

We thank the reviewer for allowing us to further improve the clarity of our manuscript. We considered the comment, have revised the section 3.2.3 accordingly and added a relevant sentence to the conclusion. Please find our reply here below. We also submitted a track changes manuscript and the supplement with the technical corrections asked by editorial office. We hope that this revised version is now suitable for publication in ACP.

### **Reply to reviewer**

#### Comment:

*I have reviewed responses to first round reviews and found items to be adequately addressed. In the case of Section 3.2.3, additional insight into the increase in acidity due to uptake of water onto organics would be useful. For example, did the increased water cause more nitric acid uptake? Or, did NH<sub>3</sub> in the gas-phase increase? Is there evidence of a discontinuity when organic water is added that could be leading to an artifact?*

#### Response:

Addition of organic aerosol water most of the times tends to reduce acidity and elevate pH, as shown by Kakavas et al. (2022) and other related studies. However, under conditions where organic aerosol water content can dominate the aerosol water however, it is possible that acidity can be increased. In the discussed case, the addition of organics and the subsequently increase of the aerosol water resulted in an increase in the partitioning of all three semi volatiles (NH<sub>3</sub>, HNO<sub>3</sub> and HCl) from the gas phase to the aerosol phase. The gas phase NH<sub>3</sub>, HNO<sub>3</sub> and HCl concentrations decreased and the respective concentrations of the aerosol phase increased. Gas phase NH<sub>3</sub> did not increase. The addition of considerable amounts of water affected the activity coefficients of all ionic species (especially sulfate/bisulfate ions and NH<sub>4</sub><sup>+</sup>) which shifted the ionic balance slightly. The resulting changes from the addition of OA are consistent with increases in aerosol water that depend on RH, changes in the partitioning of semivolatiles, the concentrations of which increased in the aerosol phase and decreased in the gas phase, as well as in changes in the activity coefficients of all ionic species. The increase in the concentrations of the acids exceeded that of ammonium resulting in a decrease of the pH. Note also that as shown in eq. 1 in the manuscript, we are using the pH<sub>F</sub> proxy for the pH (free H<sup>+</sup> approximation of pH that does not consider shifts in the activity coefficient in H<sup>+</sup>; Pye et al., Atmos. Chem. Phys., 2020).

Section 3.2.3 has been rephrased accordingly:

“ In order to investigate the potential effect of OA on the aerosol pH levels, ISORROPIA-lite was also run considering only the inorganic components of the aerosol (i.e. setting the OA concentration to zero). The mean difference between the aerosol pH calculated considering all aerosol components, including organics and the one accounting only for the inorganic content of PM<sub>2.5</sub> is shown in Figs. 3b and d for January 2020 and summer 2019, respectively. The water associated with the OA in most cases reduces the H<sup>+</sup> concentration and therefore increases the aerosol pH (Kakavas et al., 2022). However, this expected increase in aerosol pH due to OA was not always found at all sites, because of the resulting changes in the partitioning of the semivolatile compounds from the gas phase to the aerosol phase. This partitioning affects the OA induced change in the H<sup>+</sup> concentration (H<sup>+</sup><sub>air</sub> concentration in eq. 1), which together with aerosol water determine the aerosol pH.

In January at IOA, THI and PTR, the addition of aerosol water associated with the OA did not always increase the overall aerosol pH. In fact, a mean decrease of about 0.3 pH units was found at IOA, which had the highest OA concentrations among the 3 sites. Figure 5a depicts the aerosol water associated only with the inorganics along with the total one (i.e. including the OA water) and relative humidity and

in Fig 5b the timeseries of the aerosol pH at IOA is shown in which again the one associated only with the inorganics and the one including the OA water (total aerosol pH) is depicted. An increase in the aerosol pH as a result of the addition of the organics is clear only at the end of January (from 26-01 to 29-01); the total aerosol pH was higher than the one when OA was absent (by 0.19 pH units on average). This was due to the high aerosol water content, which resulted from high relative humidity (above 80%). The addition of the OA increased aerosol water even more (Fig 5a). On all the other days in January with lower relative humidity, the addition of OA resulted in relative small increases in aerosol water. The partitioning of the semivolatile species to the aerosol phase increased, by decreasing the gas phase concentration (change up to  $0.10 \mu\text{g}/\text{m}^3$  for  $\text{NH}_3$ , 0.18 for  $\text{HNO}_3$  and 0.12 for  $\text{HCl}$ ), and similarly increasing the corresponding aerosol phase ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ). Furthermore, addition of considerable amounts of aerosol water affects the activity coefficients of all ionic species (especially sulfate/bisulfate ions and  $\text{NH}_4^+$ ), which shifts the ionic balance slightly. In addition, the free  $\text{H}^+$  approximation of pH that we are using (eq.1) does not consider shifts in the activity coefficient in  $\text{H}^+$  (Pye et al., 2020). Overall, the increase in the concentrations of the acids exceeded that of ammonium, therefore, the concentration of  $\text{H}^+$  increased. The increase in aerosol water did not counterbalance the increase in  $\text{H}^+$  concentration resulting in a more acidic aerosol (lower aerosol pH). The highest decreases in pH were observed in days where high aerosol pH occurred (inorganic aerosol pH above 4.5 units, mean pH decrease 0.58 units). At the other two sites the aerosol pH decreased by about 0.08 pH units at THI and 0.01 at PTR. These relatively rare, but still important, set of conditions require further tests of thermodynamic model pH predictions.

At FKL, XAN and LAP a small increase in aerosol pH was found; 0.001, 0.05, 0.05 pH units increase respectively. In the summer (July and August), the pH increased at all sites when considering OA water, with the highest predicted increase of about 0.15 at IOA. At the other sites the aerosol pH increased by about 0.09 units at FKL and 0.11 at THI. Therefore, the effect of the organics on the pH at all sites was on average less than 0.3 units.”

The following sentences have been added to the Conclusions:

“This behavior associated with aerosol pH above 4 units is the result of increased partitioning of semivolatiles to the aerosol phase and of changes in the activity coefficients. Such conditions are good benchmark for testing the thermodynamic model predictions of pH.”