Investigating Organic Nitrogen Chemistry in Atmospheric Particles using High Resolution Aerosol Mass Spectrometry

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Keywords: Organic nitrogen (ON), AMS, organic aerosol chemistry
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Organic nitrogen (ON) compounds are a ubiquitous component of atmospheric particles and cloud and fog waters and usually account for a significant fraction of the total nitrogen content in atmospheric condensed phases (*Cape et al., 2011*). Understanding the properties and lifecycle processes of atmospheric ON is therefore important for addressing critical environmental issues such as global nitrogen cycling and aerosol's impacts on climate change, human health, and air quality. However, the chemistry of atmospheric ON has so far remained poorly studied, mainly due to the chemical complexity of ON compounds and a lack of highly time-resolved measurement techniques. In this work, we optimize the method of using high resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS) to analyze ON components in atmospheric particles and water drops. A large number of different types of ON compounds, including amines, amino acids, amides, organic nitrates, nitriles, and nitrogen-containing heterocylics, were analyzed using an HR-ToF-AMS and their mass spectra thoroughly analyzed. As expected, N-containing ions such as $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ are commonly observed in the HR-ToF-AMS spectra of ON compounds. In addition, ions that are commonly attributed to inorganic species such as ammonium and nitrate, i.e., NH_x^+ and NO_x^+ ions, in the ON spectra, are frequently detected too. In addition, CH_2N^+ (*m/z* = 28) is also found to present in the HR-ToF-AMS spectra of various ON compounds. However, this ion is hard to quantify in ambient aerosols due to interference from the N_2^+ ion signal of air. Overall, we estimate that the average nitrogen-to-carbon (N/C) ratio in atmospheric organic aerosols is underestimated by ~ 20% using the standard calibration factor reported in *Aiken et al.* (2008). In addition, we characterize the mass spectral features of various types of ON species and use this information to interpret ON composition in ambient aerosols and fog and cloud waters. The temporal variation profiles and diurnal cycles of major $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ ions are studied, as well their correlations with common AMS tracer ions, such as $C_4H_9^+$ (*m/z* = 57) for hydrocarbon-like organic aerosol (HOA, representing urban primary OA), CO_2^+ (*m/z* = 44) for oxygenated OA (OOA, representing secondary OA), and $C_2H_4O_2^+$ (*m/z* = 60) for biomass burning OA (BBOA). Our findings provide valuable insights into the chemical composition, sources, and processes of ON species in atmospheric condensed phases.

This work was supported by the by the Electric Power Research Institute (EP-P41521/C18264) and the California Agricultural Experiment Station (Projects CA-D-ETX-2102-H.

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