

## RE: A point-to-point response to Reviewer #2's comments

“Detection of atmospheric gaseous amines and amides by a high resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions” (acp-2016-484) by Lei Yao, Ming-Yi Wang, Xin-Ke Wang, Yi-Jun, Liu, Hang-Fei Chen, Jun Zheng, Wei Nie, Ai-Jun Ding, Fu-Hai Geng, Dong-Fang Wang, Jian-Min Chen, Douglas R. Worsnop, and Lin Wang

We are grateful to the helpful comments from this anonymous referee, and have carefully revised our manuscript accordingly. A point-to-point response to Reviewer #2's comments, which are repeated in italic, is given below.

### Reviewer #2's comments:

1. *Lines 93-94: C3 amines include trimethylamine, methyl-ethylamine and propylamine (formally also azetidine and the various methylaziridines, which have a different sum formula)*

Reply: The reported concentrations are the sum of propylamine (PA) and trimethylamine (TMA) (Kieloaho et al. 2013). This statement has been rephrased as “the sum of propylamine (PA) and trimethylamine (TMA)”.

2. *Lines 166-167: It is stated that the amines and amides reacted dominantly with protonated ethanol (through proton transfer reactions). This statement requires some clarification. The authors state in the lines preceding that most abundant reagent ion is protonated ethanol dimer (illustrated in Fig. S1).*

Reply: Under our CIMS setup, the most abundant reagent ion is the protonated ethanol dimer with the second most dominant ions being protonated ethanol monomer and trimer. The ion-molecule reactions between the analytes and reagent ions leads to the formation of protonated analytes (clustering with up to one molecule of ethanol), which is somehow similar to the conventional proton transfer reactions of hydronium ions. We now clarify (Line 179-181) that “Amines and amides reacted dominantly with protonated ethanol ions  $((\text{C}_2\text{H}_5\text{OH})_n \cdot \text{H}^+, n=1, 2 \text{ and } 3)$ , compared to water clusters, with the formation of protonated amines/amides clustering with up to one molecule of ethanol.”.

3. *3.1.2 Effects of RH and organics: The influence of RH on the instrument sensitivity is described and illustrated for three simple amines. The observed effect requires some explanation. Have the authors calculated the PTR rate coefficients for the different reagent ions? Does the reagent ion distribution change significantly?*

Reply: As shown in Figure S1,  $(\text{H}_2\text{O})_m\text{H}^+$  ( $m=1, 2 \text{ and } 3$ ) and  $\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O} \cdot \text{H}^+$  are present under elevated RH conditions, both of which are likely more reactive than protonated ethanol dimer (Nowak et al., 2002). Hence, proton transfer reactions of  $(\text{H}_2\text{O})_m\text{H}^+$  and  $\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O} \cdot \text{H}^+$  with

amines and amides may take place leading to the formation of protonated amines and amides. We have now (Line 319-322) state that

“At elevated RH, high concentrations of water resulted in the production of  $(\text{H}_2\text{O})_m\text{H}^+$  ( $m=1,2$  and  $3$ ) and  $\text{C}_2\text{H}_5\text{OH}\cdot\text{H}_2\text{O}\cdot\text{H}^+$  ions (Figure S1) (Nowak et al., 2002). Proton transfer reactions of  $(\text{H}_2\text{O})_m\text{H}^+$  ( $m=1, 2$  and  $3$ ) and  $\text{C}_2\text{H}_5\text{OH}\cdot\text{H}_2\text{O}\cdot\text{H}^+$  with amines and amides might occur leading to the formation of additional protonated amines and amides.”

We didn't calculate the reaction rates of amines and amides with different reagent ions. Calibration curves with known concentrations of authentic standards were used to derive their ambient concentrations instead, although those curves were obtained at ~0% RH. However, in our ambient measurements, we used high purity nitrogen to dilute the sample flow resulting in an overall RH < 20%, under which RH no significant effect on reagent ions distribution was observed.

4. *Line 314: "oxomide" should be "oxamide"*

Reply: We have replaced “oxomide” by “oxamide”.

5. *Figure 3 requires some additional information/clarification. First, the peak-shape is not discussed. Second, the curve-fitting includes a listing "Isotopes and other compounds". It is not obvious to the reader which "isotopes and other compounds" that are actually included in the analyses. As an example the region around m/z 60 must clearly contain a signal from the 13-C isotope of acetone (60.053), but this appears not to be the case.*

Reply: Clarification is now provided in the figure legend, the figure caption, and the main text. The exact formulas for “Isotopes and other compounds” have been provided in the figure legend. The new figure caption reads “**Figure 3.** High-resolution single peak fitting (custom shape) for amines and amides. During the peak deconvolution, only peaks whose areas are more than 0.5% of the total will be included in the figure legend.”

Also, we state (Line 348-349) in the main text that “The assignment of molecular formulas for these species is within a mass tolerance of < 10 ppm, and the fitted area ranges from 99% to 101%”.

We observed protonated acetone ( $m/z$  59.0491) (Table S1) but its arbitrary signal was much less than that of protonated C<sub>2</sub>-amide. Hence, the 13-C isotope of acetone, whose abundance is 3.3% of acetone, did not stand out in our mass spectra.

## Reference:

- Kieloaho, A.-J., Hellén, H., Hakola, H., Manninen, H. E., Nieminen, T., Kulmala, M., and Pihlatie, M.: Gas-phase alkylamines in a boreal Scots pine forest air, *Atmos. Environ.*, 80, 369-377, 10.1016/j.atmosenv.2013.08.019, 2013.
- Nowak, J. B.: Chemical ionization mass spectrometry technique for detection of dimethylsulfoxide and ammonia, *J. Geophys. Res. Atmos.*, 107, 10.1029/2001jd001058, 2002.