Geophysical Research Abstracts, Vol. 7, 07661, 2005
SRef-ID: 1607-7962/gra/EGU05-A-07661

A new Source of Nitrous Acid: NO_2 Photochemistry on various organic Surfaces

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The photolysis of nitrous acid (HONO) is of considerable atmospheric interest as it produces the OH radical, a key species in the atmospheric oxidation reactions of many air pollutants and a crucial intermediate in the formation of photochemical smog in the troposphere. Many studies have shown that nitrous acid can accumulate during nighttime before undergoing photolysis in the early morning, which creates an important morning OH radical burst. Despite many studies, to date the formation mechanism of HONO in the atmosphere is still not completely understood.

New highly sensitive field measurements, which allowed the determination of the photo-depleted daytime HONO concentrations, showed a significant imbalance between the known sources and the observed concentrations. These observations imply that during the day a significantly enhanced HONO formation occurs in the boundary layer and that HONO photolysis can be the dominant source of OH radicals throughout the day in the investigated environments.

In this collaborative study, we discuss the heterogeneous photochemical production of HONO and show that environmental relevant surfaces can act as very efficient substrate for the photochemical conversion of NO_2 to HONO.

By means of laboratory experiments, it is shown that light absorbing organic material reduces NO_2 very efficiently, when irradiated at different wavelength ranges of the solar spectrum. The HONO formation is discussed mechanistically on a molecular level by using simplified organic model substances as light absorbers and electron

donors and quantitatively by the investigation of complex natural substrates (as soil) under environmental relevant conditions. It is shown that this surface photochemistry is likely an important source of atmospheric HONO.