Atmos. Chem. Phys. Discuss., 14, 14833–14854, 2014
www.atmos-chem-phys-discuss.net/14/14833/2014/
doi:10.5194/acpd-14-14833-2014

Atmospheric Chemistry and Physics Discussions
Open Access

Contribution of liquid, NAT and ice particles to chlorine activation and ozone depletion during Antarctic winter and spring

O. Kirner[1], R. Müller[2], R. Ruhnke[3], and H. Fischer[3]

[1]Karlsruhe Institute of Technology, Steinbuch Centre for Computing (SCC), Karlsruhe, Germany
[2]Institute of Energy and Climate Research – Stratosphere (IEK-7), Research Centre Jülich GmbH, Jülich, Germany
[3]Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research (IMK), Karlsruhe, Germany

Received: 24 April 2014 – Accepted: 10 May 2014 – Published: 5 June 2014

Correspondence to: O. Kirner (ole.kirner@kit.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Heterogeneous reactions in the Antarctic stratosphere are the cause of chlorine activation and ozone depletion, but the relative roles of different types of PSCs in chlorine activation is an open question. We use multi-year simulations of the chemistry-climate model EMAC to investigate the impact that the various types of PSCs have on Antarctic chlorine activation and ozone loss.

One standard and three sensitivity EMAC simulations have been performed. The results of these simulations show that the significance of heterogeneous reactions on NAT and ice particles, in comparison to liquid particles, is subordinate regarding chlorine activation and ozone depletion in Antarctic winter and spring. The heterogeneous chemistry on liquid particles is sufficient to activate at least 90 % of the chlorine reservoir species. With the exception of the upper PSC regions between 10 and 30 hPa where temporarily the ice particles have a relevant contribution to the chlorine activation and during the initial PSC occurrence with short NAT contributions the liquid particles alone are sufficient to activate almost all of the available chlorine.

In the model simulations heterogeneous chemistry on liquid particles is responsible for more than 90 % of the ozone depletion in Antarctic spring. Only up to 5 DU of column ozone in high southern latitudes is depleted by chlorine activation due to additional heterogeneous chemistry on ice particles and less than 0.5 DU due to additional heterogeneous chemistry on NAT particles.

1 Introduction

Polar Stratospheric Clouds (PSCs) consist of supercooled ternary solution (STS, type 1b PSC), Nitric Acid Trihydrate (NAT, type 1a PSC) and ice particles (type 2 PSC). An accurate representation of PSCs and cold binary solutions of the sulphuric acid background/water aerosol is essential for chlorine activation and polar ozone depletion in chemistry-climate-models (CCMs). The liquid (cold binary aerosols and STS particles) and solid particles (NAT and ice particles) allow heterogeneous reactions to proceed, which cause the activation of chlorine reservoirs to chlorine radicals leading to ozone destruction and for the stratospheric denitrification (through NAT particles) resulting in a delay in the deactivation of this active chlorine in polar spring (e.g., Solomon et al., 1986; Lowe and MacKenzie, 2008).

To consider the relevance of PSCs for polar chlorine activation, a new algorithm based on an efficient growth of NAT particles, developed by van den Broek et al. (2004), has been implemented into the submodel PSC of the chemistry-climate model ECHAM5/MESSy for Atmospheric Chemistry (EMAC) to improve the representation of the PSCs in this model. The submodel PSC and the new NAT parameterisation are described in Kirner et al. (2011).

Over the last years a discussion developed about the contribution of cold binary aerosols, STS, NAT and ice particles to chlorine activation. Drdla and Müller (2012) have raised the question of the necessity of NAT and ice particles for reaching the full polar stratospheric chlorine activation. They also argue that assuming only liquid particles or even liquid binary particles only leads to a minor reduction of the simulated chlorine activation and ozone loss.

Wegner et al. (2012) examined the importance of the cold binary aerosols for chlorine activation in the Arctic winters 2004/2005 and 2009/2010 with the help of in-situ observations. They concluded that the surface area provided by PSCs did not significantly impact chlorine activation rates in these both winters. Wohltmann et al. (2013) showed, based on simulations of the Arctic winter 2009/2010 with the Lagrangian model ATLAS that liquid aerosols alone allow to explain the observed mixing ratios of active chlorine and ozone from MLS, ACE-FTS and in-situ measurements.

However in these Arctic studies the contribution of ice particles to chlorine activation was not investigated and there is still the question if liquid particles are also sufficient to activate the complete inorganic chlorine during Antarctic winters. Therefore we performed a standard EMAC simulation from 2000 to 2012 and three additional sensitivity simulations from 2005 to 2012 with different assumptions for heterogeneous chemistry on stratospheric aerosol and PSC particles. By comparing the results of the EMAC standard and sensitivity simulations it is possible to determine the contribution of liquid particles (in EMAC the cold binary aerosols and STS particles are not distinguished, see Kirner et al., 2011), NAT particles and ice particles to chlorine activation in polar winter and corresponding ozone depletion in polar spring.

2 The EMAC model

The ECHAM/MESSy Atmospheric Chemistry (EMAC) model is a numerical chemistry and climate simulation system that includes submodels describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2006). It uses the Modular Earth Submodel System (MESSy) to link multi-institutional numerical codes (Jöckel et al., 2005). The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al., 2006). For the present study we applied EMAC (ECHAM5 version 5.3.01, MESSy version 1.10) in the T42L39MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approx. 2.8° by 2.8° in latitude and longitude) with 39 vertical hybrid pressure levels up to 0.01 hPa (approx. 80 km) and with a time step of 10 min.

Besides the submodel MECCA1 (Sander et al., 2005) for the calculation of gas-phase chemistry and the submodel PSC for the simulation of polar stratospheric clouds (Kirner et al., 2011) the following submodels have been used in our study: OFFLEM for offline emissions of trace gases and aerosols (Kerkweg et al., 2006b), TNUDGE for tracer nudging (Kerkweg et al., 2006b), DRYDEP for dry deposition of trace gases and aerosols (Kerkweg et al., 2006a), SEDI for the sedimentation of aerosol particles (Kerkweg et al., 2006a), JVAL for the calculation of photolysis rates (Landgraf and Crutzen, 1998), SCAV for the scavenging and liquid phase chemistry in cloud and precipitation (Tost et al., 2006a), CONVECT for the parameterisation of convection (Tost et al., 2006b), LNOX for the source of NO_x produced by lightning (Tost et al., 2007b), PTRAC for additional prognostic tracers (Jöckel et al., 2008), CVTRANS for convective tracer transport, TROPOP for diagnosing the tropopause and boundary layer height, H2O for stratospheric water vapour, RAD4ALL for the radiation calculation, HETCHEM for calculating reaction rate coefficients of heterogeneous reactions on aerosols (see Jöckel et al., 2006, and references therein), and CLOUD for calculating the cloud cover as well as cloud microphysics including precipitation (Tost et al., 2007a).

Reaction rate coefficients for gas phase reactions and absorption cross sections for photolysis are taken mainly from Sander et al. (2011).

3 The submodel PSC

The submodel PSC is originally based on the “Mainz Photochemical Box Model” (Crutzen et al., 1992; Müller et al., 1994; Grooß, 1996; Meilinger, 2000) and was improved and extended by Buchholz (2005) and Kirner (2008). A comprehensive description of the submodel PSC is given by Kirner et al. (2011). The submodel PSC simulates the number densities, mean radii and surfaces of liquid sulphuric acid aerosols, supercooled ternary solutions (STS), nitric acid trihydrate (NAT) particles and ice particles. Different sedimentation schemes for these particles are included. Together with the submodel HETCHEM the reaction rate coefficients of all heterogeneous reactions are calculated, which are important for the ozone depletion in polar spring. Heterogeneous reaction rates and their temperature dependencies on NAT were calculated according to the parameterisation of Carslaw et al. (1995) based on the measurements of Hanson and Ravishankara (1993). The heterogeneous reaction rate coefficients on liquid particles are taken from Hanson and Ravishankara (1994) and Hanson et al. (1994), the uptake coefficients and reaction probabilities for ice particles from Sander et al. (2011).

The formation of STS in the model is based on Carslaw et al. (1995) and takes place through uptake of nitric acid (HNO_3) by liquid sulphuric acid aerosols. The formation of ice particles in the model is based on the thermodynamic approach of Marti and

Mauersberger (1993). For the ice nucleation 50 % H_2O supersaturation is assumed to be necessary.

Besides the parameterisations for the formation of liquid and ice particles, there are two parameterisations for the formation of NAT particles included in the PSC submodel. It is possible to choose either a "thermodynamical NAT parameterisation" assuming instantaneous thermodynamical equilibrium (Hanson and Mauersberger, 1988) or a new parameterisation for NAT particles based on the efficient growth and sedimentation algorithm of Carslaw et al. (2002) and van den Broek et al. (2004) implemented into the submodel by Kirner et al. (2011). In both cases NAT formation takes place below the NAT existence temperature (T_{NAT}, depending on the pressure and on the partial pressures of HNO_3 and H_2O) with the assumption of a necessary super cooling of 3 K (Schlager and Arnold, 1990; Dye et al., 1992).

4 Performed simulations

Four different EMAC simulations were performed using the new submodel PSC: a standard simulation (*Standard*) from 2000 to 2012 with heterogeneous chemistry on liquid, NAT and ice particles and three additional sensitivity simulations from 2005 to 2012. In the three sensitivity simulations we only changed the heterogeneous chemistry on PSC particles by switching on and off the chemistry on liquid, NAT and ice particles. We performed one sensitivity simulation without heterogeneous chemistry (*NoHet*), one sensitivity simulation with heterogeneous chemistry only on liquid particles (*Liquid*) and one sensitivity simulation with heterogeneous chemistry only on liquid and NAT particles, but excluding heterogeneous chemistry on ice particles (*LiquidNAT*) (see also Table 1).

The formation and distribution of the PSC particles is the same for the four simulations. Also the denitrification caused by the sedimentation of NAT particles is simulated in all simulations consistently. Only the assumptions regarding the heterogeneous chemistry on liquid, NAT and ice particles are different.

To simulate realistic synoptic conditions we apply in all four EMAC simulations a Newtonian relaxation technique of the prognostic variables temperature, vorticity, divergence and the surface pressure. We applied this nudging technique above the boundary layer and below 1 hPa with nudging strengths as recommended in van Aalst (2005) using the ERA-Interim reanalysis (Dee et al., 2011) from the European Centre for Medium-range Weather Forecasts (ECMWF). Boundary conditions for greenhouse gases are from the IPCC-A1B scenario (IPCC, 2007), for ozone depleting substances (CFCs and halons) from the WMO-Ab scenario (WMO, 2007).

The simulation includes a comprehensive chemistry setup with 104 gas phase species, 234 gas phase reactions, 67 photolysis reactions, and 11 heterogeneous reactions on liquid aerosols, NAT- and ice particles (Jöckel et al., 2006).

5 Mean development of liquid, NAT and ice particles in EMAC and simulated denitrification

The formation and distribution of PSCs are simulated in EMAC very reasonably. For example in Fig. 1 the simulated denitrification due to NAT particles from the standard simulation is presented. After the temperature has dropped below 192 K, and thus the necessary temperature threshold is reached for NAT formation the first NAT particles are formed on 15 May 2004 over Antarctica. Due to the continued cooling from 19 to 31 May 2004 the number density of NAT increases up to 240 m^{-3} and, simultaneously, the NAT-PSCs are expanding into a larger area. In HNO_3 the first hint of denitrification due to sedimentation of NAT is visible on 19 May 2004. Ongoing NAT formation and sedimentation of NAT particles leads to less HNO_3 in the area in which NAT particles are present.

Besides the NAT particles, also ice particles and liquid particles in form of cold binary solutions ($H_2SO_4 \cdot H_2O$) and supercooled ternary solutions ($HNO_3 \cdot H_2SO_4 \cdot H_2O$) are calculated with the submodel PSC. In Fig. 2 the time development of liquid particles, NAT and ice particles is shown in form of an average over the latitudes from 80° S to 90° S and over the five years from 2005 to 2009. The illustrated results are valid for the standard and for all three sensitivity simulation, i.e. the formation and development of stratospheric aerosol and PSCs are the same for each simulation. In average NAT is in the EMAC simulations visible from mid-May until October in the area of lower temperatures. The relatively slow increase of the number density from 0 to the average maximum of over 200 m^{-3} by end of May is caused by different first NAT appearances in the individual years 2005 to 2009. The decrease between June to September is caused by the sedimentation of larger NAT particles and the related denitrification. Ice particles exist mainly from June to September with mean maxima of over 40 000 m^{-3}. In comparison to liquid and NAT particles they have the largest surface densities with values up to 38 $\mu\mathrm{m}^2\,\mathrm{cm}^{-3}$. The liquid particles have the second largest surface densities with values up to 6.8 $\mu\mathrm{m}^2\,\mathrm{cm}^{-3}$, the NAT particles the smallest with maxima of 0.11 $\mu\mathrm{m}^2\,\mathrm{cm}^{-3}$.

6 Contribution of NAT, ice and liquid particles to stratospheric chlorine activation and ozone depletion

By comparing the standard and the sensitivity simulations it is possible to determine the contribution of the heterogeneous reactivity of liquid, NAT and ice particles to polar chlorine activation and corresponding ozone depletion in polar spring. In this way it is possible to assess the impact of the liquid particles by subtraction the results of the simulation *NoHet* from the results of the simulation *Liquid*. The absolute contribution of additional NAT chemistry is calculated by subtraction the results of the simulation *Liquid* from the simulation *LiquidNAT*, and the contribution of additional heterogeneous chemistry on ice particles by subtraction the results of the simulation *LiquidNAT* from the simulation *Standard*. For a better statistics we averaged the ClO_x and O_3 results over the southern high latitudes from 80° S to 90° S and over the five year time period from 2005 to 2009 (Figs. 3 and 4) and the ozone columns as zonal mean over the same five years (Fig. 5).

In Fig. 3 (top left) the averaged development of ClO_x in the standard simulation is illustrated. The contributions of liquid, NAT and ice particles are shown in Fig. 3 (top right and two bottom panels). It is apparent that the simulated ClO_x development with maximum values of about 2.9 ppbv is mainly caused due to the heterogeneous chemistry on liquid particles with contributions up to 2.6 ppbv. There is almost no extra chlorine activation due to the additional heterogeneous chemistry on NAT particles with a contribution below 0.1 ppbv and only a slight additional chlorine activation due to heterogeneous chemistry on ice particles. The relevant contribution of the ice particles is mainly in the upper PSC region in which only few liquid particles are simulated (see Fig. 2). A maximum about 0.33 ppbv extra ClO_x is present in the region between 10 and 30 hPa from end of June until mid-September due to additional heterogeneous chemistry on ice.

The contribution of liquid particles to chlorine activation is for most of the time over 90 %. Between June and August in the region between 30 hPa and 100 hPa the contribution is almost 100 %. Only in the upper PSC region, as mentioned above, the heterogeneous chemistry of additional ice particles is relevant with maximum contributions in the range of 10 % to 15 % of the total chlorine activation. Only during the initial PSC occurrence have the NAT particles a relevant contribution to chlorine activation with up to 10 % in Mid-May in the region between 20 hPa and 50 hPa.

The ozone development resulting from the chlorine activation is shown in Fig. 4. The ozone depletion is highest from mid-September to late October forming the ozone hole (see for example Grooß et al., 2011). The largest impact to this ozone depletion comes from the chlorine activated on liquid particles with an ozone depletion of more than 2500 ppbv. In contrast in the upper PSC region only values up to 170 ppbv during the maximum ozone depletion can be attributed to the simulation of additional heterogeneous chemistry on ice particles. The contribution of NAT particles is visible in the region between 10 to 30 hPa in September and October, but the values are close to zero.

The total effect on ozone chemistry of applying heterogeneous chemistry on different PSC particles is illustrated in form of the time development of ozone columns in the Southern Hemisphere in Fig. 5. Liquid particles are mainly responsible for the ozone depletion noticeable as a decrease in ozone columns by more than 130 DU in early October in high southern latitudes. During September to October in the southern high latitudes the contribution of liquid particles to the simulated ozone depletion is at least 95 %. The contribution of additional heterogeneous chemistry on ice particles only reaches up to 5 DU and is always smaller than 5 %, the contribution of additional heterogeneous chemistry on NAT particles is less than 0.5 DU and thus almost negligible. On the other hand the NAT particles are essential for the denitrification in polar spring and thus have an additional indirect influence on the formation of the ozone hole.

7 Conclusions

The significance of heterogeneous reactions on NAT and ice particles with respect to chlorine activation and ozone depletion in Antarctic winter and spring is small compared to reactions on liquid particles in standard and sensitivity simulations performed with the EMAC model. The simulated heterogeneous chemistry on liquid particles is sufficient to activate at least about 90 % of the chlorine. With the exception of the upper PSC regions between 10 and 30 hPa, where temporarily the ice particles have relevant contribution to chlorine activation and during the initial PSC occurrence with NAT contributions, the liquid particles are sufficient to activate almost all of the available chlorine reservoirs alone.

In the model simulations, heterogeneous chemistry on liquid particles is responsible for more than 90 % of the ozone depletion in polar spring. Only up to 5 DU of column ozone in high southern latitudes is depleted by chlorine activation due to additional heterogeneous chemistry on ice particles and less than 0.5 DU due to additional heterogeneous chemistry on NAT particles.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◂◂ ▸▸
◂ ▸
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

By confirming the major contribution of liquid particles to chlorine activation some of the latest published findings could be essential for the future study of the stratospheric polar ozone development. Hence, regarding the ozone development it will on the one hand be crucial how strong the future cooling in the lower and middle stratosphere will be in polar winter and spring and how strong this will be affecting the occurrence of PSCs (i.e., Butchart et al., 2010; Bohlinger et al., 2014). On the other hand also the future development of the background stratospheric aerosol, as discussed in Solomon et al. (2011), can lead to an altered distribution of liquid particles with implications for the polar chlorine activation.

The service charges for this open access publication
have been covered by a Research Centre of the
Helmholtz Association.

References

Bohlinger, P., Sinnhuber, B.-M., Ruhnke, R., and Kirner, O.: Radiative and dynamical contributions to past and future Arctic stratospheric temperature trends, Atmos. Chem. Phys., 14, 1679–1688, doi:10.5194/acp-14-1679-2014, 2014. 14843

Buchholz, J.: Simulations of Physics and Chemistry of Polar Stratospheric Clouds with a General Circulation Model, Ph. D. thesis, Johannes Gutenberg University Mainz, Mainz, Germany, 2005. 14837

Butchart, N., Cionni, I., Eyring, V., Shepherd, T. G., Waugh, D. W., Akiyoshi, H., Austin, J., Brühl, C., Chipperfield, M. P., Cordero, E., Dameris, M., Deckert, R., Dhomse, S., Frith, S. M., Garcia, R. R., Gettelman, A., Giorgetta, M. A., Kinnison, D. E., Li, F., Mancini, E., McLandress, C., Pawson, S., Pitari, G., Plummer, D. A., Rozanov, E., Sassi, F., Scinocca, J. F., Shibata, K., and Tian, W.: Chemistry-climate model simulations of 21st century stratospheric climate and circulation changes, J. Climate, 23, 5349–5374, doi:10.1175/2010JCLI3404.1, 2010. 14843

Carslaw, K. S., Luo, B., and Peter, T.: An analytic expression for the composition of aqueous HNO_3–H_2SO_4 stratospheric aerosols including gas phase removal of HNO_3, Geophys. Res. Lett., 22, 1877–1880, doi:10.1029/95GL01668, 1995. 14837

Carslaw, K. S., Kettleborough, J. A., Northway, M. J., Davies, S., Gao, R. S., Fahey, D. W., Baumgardner, D. G., Chipperfield, M. P., and Kleinböhl, A.: A vortex-scale simulation of the growth and sedimentation of large nitric acid hydrate particles, J. Geophys. Res., 107, 8300, doi:10.1029/2001JD000467, 2002. 14838

Crutzen, P. J., Müller, R., Brühl, C., and Peter, T.: On the potential importance of the gas-phase reaction $CH_3O_2 + ClO \rightarrow ClOO + CH_3O$ and the heterogeneous reaction $HOCl + HCl \rightarrow H_2O + Cl_2$ in ozone hole chemistry, Geophys. Res. Lett., 19, 1113–1116, doi:10.1029/92GL01172, 1992. 14837

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Q. J. Roy. Meteor. Soc., 137, 553–597, doi:10.1002/qj.828, 2011. 14839

Drdla, K. and Müller, R.: Temperature thresholds for chlorine activation and ozone loss in the polar stratosphere, Ann. Geophys., 30, 1055–1073, doi:10.5194/angeo-30-1055-2012, 2012. 14835

Dye, J. E., Baumgardener, D., Gandrud, B. W., Kawa, S. A., Kelly, K. K., Lowenstein, M., Ferry, G. V., Chan, K. R., and Gary, B. L.: Particle size distributions in Arctic polar stratospheric clouds, growth and freezing of sulphuric acid droplets, and implications for cloud formation, J. Geophys. Res., 97, 8015–8034, 1992. 14838

Grooß, J.-U.: Modelling of Stratospheric Chemistry based on HALOE/UARS Satellite Data, Ph. D. thesis, Universitat Mainz, Mainz, Germany, , 1996. 14837

Grooß, J.-U., Brautzsch, K., Pommrich, R., Solomon, S., and Müller, R.: Stratospheric ozone chemistry in the Antarctic: what determines the lowest ozone values reached and their recovery?, Atmos. Chem. Phys., 11, 12217–12226, doi:10.5194/acp-11-12217-2011, 2011. 14841

Hanson, D. R. and Mauersberger, K.: Laboratory studies of the nitric acid trihydrate: implications for the south polar stratosphere, Geophys. Res. Lett., 15, 855–858, doi:10.1029/GL015i008p00855, 1988. 14838

Hanson, D. R. and Ravishankara, A. R.: Reaction of $ClONO_2$ with HCl on NAT, NAD, and frozen sulfuric acid and hydrolysis of N_2O_5 and $ClONO_2$ on frozen sulfuric acid, J. Geophys. Res., 96, 22931–22936, 1993. 14837

Hanson, D. R. and Ravishankara, A. R.: Reactiv uptake of $ClONO_2$ onto sulfuric acid due to reaction with HCl and H_2O, J. Phys. Chem., 98, 5728–5735, 1994. 14837

Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric acid aerosols: A framework for model calculations, J. Geophys. Res., 99, 3615–3629, 1994. 14837

IPCC (Intergovernmental Panel on Climate Change): Climate Change 2007: Synthesis Report, A Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Core Writing Team, Pachauri, R. K., and Reisinger, A., IPCC, Geneva, Switzerland, 2007. 14839

Jöckel, P., Sander, R., Kerkweg, A., Tost, H., and Lelieveld, J.: Technical Note: The Modular Earth Submodel System (MESSy) – a new approach towards Earth System Modeling, Atmos. Chem. Phys., 5, 433–444, doi:10.5194/acp-5-433-2005, 2005. 14836

Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerkweg, A., Lawrence, M. G., Sander, R., Steil, B., Stiller, G., Tanarhte, M., Taraborrelli, D., van Aardenne, J., and Lelieveld, J.: The atmospheric chemistry general circulation model ECHAM5/MESSy1: consistent simulation of ozone from the surface to the mesosphere, Atmos. Chem. Phys., 6, 5067–5104, doi:10.5194/acp-6-5067-2006, 2006. 14836, 14837, 14839

Jöckel, P., Kerkweg, A., Buchholz-Dietsch, J., Tost, H., Sander, R., and Pozzer, A.: Technical Note: Coupling of chemical processes with the Modular Earth Submodel System (MESSy) submodel TRACER, Atmos. Chem. Phys., 8, 1677–1687, doi:10.5194/acp-8-1677-2008, 2008. 14837

Kerkweg, A., Buchholz, J., Ganzeveld, L., Pozzer, A., Tost, H., and Jöckel, P.: Technical Note: An implementation of the dry removal processes DRY DEPosition and SEDImentation in the Modular Earth Submodel System (MESSy), Atmos. Chem. Phys., 6, 4617–4632, doi:10.5194/acp-6-4617-2006, 2006a. 14836

Kerkweg, A., Sander, R., Tost, H., and Jöckel, P.: Technical note: Implementation of prescribed (OFFLEM), calculated (ONLEM), and pseudo-emissions (TNUDGE) of chemical species in the Modular Earth Submodel System (MESSy), Atmos. Chem. Phys., 6, 3603–3609, doi:10.5194/acp-6-3603-2006, 2006b. 14836

Kirner, O.: Prozessstudien der stratosphärischen Chemie und Dynamik mit Hilfe des Chemie-Klima-Modells ECHAM5/MESSy1, Ph. D. thesis, Universität Karsruhe, Karlsruhe, Germany, 2008. 14837

Kirner, O., Ruhnke, R., Buchholz-Dietsch, J., Jöckel, P., Brühl, C., and Steil, B.: Simulation of polar stratospheric clouds in the chemistry-climate-model EMAC via the submodel PSC, Geosci. Model Dev., 4, 169–182, doi:10.5194/gmd-4-169-2011, 2011. 14835, 14836, 14837, 14838

Landgraf, J. and Crutzen, P. J.: An efficient method for online calculations of photolysis and heating rates, J. Atmos. Sci., 55, 863–878, doi:10.1175/1520-0469(1998)055<0863:AEMFOC>2.0.CO;2, 1998. 14836

Lowe, D. and MacKenzie, A. R.: Polar stratospheric cloud microphysics and chemistry, J. Atmos. Sol.-Terr. Phy., 70, 13–40, 2008. 14835

Marti, J. and Mauersberger, K.: A survey and new measurements of ice vapor pressure at temperatures between 170 and 250 K, Geophys. Res. Lett., 20, 363–366, doi:10.1029/93GL00105, 1993. 14837

Meilinger, S. K.: Heterogeneous Chemistry in the Tropopause Region: Impact of Aircraft Emissions, Ph. D. thesis, Swiss Federal Institute of Technology (ETH), Zürich, 2000. 14837

Müller, R, Peter, T, Crutzen, P. J., Oelhaf, H., Adrian, G. P., Von Clarmann, T., Wegner, A., Schmidt, U., and Lary, D.: Chlorine chemistry and the potential for ozone depletion in the arctic stratosphere in the winter of 1991/92, Geophys. Res. Lett., 21, 1427–1430, doi:10.1029/94GL00465, 1994. 14837

Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M., Hagemann, S., Koernblueh, L., Manzini, E., Schlese, U., and Schulzweida, U.: Sensitivity of simulated climate to horizontal and vertical resolution in the ECHAM5 atmosphere model, J. Climate, 19, 3771–3791, doi:10.1175/JCLI3824.1, 2006. 14836

Sander, R., Kerkweg, A., Jöckel, P., and Lelieveld, J.: Technical note: The new comprehensive atmospheric chemistry module MECCA, Atmos. Chem. Phys., 5, 445–450, doi:10.5194/acp-5-445-2005, 2005. 14836

Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E. Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011. 14837

Schlager, H. and Arnold, F.: Measurement of stratospheric gaseous nitric acid in the Winter arctic vortex using a novel rocket-borne mass spectrometer method, Geophys. Res. Lett., 17, 433–436, 1990. 14838

Solomon, S., Garcia, R. R., Rowland, F. S., and Wuebbles, D. J.: On the depletion of Antarctic ozone, Nature, 321, 755–758, 1986. 14835

Solomon, S., Daniel, J. S., Neely, R. R., Vernier, J. P., Dutton, E. G., and Thomason, L. W.: The persistently variable background stratospheric aerosol layer and global climate change, Science, 333, 866–870, doi:10.1126/science.1206027, 2011. 14843

Tost, H., Jöckel, P., Kerkweg, A., Sander, R., and Lelieveld, J.: Technical note: A new comprehensive SCAVenging submodel for global atmospheric chemistry modelling, Atmos. Chem. Phys., 6, 565–574, doi:10.5194/acp-6-565-2006, 2006a. 14836

Tost, H., Jöckel, P., and Lelieveld, J.: Influence of different convection parameterisations in a GCM, Atmos. Chem. Phys., 6, 5475–5493, doi:10.5194/acp-6-5475-2006, 2006b. 14836

Tost, H., Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., and Lelieveld, J.: Global cloud and precipitation chemistry and wet deposition: tropospheric model simulations with ECHAM5/MESSy1, Atmos. Chem. Phys., 7, 2733–2757, doi:10.5194/acp-7-2733-2007, 2007a. 14837

Tost, H., Jöckel, P., and Lelieveld, J.: Lightning and convection parameterisations – uncertainties in global modelling, Atmos. Chem. Phys., 7, 4553–4568, doi:10.5194/acp-7-4553-2007, 2007b. 14836

van Aalst, M. K.: Dynamics and Transport in the Stratosphere – Simulations with a General Circluation Model, Ph. D. thesis, Institute for Marine and Atmospheric Research, Utrecht, the Netherlands, 2005 14839

van den Broek, M. M. P., Williams, J. E., and Bregman, A.: Implementing growth and sedimentation of NAT particles in a global Eulerian model, Atmos. Chem. Phys., 4, 1869–1883, doi:10.5194/acp-4-1869-2004, 2004. 14835, 14838

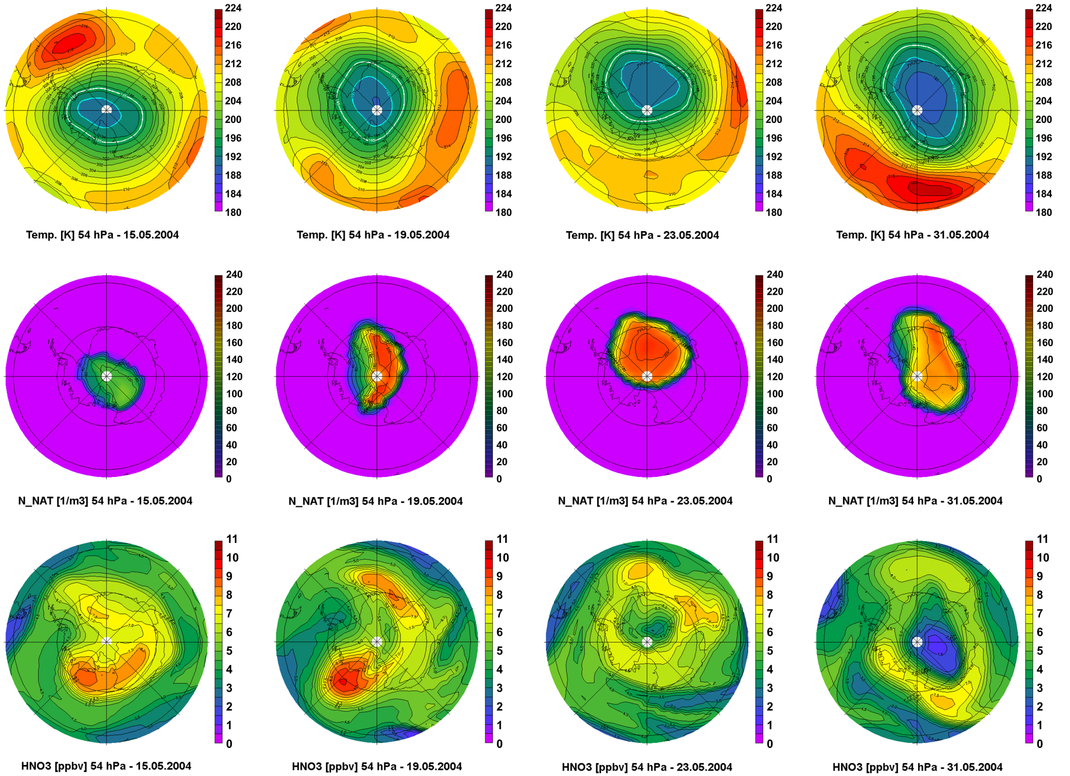
Wegner, T., Grooß, J.-U., von Hobe, M., Stroh, F., Sumińska-Ebersoldt, O., Volk, C. M., Hösen, E., Mitev, V., Shur, G., and Müller, R.: Heterogeneous chlorine activation on stratospheric aerosols and clouds in the Arctic polar vortex, Atmos. Chem. Phys., 12, 11095–11106, doi:10.5194/acp-12-11095-2012, 2012. 14835

Wohltmann, I., Wegner, T., Müller, R., Lehmann, R., Rex, M., Manney, G. L., Santee, M. L., Bernath, P., Sumińska-Ebersoldt, O., Stroh, F., von Hobe, M., Volk, C. M., Hösen, E., Ravegnani, F., Ulanovsky, A., and Yushkov, V.: Uncertainties in modelling heterogeneous chemistry and Arctic ozone depletion in the winter 2009/2010, Atmos. Chem. Phys., 13, 3909–3929, doi:10.5194/acp-13-3909-2013, 2013. 14835

WMO (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project–Report No. 50, Geneva, Switzerland, 2007. 14839

Table 1. The four performed EMAC simulations with different assumptions for heterogeneous chemistry.

Simulations	Time period	Heterogeneous chemistry
Standard	2000–2012	on liquid, NAT and ice particles
NoHet	2005–2012	none
Liquid	2005–2012	on liquid particles
LiquidNAT	2005–2012	on liquid and NAT particles



Temp. [K] 54 hPa - 15.05.2004 Temp. [K] 54 hPa - 19.05.2004 Temp. [K] 54 hPa - 23.05.2004 Temp. [K] 54 hPa - 31.05.2004

N_NAT [1/m3] 54 hPa - 15.05.2004 N_NAT [1/m3] 54 hPa - 19.05.2004 N_NAT [1/m3] 54 hPa - 23.05.2004 N_NAT [1/m3] 54 hPa - 31.05.2004

HNO3 [ppbv] 54 hPa - 15.05.2004 HNO3 [ppbv] 54 hPa - 19.05.2004 HNO3 [ppbv] 54 hPa - 23.05.2004 HNO3 [ppbv] 54 hPa - 31.05.2004

Figure 1. Denitrification in the standard simulation – time series of the temperature in K (top row) and the distribution of N_{NAT} in m^{-3} (second row) and $\mathrm{HNO_3}$ in ppbv (bottom row) for southern polar latitudes on 54 hPa (approx. 20.5 km) for the times 15 May 2004, 19 May 2004, 23 May 2004, and 31 May 2004. In the temperature plots the isothermes of 195 K (white) and 192 K (light blue) are marked.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
I◀ ▶I
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

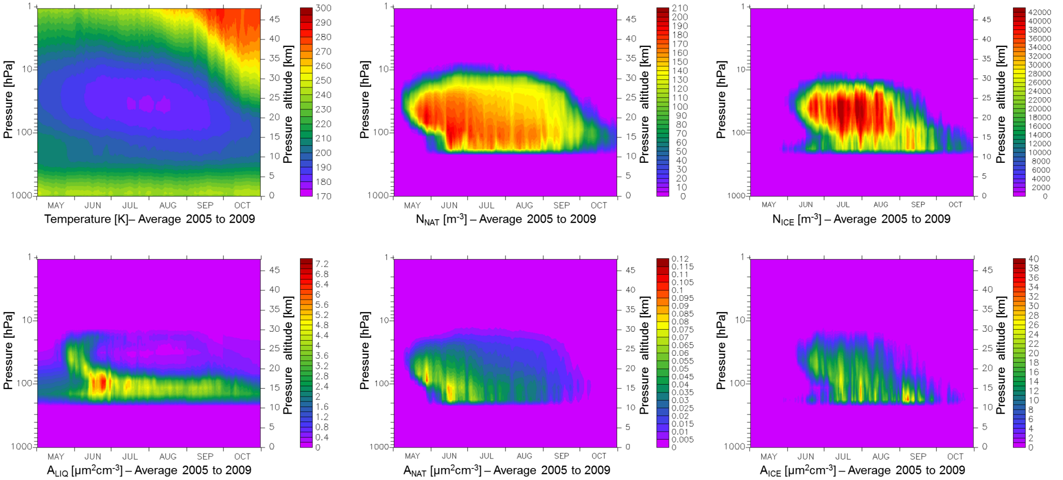


Figure 2. Stratospheric temperature, liquid and solid particles – time series averaged from 80° to 90° S and over the years 2005 to 2009 for temperature in K (top left), number densities of NAT (N_{NAT}) and ice particles (N_{ICE}) in m^{-3} (top center and right), as well as surface densities of liquid particles (A_{LIQ}), NAT (A_{NAT}) and ice particles (A_{ICE}) in $\mu\mathrm{m}^2\,\mathrm{cm}^{-3}$ (bottom left to right).

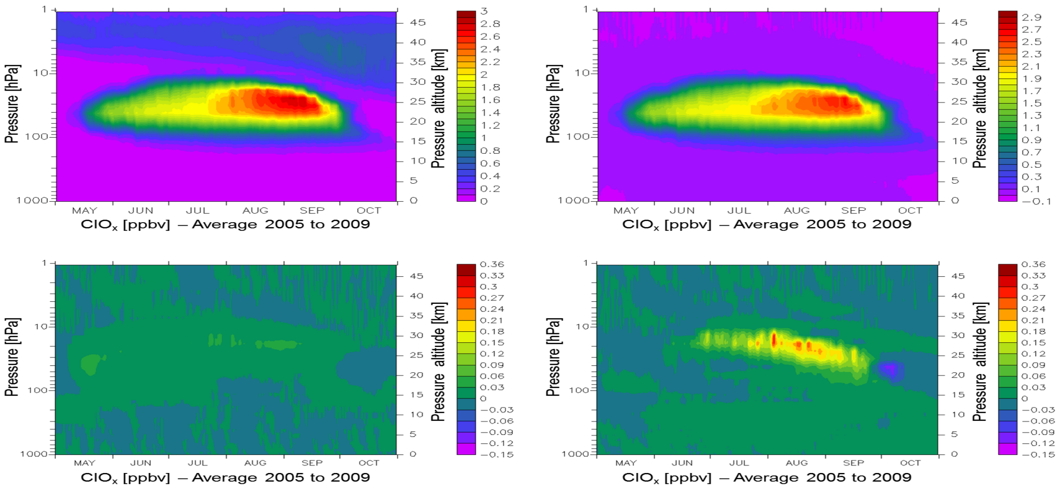


Figure 3. Chlorine activation – time series of ClO_x in ppbv in the standard simulation during Antarctic winter and spring in 80° to 90° S averaged over the years 2005 to 2009 (top left) and contribution of liquid particles (top right), additional contribution by activation on NAT particles (bottom left) and additional contribution by activation on ice particles (bottom right). ClO_x is defined as the sum of $ClO + OClO + HOCl + 2Cl_2 + 2Cl_2O_2$.

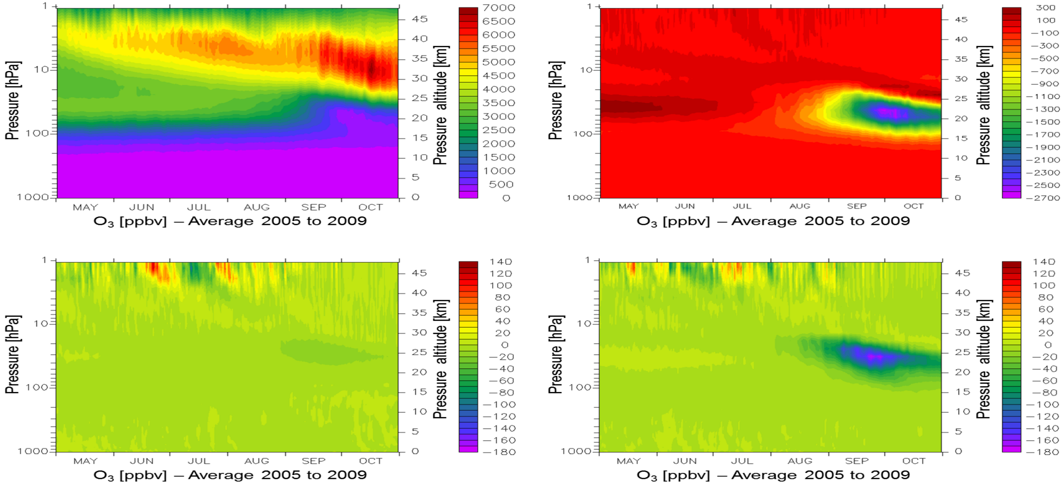


Figure 4. Ozone depletion – time series of O_3 in ppbv in the standard simulation during Antarctic winter and spring in 80° to 90° S averaged over the years 2005 to 2009 (top left) and contribution of liquid particles (top right), additional NAT particles (bottom left) and additional ice particles (bottom right). Note that the color bars have diffent units.

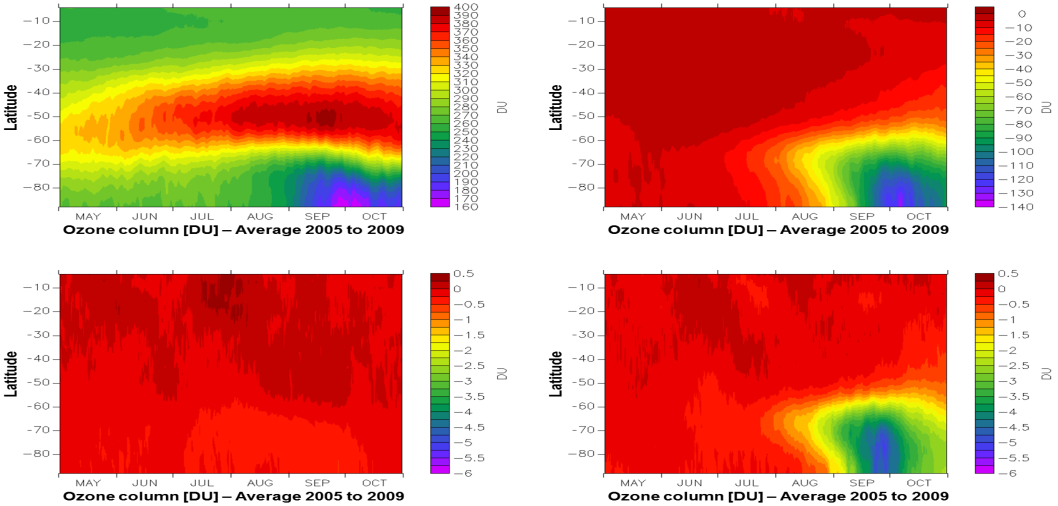


Figure 5. Ozone columns – development of ozone column in DU in the standard simulation during Antarctic winter and spring in the Southern Hemisphere averaged over the years 2005 to 2009 (top left) and contribution of liquid particles (top right), additional NAT particles (bottom left) and additional ice particles (bottom right) to ozone depletion. Note that the color bars have diffent units.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
|◀ | ▶|
◀ | ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion