

Emission of nitrous acid from soil and biological soil crusts as a major source of atmospheric HONO on Cyprus

Hannah Meusel (1), Alexandra Tamm (1), Dianming Wu (1), Uwe Kuhn (1), Anna-Lena Leifke (1), Bettina Weber (1), Hang Su (1), Jos Lelieveld (2), Thorsten Hoffmann (3), Ulrich Pöschl (1), and Yafang Cheng (1)

(1) Max Planck Institute for Chemistry (Multiphase Chemistry Department), Mainz, Germany , (2) Max Planck Institute for Chemistry (Atmospheric Chemistry Department), Mainz, Germany , (3) Johannes Gutenberg University, Institute for Inorganic and Analytical Chemistry, Mainz, Germany

Elucidation of the sources and atmospheric chemistry of nitrous acid (HONO) is highly relevant, as HONO is an important precursor of OH radicals. Up to 30% of the OH budget are formed by photolysis of HONO, whereas major fractions of HONO measured in the field derive from yet unidentified sources. Heterogeneous conversion of nitrogen dioxide (NO₂) to HONO on a variety of surfaces (soot, humic acid aerosol) is assumed to be a major HONO source (Stemmler et al., 2007, Ammann et al., 1998). In rural regions, however, NO₂ concentrations were found to be too low to explain observed HONO concentrations, as e.g., in the case of a recent field study on the Mediterranean island of Cyprus (Meusel et al., 2016). In this study a good correlation between missing sources of HONO and nitrogen oxide (NO) was found indicating a common origin of both reactive nitrogen compounds. Simultaneous emission of HONO and NO from soil was reported earlier (Oswald et al., 2013), and enhanced emission rates were found when soil was covered by biological soil crusts in arid and semi-arid ecosystems (Weber et al., 2015). In the present study we measured HONO and NO emissions of 43 soil and soil crust samples from Cyprus during full wetting and drying cycles under controlled laboratory conditions by means of a dynamic chamber system. The observed range of HONO and NO emissions was in agreement with earlier studies, but unlike the study of Weber et al. (2015), we found highest emission from bare soil, followed by soil covered by light and dark cyanobacteria-dominated biological soil crusts. Emission rates correlated well with the nitrite and nitrate contents of soil and biological soil crust samples, and higher nutrient contents of bare soil samples, as compared to the previous biological soil crust study, explain the higher bare soil emissions. Integrating the emission rates of bare soil and the different types of biological soil crusts, based on their local relative abundance, the calculated total community flux of NO was found to be by far too low to explain the NO missing source observed during the Cyprus field campaign. For HONO, the calculated community flux was in good agreement with the mean of the missing HONO source found during the field study in Cyprus, indicating that soil and the biological soil crust communities represent a dominant source in remote or rural areas.

Ammann, M. et al.: Heterogeneous production of nitrous acid on soot in polluted air masses, *Nature*, 395, 157-160, 1998.

Meusel, H. et al.: Daytime formation of nitrous acid at a coastal remote site in Cyprus indicating a common ground source of atmospheric HONO and NO, *Atmos. Chem. Phys.*, 16, 14475-14493, 2016.

Oswald, R. et al.: HONO Emissions from Soil Bacteria as a Major Source of Atmospheric Reactive Nitrogen, *Science*, 341, 1233-1235, 2013.

Stemmler, K. et al.: Light induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol, *Atmos. Chem. Phys.*, 7, 4237-4248, 2007.

Weber, B. et al.: Biological soil crusts accelerate the nitrogen cycle through large NO and HONO emissions in drylands, *Proceedings of the National Academy of Sciences of the United States of America*, 112, 15384-15389, 2015.