

## **RE: A point-to-point response to Reviewer #3'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 #3's comments, which are repeated in italic, is given below.

### **Reviewer #3's comments:**

*The manuscript presents a method for the quantitative measurement of various amines and amides in the ppt range by Chemical Ionization using a High - Resolution Time - of - Flight mass spectrometer with protonated ethanol reagent ions. Calibrations are presented and the influence of humidity is characterized in the laboratory. Several weeks of ambient measurements in Shanghai are presented. 85 nitrogen - containing species with  $m/z < 163$  Th are identified in the ambient air including numerous amines and amides. Amines reach mixing ratios up to more than 100 pptv. Amides reach maximum mixing ratios of several ppbv. Diurnal variations of specific amines and amides are studied.*

*The paper is well written, concise and well structured. Measurements are made with ethanol as reagent ions, a reagent ion that had not been tested in detail before. Atmospheric measurements of amides with CIMS have not been presented before. The paper is suitable for publication in ACP. Some minor comments should be taken into account.*

Reply: We are very grateful to the positive viewing of our manuscript by Reviewer #3, and have now revised our manuscript accordingly.

### **Minor comments:**

1. l. 86: *some important earlier references are missing: Murphy et al., ACP, 7, 2313–2337, 2007; Kurten et al., ACP, 8, 4095–4103, 2008; Berndt et al., ACP, 10, 7101–7116, 2010.*

Reply: These three references have been added.

2. l. 88: *also Bzdek et al., ACP, 10, 3495–3503, 2010 and Kupianinen et al., ACP, 12, 3591–3599, 2012, should be cited.*

Reply: These two references have been added.

3. l. 103 - 105: *compare also with the much lower amine concentrations measured with CIMS in Hyytiälä as presented by Sipilä et al., AMT, 8, 4001–4011, 2015.*

Reply: Inter-comparison with results from Sipilä et al. (2015) is added. We now state (Line 114-117) that “Additionally, at the same site, DMA concentration was measured to be less than 150 ppqv (parts per quadrillion by volume) in May-June 2013 by an atmospheric pressure CIMS based on bisulfate-cluster method for DMA detection (Sipilä et al. 2015).”

4. l. 122 - 123: *Also Sipilä et al. 2015, and Simon et al., AMT, 9, 2135 - 2145, 2016, should be cited.*

Reply: These two references have been cited.

5. l. 139 - 140. *Avoid exact repetition of sentences from the abstract.*

Reply: We have revised our manuscript accordingly.

6. l. 366 - 367: *compare also with the results of Sipilä et al., AMT, 2015.*

Reply: We have added the inter-comparison in discussion section 3.2.2 (line 407-411). We have now state that

“The concentrations of amines in Shanghai are generally smaller than those in Hyytiälä, Finland (Hellén et al., 2014; Kieloaho et al., 2013; Sellegri et al., 2005) except for one study that, as stated by the authors, should be treated with caution (Sipilä et al. 2015), potentially hinting that sources for amines existed in the forest region of Hyytiälä, Finland.”

7. *Table 2: include also Sipilä et al., AMT, 8, 4001–4011, 2015, and Kürten et al., ACPD, doi:10.5194/acp - 2016 - 294, 2016 in the inter - comparison.*

Reply: These two references have been added. We have now state that (line 407-413)

“The concentrations of amines in Shanghai are generally smaller than those in Hyytiälä, Finland (Hellén et al., 2014; Kieloaho et al., 2013; Sellegri et al., 2005) except for one study that, as stated by the authors, should be treated with caution (Sipilä et al. 2015), potentially hinting that sources for amines existed in the forest region of Hyytiälä, Finland. Our C<sub>1</sub>- and C<sub>2</sub>-amines are generally more abundant than those in agricultural, coastal, continental, suburban, and urban areas (Freshour et al., 2014; Hanson et al., 2011; Kieloaho et al., 2013; Kürten et al., 2016; Sellegri et al., 2005; You et al., 2014).”

8. *Figure 3, upper right hand panel: some discussion of the “isotopes and other compounds” peaks needs to be given. Some more discussion of the uncertainties of the peak separation is necessary. Please discuss why the main peak needs to be separated into the two peaks as indicated. How large are the uncertainties in mass and signal intensity for the “isotopes and other compounds” peak?*

Reply: Clarification is now provided in the figure legend and the figure caption. 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%”.

**Technical corrections:**

1. l. 5: *omit comma between Yi - Jun and Liu*

Reply: We have revised our manuscript accordingly.

2. l. 158: *...was THE protonated ethanol...*

Reply: We have revised our manuscript accordingly.

3. l. 159: *... with the SECOND MOST dominant ions being THE protonated ethanol monomer...*

Reply: We have revised our manuscript accordingly.

4. l. 160: *... and THE protonated ethanol trimer*

Reply: We have revised our manuscript accordingly.

5. l. 163: *... the ratios of THE oxygen...*

Reply: We have revised our manuscript accordingly.

6. l. 168: *(...NR<sub>3</sub>, with R BEING EITHER A HYDROGEN ATOM or an alkyl group)*

Reply: We have revised our manuscript accordingly.

7. l. 169: *(... WITH R` BEING EITHER A HYDROGEN or ...)*

Reply: We have revised our manuscript accordingly.

8. l. 169 - 170: *... can be REPRESENTED BY THE FOLLOWING REACTIONS (Yue...*

Reply: We have revised our manuscript accordingly.

9. l. 209: *mixed WITH the amine/amide...*

Reply: We have revised our manuscript accordingly.

10. l. 359: ...each DATA point...

Reply: We have revised our manuscript accordingly.

11. l. 421: A Lagrangian...

Reply: We have revised our manuscript accordingly.

12. l. 425: ... are SHOWN for air masses

Reply: We have revised our manuscript accordingly.