

On the upgrade of heterogeneous chemistry in TM5

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Abstract

In this report we describe the modifications to the TM5 code regarding the heterogeneous reactions in the troposphere. We now make full use of aerosol SAD as computed by M7, and include heterogeneous reactions for N₂O₅, HO₂ and NO₃ on liquid and ice cloud and aerosol. The inclusion of HO₂ uptake leads to an increase in methane lifetime by ~0.5yr, and associated changes in O₃ and CO budget, mainly due to heterogeneous chemistry on liquid cloud. The new source code allows for a flexible implementation of varying efficiencies of reactions on different surfaces.

Introduction

The chemistry benchmark version 3 of TM5 (TM5-chem-v3, Huijnen et al., 2010) included heterogeneous reaction of N₂O₅, based on historic parameterizations by Dentener (1993) for aerosol, and more recent work (Williams et al., 2009) for liquid and ice cloud. For heterogeneous reactions on aerosol only sulphate, MSA and nitrate were applied, hence neglecting the availability of all M7 aerosol. Furthermore, only heterogeneous reactions for N₂O₅ were considered, neglecting HO₂, NO₃ and other reactions (Jacob, 2000; Amman et al., ACP 2013). The uptake coefficients for N₂O₅ seem outdated considering recent literature. Until now, γ (N₂O₅) = 0.04 on aerosol (including only aerosol types MSA, SO₄ and NO₃⁻) and γ (N₂O₅) = 0.02 on liquid and ice cloud are adopted. In this report we describe the updates to the modelling of heterogeneous chemistry, assess the changes of introducing HO₂ reactions, and compare this to results from C-IFS (Huijnen et al., 2013).

1.1 Modeling Heterogeneous uptake on surfaces

Heterogeneous reactions on aerosol and cloud particles are described by a pseudo first-order rate constant k_{het} using the theory of Schwartz (1986):

$$k_{het} = \left(\frac{r_e}{D_g} + \frac{4}{c\gamma} \right)^{-1} A \quad (1)$$

Where r_e (cm) is the particle effective radius, D_g (cm²s⁻¹) is the gas phase diffusion coefficient, γ is the uptake coefficient, c (cm s⁻¹) is the mean molecular speed, and A is the cloud or aerosol surface area density (SAD, cm²cm⁻³). The SAD for liquid cloud and aerosol particles is computed as:

$$A = \frac{3M}{\rho r_e} \quad (2)$$

with M being the particle mass density in the ambient air (gr cm⁻³) and ρ (gr cm⁻³) the density of the particle. Here we assume spherical particles. The effective cloud particle radius ($r_{e,cloud}$) is in this study computed by the rather simple empirical relationship of Fouquart et al. (1990):

$$r_{e,cloud} = 4 + 11LWP \quad (3)$$

With LWP being the liquid water path (g m^{-2}), integrated per grid cell from the cloud liquid water content, and $r_{e,cloud}$ in units (μm). Cloud radius is slightly reduced as the optical radius is typically somewhat larger than the physical radius (Linacre and Geerts, 1997). For the computation of ice cloud SAD we apply the parameterization developed by Heymsfield and McFarquhar (1996):

$$A_{ice} = 10^{-4}IWC^{0.9} \quad (4)$$

Compared to observations, Popp et al. (2004) found that A_{ice} is too low, therefore Schmitt and Heymsfield (2005) suggested a multiplication by a factor 10 to account for irregularities in the ice particles. The effective ice particle radius $r_{e,ice}$ are computed according to the parameterization of Fu (1996):

$$r_{e,ice} = \frac{\sqrt{3}}{3\rho_{ice}} \frac{IWC}{A} \quad (5)$$

Effective wet aerosol particle radii for every mode, along with their particle densities and mass density per cubic meter of air, needed for the computation of aerosol SAD, are taken over from the M7 aerosol module. Additionally nitrate and ammonium aerosol as computed by Eqsam (Metzger et al. 2002) are included for the computation of heterogeneous reactions, assuming a mean density of 1.7gr/cm^3 and a particle radius of $1.8 \mu\text{m}$. DMS aerosol is neglected so far.

Subgrid-scale information is used by scaling the LWC, LWP and IWC to the cloud cover, such that the liquid and ice cloud droplet effective radius, and hence SAD, is relevant for the cloudy part of the grid cell only. Considering this, the corresponding heterogeneous reaction rate is also scaled by the cloud cover. The new scaling of LWP, and the corresponding changes in the cloud effective radius, affects the photolysis rates as compared to the original model version TM5-chem-v3.0.

With the lack of subgrid-scale information on aerosol spatial distribution, we compute heterogeneous reactions on aerosol that are representative for the full grid cell.

Selection of heterogeneous reactions

The heterogeneous reactions of N_2O_5 on cloud and aerosol surfaces which form nitric acid (HNO_3) are included in TM5, Table 1. In addition, NO_3 loss on aerosol is assumed to take place with $\gamma(\text{NO}_3) = 10^{-3}$ following Jacob (2000), Table 2.

No consensus has been reached yet regarding the most relevant value for $\gamma(\text{HO}_2)$ for aerosol particles. Therefore we make little attempt to optimize our HO_2 uptake parameterization on aerosol, but rather choose to select a lower limit as discussed in Abbatt et al. (2012), see Table 3. Huijnen et al., (in preparation for ACPD, 2013) perform a sensitivity study where they set $\gamma(\text{HO}_2)$ to 0.7 on aerosol types that are mostly associated to anthropogenic origin (SO_4^{2-} , NO_3^- , BC), for which high values for $\gamma(\text{HO}_2)$ have been observed (Liang et al., 2013, Taketani et al., 2012). This provides an estimate of the upper limit of the impact on atmospheric composition of HO_2 uptake on aerosol.

Only few publications report on the actual uptake efficiency of HO₂ on clouds, despite its apparent importance (e.g., Jacob et al., 2000, Tilgner et al., 2005). Here we assume γ (HO₂) on liquid cloud to be 0.06, in line with Ervens et al. (2003). For the uptake of HO₂ on ice particles we follow the IUPAC recommendation based on Cooper and Abbatt (1996).

Table 1. The uptake coefficients applied for N₂O₅ on the various heterogeneous surfaces.

Surface type	γ	Reference
SS, OM, SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄	0.02	Macintyre and Evans (2010)
Liquid cloud	$2.7 \times 10^{-5} \exp(1800/T)$	IUPAC
DD, BC	0.02	
Ice cloud	0.02	IUPAC

Table 2. The uptake coefficients applied for NO₃ on the various heterogeneous surfaces.

Surface type	γ	Reference
All aerosol	0.001	Jacob (2000)
Liquid cloud	N/A	
Ice cloud	N/A	

Table 3. The uptake coefficients used for the heterogeneous scavenging of HO₂ onto various types of particle surface

Surface type	γ	Reference
All aerosol ^a	0.06	Abbatt et al. (2012)
Liquid cloud	0.06	Ervens et al. (2003)
Ice cloud	0.025	Cooper and Abbatt (1996)

^a Optionally on a selection of aerosol related to anthropogenic origin (SO₄²⁻, NO₃⁻, BC^a), a higher value for γ ($\gamma = 0.7$) may be appropriate (Taketani et al., 2012 ; Liang et al. 2013), but this is not yet assumed standard.

Sensitivity run

Two sensitivity runs have been carried out, 1) with HO₂ uptake on aerosol and 2) with HO₂ uptake on aerosol and cloud switched on. This revealed that the impact of aerosol uptake on the CO budget is relatively low (~2Tg increase, i.e. 0.8%) compared to the impact on cloud. The additional heterogeneous chemistry on cloud leads to an increase in CO trop. burden of ~12 Tg, i.e. 4%, see also the evaluation by Philippe Le Sager.

Summary

We implemented a new formulation for heterogeneous chemistry in TM5, making full use of available meteorological information of liquid and ice clouds, and M7 aerosol fields. The new code allows for a simple implementation of variable heterogeneous

reaction rates on different type of cloud and aerosol particles. The cloud, ice and aerosol surface area densities are exported as monthly mean fields for diagnostics purposes.

The changes in the chemistry budgets with respect to the inclusion of HO₂ heterogeneous reactions indicate that for the global HO₂ uptake, cloud SAD contributes ~10x more than aerosol SAD. The inclusion of HO₂ uptake leads to a decrease in O₃ production and loss budget of ~5% and a corresponding increase in methane lifetime and CO burden.

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