Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union










Atmos. Chem. Phys., 9, 1817-1829, 2009
www.atmos-chem-phys.net/9/1817/2009/


# HOCl chemistry in the Antarctic Stratospheric Vortex 2002, as observed with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS)

T. von Clarmann[1,*], N. Glatthor[1], R. Ruhnke[1], G. P. Stiller[1], O. Kirner[1], T. Reddmann[1], M. Höpfner[1], S. Kellmann[1], W. Kouker[1], A. Linden[1], and B. Funke[2]

[1]Forschungszentrum Karlsruhe and Karlsruhe University, Institut für Meteorologie und Klimaforschung, Karlsruhe, Germany

[2]Instituto de Astrofísica de Andalucía, CSIC, Granada, Spain

[*]now also at: Univ. de Toulouse, UPS, CNRS, Laboratoire d'Aérologie, 14 avenue Edouard Belin, 31400 Toulouse, France

Abstract. In the 2002 Antarctic polar vortex enhanced HOCl mixing ratios were detected by the Michelson Interferometer for Passive Atmospheric Sounding both at altitudes of around 35 km (1000 K potential temperature), where HOCl abundances are ruled by gas phase chemistry and at around 18–24 km (475–625 K), which belongs to the altitude domain where heterogeneous chlorine chemistry is relevant. At altitudes of 33 to 40 km polar vortex HOCl mixing ratios were found to be around 0.14 ppbv as long as the polar vortex was intact, centered at the pole, and thus received relatively little sunlight. This is the altitude region where in midlatitudinal and tropic atmospheres peak HOCl mixing ratios significantly above 0.2 ppbv (in terms of daily mean values) are observed. After deformation and displacement of the polar vortex in the course of a major warming, ClO-rich vortex air was more exposed to sunlight, where enhanced $HO_x$ abundances led to largely increased HOCl mixing ratios (up to 0.3 ppbv), exceeding typical midlatitudinal and tropical amounts significantly. The HOCl increase was preceded by an increase of ClO. Model runs could reproduce these measurements only when the Stimpfle et al. (1979) rate constant for the reaction $ClO+HO_2 \rightarrow HOCl+O_2$ was used but not with the current JPL recommendation. At an altitude of 24 km, HOCl mixing ratios of up to 0.15 ppbv were detected. This HOCl enhancement, which is already visible in 18 September data, is attributed to heterogeneous chemistry, which is in agreement with observations of polar stratospheric clouds. The measurements were compared to a model run where no polar stratospheric clouds appeared during the observation period. The fact that HOCl still was produced in the model run suggests that a significant part of HOCl was generated from ClO rather than directly via heterogeneous reaction. Excess ClO, lower $ClONO_2$ and earlier loss of HOCl in the measurements are attributed to ongoing heterogeneous chemistry which is not reproduced by the model. On 11 October, polar vortex mean daytime mixing ratios were only 0.03 ppbv.

Final Revised Paper (PDF, 7233 KB) Discussion Paper (ACPD)

Citation: von Clarmann, T., Glatthor, N., Ruhnke, R., Stiller, G. P., Kirner, O.,

Reddmann, T., Höpfner, M., Kellmann, S., Kouker, W., Linden, A., and Funke, B.: HOCl chemistry in the Antarctic Stratospheric Vortex 2002, as observed with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), Atmos. Chem. Phys., 9, 1817-1829, 2009. Bibtex EndNote Reference Manager