

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.
- De Haan, D. O.; Tolbert, M. A.; Jimenez, J. L. Atmospheric condensed-phase reactions of glyoxal with methylamine. *Geophys. Res. Lett.* 36, L11819,2009.
- 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.