-1254.

Saarikoski, S., Carbone, S., Decesari, S., Giulianelli, L., Angelini, F., Canagaratna, M., Ng, N. L., Trimborn, A., Facchini, M. C., Fuzzi, S., Hillamo, R., & Worsnop, D. (2012). Chemical characterization of springtime submicrometer aerosol in Po Valley, Italy. *Atmospheric Chemistry and Physics*, *12*(18), 8401-8421.