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Detection of atmospheric gaseous amines and amides by a high resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions

By Yao et al.

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.

General comments:

- 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.

- 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.

Schmeltz, I.; Hoffmann, D. Nitrogen-Containing Compounds in Tobacco and Tobacco Smoke. Chem. Rev. 1977, 77, 295−311

Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Sources of Fine Organic Aerosol. 1. Charbroilers and Meat Cooking Operations. Environ. Sci. Technol. 1991, 25, 1112− 1125.

Sollinger, S.; Levsen, K.; Wünsch, G. Indoor Pollution by Organic Emissions from Textile Floor Coverings: Climate Test Chamber Studies Under Static Conditions. Atmos. Environ. 1994, 28, 2369− 2378.

Cheng, Y.; Li, S.; Leithead, A. Chemical Characteristics and Origins of Nitrogen-Containing Organic Compounds in PM2.5 Aerosols in the Lower Fraser Valley. Environ. Sci. Technol. 2006, 40, 5846−5852.

Laskin, A.; Smith, J. S.; Laskin, J. Molecular Characterization of Nitrogen-Containing Organic Compounds in Biomass Burning Aerosols Using High-Resolution Mass Spectrometry. Environ. Sci. Technol. 2009, 43, 3764−3771.

Raja, S.; Raghunathan, R.; Kommalapati, R. R.; Shen, X.; Collett, J. L., Jr.; Valsaraj, K. T. Organic Composition of Fogwater in the Texas−Louisiana Gulf Coast Corridor. Atmos. Environ. 2009, 43, 4214−4222.

- 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.

  Roberts, J. M.; Veres, P. R.; Cochran, A. K.; Warneke, C.; Burling, I. R.; Yokelson, R. J.; Lerner, B.; Gilman, J. B.; Kuster, W. C.; Fall, R.; de Gouw, J. Isocyanic acid in the atmosphere and its possible link to smoke-related health effects. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 8966-8971.

- 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.

- 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.

- 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?

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

Specific comments:

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

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.

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

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.)

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?

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

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.

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.

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.

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

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.

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.

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?

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

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

Missing reviews on organic nitrogen:

Cape, J. N.; Cornell, S. E.; Jickells, T. D.; Nemitz, E. Organic nitrogen in the atmosphere - Where does it come from? A review of sources and methods. *Atmos. Res.* **2011**, *102*, 30-48.

Fowler, D.; Coyle, M.; Skiba, U.; Sutton, M. A.; Cape, J. N.; Reis, S.; Sheppard, L. J.; Jenkins, A.; Grizzetti, B.; Galloway, J. N.; Vitousek, P.; Leach, A.; Bouwman, A. F.; Butterbach-Bahl, K.; Dentener, F.; Stevenson, D.; Amann, M.; Voss, M. The global nitrogen cycle in the twenty-first century. *Philos. Trans. R. Soc. London, Ser. B* **2013**, *368*.

Missing reference on imines:

Bunkan, A. J. C.; Tang, Y.; Selleveg, S. R.; Nielsen, C. J. Atmospheric gas phase chemistry of CH2=NH and HNC. A first-principles approach. *J. Phys. Chem. A* **2014**, *118*, 5279-5288.

One of a few more missing reference on gas-phase amine measurements:

Dawson, M. L.; Perraud, V.; Gomez, A.; Arquero, K. D.; Ezell, M. J.; Finlayson-Pitts, B. Measurement of gas-phase ammonia and amines in air by collection onto an ion exchange resin and analysis by ion chromatography. *Atmos. Meas. Tech.* **2014**, *7*, 2733-2744, 12 pp.

Technical comments:

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

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

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

Line 187: delete “referred to that as”

Lines 328-329: check syntax of the sentence.

Lines 433-436: check syntax of the sentence.

Line 487: progress is misspelled.