

RE: A point-to-point response to Reviewer #1'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 #1's comments, which are repeated in italic, is given below.

Reviewer #1's comments:

The authors make simultaneous measurements of amines and amides using a recently developed online instrument, the HR-ToF-CIMS. They use ethanol as the reagent ion to optimize the detection of nitrogen-containing molecules. The instrument characteristics within the laboratory context are thorough and well presented, and include calibrations, relative humidity dependence measurements and organic effect on the measured concentrations.

The calibrated HR-ToF-CIMS was then employed to make ambient air measurements of a wide range of amines and amides at an urban site in Shanghai. The ambient measurements answer some questions about sources, sinks and transport of amines and amides and has the potential to be a useful reference for future work on the fate of organic nitrogen compounds in the atmosphere.

In particular, the manuscript is well presented with clear experimental detail. However, the referencing is generally incomplete and careful attention should be taken to research the literature accurately.

Reply: We are very grateful to the positive viewing of our manuscript by Reviewer #1, and have now revised our manuscript accordingly.

General comments:

- 1. The introduction section describing previous measurements of amines and amides is a little tedious to read. Table 2 serves as a good summary and a clear reference and so perhaps the introduction could solely focus on identified trends in season, location, etc. It would also be important to keep referencing Table 2 in the discussion section. Finally, there could be value in making two tables, one for amines and one for amides. This arrangement would also highlight how few amide measurements exist. Also, see comment below for missing references.*

Reply: We have revised our manuscript accordingly. Table 2 has now been divided into two tables, and previous works on amides are shown in Table 3. The main text in the discussion has been

revised accordingly.

2. *The referencing for previous work on amides is incomplete. Amides have been measured and speciated in the context of cigarette smoke and in charbroiling burgers. In addition, they have been identified in PM. See the following references for examples.*

Reply: We have added the related references, although particulate amides are not a focus of this study.

3. *In Table S1, CHNO-H+ at m/z 44 is not reported and the authors explain that the proton affinity of HNCO is higher than that of ethanol in their response. Nonetheless, it would be important to mention this simply because of the growing interest in HNCO in our community.*

Reply: Statements on detection of HNCO have been added in the main text, which reads (line 376-379),

“One important atmospheric nitrogen-containing compound, isocyanic acid (HNCO) (Roberts et al., 2011) is not listed in Table S1, because the proton affinity of isocyanic acid is $180.0 \text{ kcal mol}^{-1}$, which is less than that of ethanol ($185.6 \text{ kcal mol}^{-1}$). Hence, the ethanol reagent ions are not sensitive to the detection of isocyanic acid.”

4. *2-aminoethanol (m/z 62) is an important industrial compound, especially in carbon capture and storage technologies and is listed in Table S1. Did the concentrations of this compound show high concentrations and/or wind speed/direction dependencies? Perhaps add a short discussion in section 3.2.1.*

Reply: No calibration was performed for 2- aminoethanol, which pre-excludes the determination of its concentration in this study. In addition, no correlation was found between 2-aminoethanol and C₃-amide.

5. *The authors mention the use of the FIGAERO inlet and it is fair that they plan on reporting the particle measurements elsewhere. However, in the context of organic nitrogen it could be important to include a short discussion on how the gas phase and particle phase concentrations of organic nitrogen differ.*

Reply: A previous study reported that the concentrations of particulate primary amines measured with Fourier transform infrared spectroscopy (FTIR) from micron and submicron particles were 2 orders of magnitude higher than those of gas-phase amines (You et al., 2014). As a conclusion from that specific study, most of amines existed in particles.

We are now working on an optimized quantification method for particulate amines and amides, and other organic nitrogen compounds. It is premature from our dataset to make any statement on how the gas phase and particle phase concentrations of organic nitrogen differ at this stage.

6. *How confident are the authors that their reported concentrations are solely gas phase? What possible contribution could there be from amines and amides in the particle phase?*

Reply: First of all, the FIGAERO inlet has two separate sampling ports: one for gases, and the other for particle collection and subsequent thermal desorption (Lopez-Hilfiker et al., 2014). The temperature of IMR (ion-molecule reactions chamber) was set at 50 °C to minimize the absorption and adsorption of amines and amides on the surface of IMR. Also, our inlet memory tests clearly suggest that the particle analysis (of amines and amides) will not have an impact on the gas sample analysis.

We do not filter out particles in the flow when we analyze gas samples. However, given the pressure in IMR (~100 mbar) and the existence state of amines and amides in aerosols, particulate amines and amides are unlikely to evaporate and react with reagent ions (protonated ethanol ions) to make product ions that can be detected by the mass spectrometer. Hence, the interference for amines and amides from particles were negligible.

7. *Many references and important discussions are included in the conclusion section but would perhaps be more appropriate in the discussion section.*

Reply: We have revised the conclusion section and emphasized on discussions in the discussion section. For example, we moved the following statement from the conclusion section to the discussion section (line 368-372).

“Berndt et al. (2014) reported that pyridine was able to enhance nucleation in H₂SO₄/H₂O system. Also, proton affinities of most of these heterocyclic nitrogen-containing compounds are higher than that of ammonia, hence they potentially have the capacity to neutralize atmospheric acidic species (e.g. H₂SO₄, HNO₃ and organic acids) to contribute to secondary particle formation and growth”.

Also, statements in the conclusion section have been moved into the introduction (line 89-91), “Compared with amines, acetamide has a very weak positive enhancement on the nucleation capability of sulfuric acid (Glasoe et al., 2015).”

Specific comments:

1. *Lines 107-108: Could these authors specify what differences they are referring too? Diurnals? Absolute value? Etc.*

Reply: We meant to state that the absolute concentrations were not significantly different in different urban locations, which is clarified in our revised text

2. *Line 125: I believe that the Borduas et al. and Bunkan et al. references used PTR-MS to measure amides and amines and not CIMS. The authors should double check these references.*

Reply: The principle of PTR-MS is similar to CIMS. Both of them utilize chemical ionization

methodology to charge the analytes. Hence, PTR-MS is considered as a sub-category of CIMS.

3. *Line 170: Please clarify this sentence. “Dominantly protonated” compared to the water clusters?*

Reply: We now state (Line 179-181) that “Amines and amides reacted dominantly with protonated ethanol ions ($(\text{C}_2\text{H}_5\text{OH})_n\cdot\text{H}^+$, $n=1, 2$ and 3), compared to water clusters, with the formation of the protonated amines/amides clustering with up to one molecule of ethanol”.

4. *Line 200: When the authors are referring to total ethanol signal, mean the sum of first three dimers with ethanol correct? (also, this sentence seems a bit out of place.)*

Reply: “Total ethanol signal” refers to the sum of the protonated ethanol monomer, dimer and trimer. The variation in total reagent ions between in laboratory calibration and during field measurements is taken into account when ambient concentrations of amines and amides are calculated. We clarify here (Line 211-214) that “The total ethanol reagent ion signals, i.e., the sum of the protonated ethanol monomer, dimer and trimer, during the laboratory calibration were typically ~ 0.32 MHz, which yields a small correction because of the variation in total reagent ions between in laboratory calibration and during field measurements as stated in section 2.4”.

5. *Lines 296-304: Do the authors have a hypothesis as to why the enhancement is larger with amines than with amides? Perhaps because of differences in proton affinity?*

Reply: We now state (Line 319-324) that “At elevated RH, high concentrations of water vapor result 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. In addition, the proton affinities of amines are generally higher than those of amides. Thus, the relative enhancement was more significant for amines.

6. *Lines 305-312: What is the context of this experiment? Have others observed interferences with organics? Give context and appropriate references.*

Reply: We now state (Line 325-328) that “Since a large number of ambient organics can be detected by this protonated ethanol reagent ion methodology as shown later, laboratory measurements of amines and amides in presence of and in absence of organics formed from photo oxidation of α -pinene and p-xylene, respectively, were carried out to examine the influence of organics on detection of amines and amides”.

7. *Lines 345-346: This is an important finding. Since a majority of nitrogen-containing compounds are oxygenated, it would be interesting to see examples of diurnals and to compare them with the amide diurnals. I would encourage the authors to emphasize this point and discuss further the implications of higher order nitrogen-containing compounds, including in the context of particle formation.*

Reply: This is an excellent suggestion, but determination of nitrogen-containing species with $m/z > 163$ from the ambient mass spectra is beyond the scope of this manuscript.

8. *Line 363: “C5 and C6 amines standards are unavailable” is difficult to believe, especially since the authors build their own permeation tubes for the most part. I would recommend the authors clarify or remove this statement.*

Reply: We now state (Line 396-397) that “Since the sensitivities of C₅- to C₆-amine were not determined, the sensitivity of DEA by HR-ToF-CIMS was adopted to quantify C₅- to C₆-amines”

9. *Line 383: a value of 778 +/- 899 is a little bizarre. How were the errors calculated? Line 385-386: I would recommend moving this sentence to the paragraph discussing these high values in section 3.2.4.*

Reply: The error here represents one standard deviation, which is derived from the significant fluctuation in the C₃-amide concentration as shown in Figure 5.

The sentence regarding the high concentration of C₃-amides has been moved to section 3.2.4.

10. *Lines 393-397: What could be the role of particle phase chemistry on the observed diurnals?*

Reply: According to our preliminary uptake experiments of amides by suspended H₂SO₄ particles and published uptake coefficient of amines by sulfuric acid (Wang et al., 2010), heterogeneous chemistry does not show a major preference between amines and amides. The lower RH in the daytime will generally lead to higher particle acidity, but not in the range of acidity that has been studied (Wang et al., 2010). Hence, the role of heterogeneous chemistry is not discussed here.

In the atmospheric condensed-phase material and cloud droplets, amines (e.g. methylamine) can react with aldehydes (e.g. methyglyoxal and glyoxal) to form oligomers that contribute to secondary organic aerosols (De Haan et al., 2009, 2011; Galloway et al., 2014). However, no data on aldehydes in the condensed-phase material and cloud droplets were available during our ambient campaign. Hence, we decided not to estimate the contribution of particle phase chemistry to the observed diurnals.

11. *Figure 2 – Can the authors estimate the concentrations of pinene and xylene used in these experiments? This information would be useful to include in the experimental section starting on line 210.*

Reply: The estimated concentrations of α -pinene and p-xylene were both ~200ppb. We have added the concentrations of these two compounds in main text.

12. *Figure 4 is an important analysis and can be used to discuss functional group interconversion and trends. I would recommend the authors spend a bit more time analyzing these graphs and discussing them.*

Reply: The high-resolution mass spectrometer allows us to determine the molecular formulas of these nitrogen-containing species and hence their mass defects, but would not permit a direct determination of the functional groups. The focus of this manuscript is detection of amines and amides. Interested readers can refer to the supplementary Table S1 that lists the tentative formula assignments for these nitrogen-containing species

13. *Figure 6 is not convincing. The amines and amides seem to have decreased prior to rain fall. Are RH measurements available? Perhaps a better correlation can be seen with RH instead of rainfall?*

Reply: In figure 6, the concentrations of amines and amides started to decrease right after the sunrise on August 21, 2015 (i.e., before the actual rain fall), which is in fact consist with their typical diurnal cycles. We meant to show in Figure 6 that the concentrations of amines and amides are generally maintaining at a low level on raining days, hinting the role of wet deposition. In addition, no clear correlation between RH and the concentrations of amines and amides were observed.

14. *Line 459: specify what is meant by “slightly better”. Because of detection limits, or choice of reagent ion, or?*

Reply: We now state (Line 494-495) that “...are slightly better than those in previous studies using a similar protonated ethanol-CIMS method”, which clarifies that both sensitivities and detection limits are slightly better. .

15. *Lines 480-481: added references: Barnes et al., Borduas et al., Bunkan et al.*

Reply: We have added these references.

Technical comments:

1. *Line 47: missing the word “the” before the word detection.*

Reply: We have revised our manuscript accordingly.

2. *Lines 53-54: separate the sentences; one thought on the diurnal profile of amines and another on the diurnal profiles of amides.*

Reply: We now state (Line 53-54) that “the diurnal profiles and backward trajectory analysis suggest that in addition to the secondary formation of amides in the atmosphere, industrial emissions could be important sources of amides in urban Shanghai”.

3. *Lines 88, 121: physio-chemical should be written as physico-chemical. I think the authors are referring to physical properties and not to physiology properties.*

Reply: We have revised our manuscript accordingly.

4. *Line 187: delete “referred to that as” Lines 328-329: check syntax of the sentence.*

Reply: Line 187 (now Line 198): “referred to that as” has been removed.

Lines 328-329 (now lines 352-354): we now state that “In addition to the protonated C₁ to C₆-amines and amides, the presence of their clusters with one ethanol molecule is evident, which further confirms the identification of these species”.

5. *Lines 433-436: check syntax of the sentence. Line 487: progress is misspelled.*

Reply: Lines 433-436 (now lines 468-471): we now state “Three-day backward retroplumes (100 m above the ground level) from the Fudan sampling site are shown for air masses with mixing ratios of C₃-amides > 2670 pptv in Figure 8, and for air masses with the C₃-amide concentration range between 1340 pptv and 2650 pptv in Figure S10, respectively.”

Line 487: we revised our manuscript accordingly.

References:

- Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tome, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359-363, 10.1038/nature12663, 2013.
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- De Haan, D. O.; Hawkins, L. N.; Kononenko, J. A.; Turley, J. J.; Corrigan, A. L.; Tolbert, M. A.; Jimenez, J. L. Formation of nitrogencontaining oligomers by methylglyoxal and amines in simulated evaporating cloud droplets. *Environ. Sci. Technol.* 45 (3), 984– 991,2011.
- Galloway, M. M.; Powelson, M. H.; Sedehi, N.; Wood, S. E.; Millage, K. D.; Kononenko, J. A.; Rynaski, A. D.; De Haan, D. O. Secondary Organic Aerosol Formation during Evaporation of Droplets Containing Atmospheric Aldehydes, Amines, and Ammonium Sulfate. *Environ. Sci.*

Technol. 2014, 48 (24), 14417–14425.

- Nowak, J. B.: Chemical ionization mass spectrometry technique for detection of dimethylsulfoxide and ammonia, *J. Geophys. Res. Atmos.*, 107, 10.1029/2001jd001058, 2002.
- Pratt, K. A., Hatch, L.E., Prather, K. A.: Seasonal volatility dependence of ambient particle phase amines, *Environ. Sci. Technol.*, 43, 5276-5281, 10.1021/es803189n, 2009.
- Wang, L., Lal, V., Khalizov, A. F., and Zhang, R. Y.: Heterogeneous Chemistry of Alkylamines with Sulfuric Acid: Implications for Atmospheric Formation of Alkylammonium Sulfates, *Environ. Sci. Technol.*, 44, 2461-2465, 10.1021/es9036868, 2010.
- You, Y., Kanawade, V. P., de Gouw, J. A., Guenther, A. B., Madronich, S., Sierra-Hernández, M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H., and Lee, S. H.: Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS), *Atmos. Chem. Phys.*, 14, 12181-12194, 10.5194/acp-14-12181-2014, 2014.

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

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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 C₂-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.

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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 C₁- and C₂-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: *(...NR₃, 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.