Geophysical Research Abstracts
Vol. 15, EGU2013-10891, 2013
EGU General Assembly 2013

Long-term uptake of hydrogen peroxide to ice – a laboratory study

Thomas Ulrich, Markus Ammann, and Thorsten Bartels-Rausch
Paul Scherrer Institut (PSI), Villigen PSI, Switzerland (thorsten.bartels-rausch@psi.ch)

The trace gas hydrogen peroxide is chemical very reactive both in the atmosphere and in surface snow and its concentration may significantly determine gas-phase OH_x and thus O_3 levels. It is further the only major atmospheric oxidant that is directly taken up by snow and ice. This removal process might have direct impact on its gas-phase concentration and thus on the oxidations capacity of the atmosphere. Further, reconstructions of its atmospheric concentration from ice core records can deliver crucial information about past atmosphere and are of great interest [1].

Characterizing the physical exchange of H_2O_2 between the snow grains or ice surfaces and the surrounding air has consequently received much attention in laboratory-based studies. In one type of studies that focused on short time scales, a detailed description of the adsorption equilibrium between the gas phase and ice was derived [2,3]. These studies, done on very thin ice films, did not give any indication that H_2O_2 is incorporated into the bulk ice. Earlier studies with packed snow samples have shown a different picture of the H_2O_2 – ice interaction, where surface adsorption and accommodation into the bulk ice governed the overall uptake in long-lasting experiments [4]. Moreover, the uptake decreased strongly with increasing temperatures, before it slightly increase at temperatures above approximately 261 K. These different temperature dependences of the equilibrium may reflect the interaction with ice at very low temperatures and the uptake in to a liquid fraction at higher temperatures.

In summary, 3 processes – surface adsorption, bulk uptake, dissolution into liquid – that might govern the interaction of H_2O_2 with snow at environmentally relevant temperatures have been identified in some studies. Other studies indicate that only surface adsorption governs the exchange with the gas-phase and give no indication of long-lasting uptake to the bulk of the ice. Further, the detailed parameterization of the adsorption equilibrium is not consistent between the two studies [2,3]. To predict the partitioning of H_2O_2 to surface snow under varying environmental settings, the importance, the kinetics, and the precise mechanism of each process needs further investigation. Here, we present results from a laboratory study that might help to explain the deviating results of recent studies.

In this study the H_2O_2 – ice interaction was investigated over long time-scales of hours. For these experiments about 4×10^{10} molecules $H_2O_2\ \mathrm{cm}^{-3}$ in nitrogen were passed through an ice coated wall flow tube at atmospheric pressure. Temperature was varied between 230 K and 260 K. The concentration of H_2O_2 in the gas-phase was monitored with time upon exposure to the ice to derive the amount of H_2O_2 lost to the ice phase. Additionally, the H_2O_2 was directly determined in the ice phase in some experiments. These experiments quantitatively confirm that H_2O_2 reversibly adsorbs to thin ice films in agreement with previous studies on thin ice films [3]. However, additionally a long-lasting uptake of H_2O_2 to thin ice films is observed for the first time. The total amount of H_2O_2 taken up by the ice film via this slow process might easily exceed the adorbed H_2O_2 under environmental time-scales. Possible mechanisms of this long-lasting uptake (in absence of liquid) and the reversibility are discussed.

[1] Bartels-Rausch, T., Jacobi, H. W., Kahan, T. F., Thomas, J. L., Thomson, E. S., Abbatt, J. P. D., Ammann, M., Blackford, J. R., Bluhm, H., Boxe, C. S., Domine, F., et al.: Relationship between snow microstructure and physical and chemical processes, Atmos. Chem. Phys. Discuss., 12(11), 30409–30541, doi:10.5194/acpd-12-30409-2012, 2012.

[2] Clegg, S. M. and Abbatt, J. P. D.: Uptake of Gas-Phase SO_2 and H_2O_2 by Ice Surfaces: Dependence on Partial Pressure, Temperature, and Surface Acidity, J. Phys. Chem. A, 105(27), 6630–6636, doi:10.1021/jp010062r, 2001.

[3] Pouvesle, N., Kippenberger, M., Schuster, G. and Crowley, J. N.: The interaction of H_2O_2 with ice surfaces between 203 and 233 K, Phys. Chem. Chem. Phys., 12(47), 15544–15550, doi:10.1039/C0cp01656j [online] Available from: http://pubs.rsc.org/en/Content/ArticleHTML/2010/CP/C0CP01656J, 2010.

[4] Conklin, M. H., Sigg, A., Neftel, A. and Bales, R. C.: Atmosphere-Snow Transfer-Function for H_2O_2 - Microphysical Considerations, J. Geophys. Res., 98(D10), 18367–18376, doi:10.1029/93JD01194, 1993.