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Diurnal cycles of ammonia, nitrous acid and nitric acid at a forest site in Finland in summer 2010

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Background

In July – August 2010 a large campaign "Hyytiälä United Measurements of Photochemistry and Particles in Air - Comprehensive Organic Precursor Emission Concentration 2010 (HUMPPA – COPEC-10)", was conducted in a boreal forest at the SMEAR II station in Hyytiälä, southwestern central Finland. The campaign was organized by the Max Planck Institute for Chemistry and the University of Helsinki. The general goal was to study links between gas phase oxidation chemistry and particle properties and processes.

The Finnish Meteorological Institute contributed to the campaign with an on-line analyzer MARGA 2S (Ten Brink et al., 2007) for semi-continuous (1-hr time resolution) measurement of water-soluble gases and ions. Concentrations of gases (HCl, HNO_3, HNO_2, NH_3, SO_2) and major ions in particles (Cl, NO_3, SO_4, NH_4, Na, K, Mg, Ca) were measured in two size fractions: PM2.5 and PM10. The MARGA has been operational at SMEAR II since 21 June. Here we discuss data collected until 4 September, 2010, and restrict the analysis to the nitrogen-containing gases. NH_3 plays a key role in neutralizing acidic atmospheric compounds and in aerosol formation. The concentration of semi-volatile aerosol species such as ammonium nitrate and ammonium chloride is strongly dependent on the gas phase precursors, NH_3, HNO_3 and HCl. HONO is of atmospheric importance due to its expected significant contribution to the production of OH radicals.

Results and discussion

The median concentrations of ammonia (NH_3), nitrous acid (HONO) and nitric acid (HNO_3) during whole period of 21 June – 4 September were 0.24 ppb, 0.069 ppb and 0.22 ppb, respectively. A very clear diurnal cycle of all these gases was observed, especially in July. All data were classified according to the measurement hour. In July the highest median concentration of ammonia, 0.59 ppb was observed in the afternoon at 15:00 and the lowest, 0.17 ppb at 05:00. Similarly, the highest median concentration of nitric acid, 0.32 ppb was observed at 15:00 and the lowest, 0.20 ppb at 04:00. The clear diurnal cycles of ammonia and nitric acid suggest that they may at least partly be due to evaporation of ammonium nitrate particles in the hottest time of the warm July 2010 and condensation on particles at the cooler night. For nitrous acid the diurnal variation was the opposite: the highest median concentration 0.20 ppb was observed very early in the morning at 03:00 and the minimum concentration 0.045 ppb in the evening at 18:00, in agreement with the photolysis of HONO. Towards the end of the campaign both the concentrations and their diurnal variations decreased. In 25 August to 04 September the median concentrations of ammonia, nitrous acid and nitric acid were 0.10 ppb, 0.061 ppb, and 0.18 ppb, respectively. From the 24-hour classification the medians of daily maximum and minimum concentrations were 0.16 and 0.069 ppb for ammonia, 0.094 and 0.021 ppb for nitrous acid, and 0.20 and 0.17 ppb for nitric acid.

Acknowledgement

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Reference

Ten Brink H., Otjes R., Jongejan P., Slanina S. (2007) An instrument for semi-continuous monitoring of the size-distribution of nitrate, ammonium, sulphate and chloride in aerosol, Atm. Environ. 41, 2768-2779.