

On the importance of aqueous-phase chemistry on the oxidative capacity of the troposphere: A 3-dimensional global modeling study

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Tropospheric oxidants present in the gas phase of the atmosphere are driving tropospheric chemistry of gases and secondary aerosols and control the lifetimes of chemical reactive greenhouse gases. They determine the removal rates and abundances of gaseous pollutants. Oxidants can be also transferred from the gas phase into the aqueous phase of the atmosphere and vice versa. Fenton reactions involving $\text{Fe}^{2+}/\text{Fe}^{3+}$ significantly affect HOx radical cycling in the aqueous-phase and therefore the oxidizing capacity of the troposphere. The impact of aqueous phase chemistry on the oxidation capacity of the troposphere is here investigated using a global 3D chemistry transport model TM4-ECPL.

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1 Introduction

Hydroxyl radical (OH) – the detergent of the atmosphere – is the most important oxidant in the troposphere, controlling the formation and removal rates of numerous trace gases and thus their atmospheric abundance. The production of OH is driven by O₃ abundance in the presence of humidity and solar irradiance, while in turn CO and volatile organic compounds (VOC) oxidation initiated by reactions with OH, leads to secondary organic aerosol formation (SOA) as well as O₃ production in the troposphere when sufficient nitrogen oxides (NO_x=NO+NO₂) are present (Logan et al. 1981). OH also governs the chemical loss of methane (CH₄), an important contributor to the greenhouse effect. Oxidation of VOC starts radical cycling via HO_x (sum of OH and HO₂ radicals) and NO_x (sum of NO and NO₂) chemistry in the troposphere, that drives numerous chemical processes, including O₃ and secondary organic aerosol (SOA) formation. Recent field studies reveal a significant underestimation by the models of HO_x recycling in remote environments (e.g. Lelieveld et al. 2008).

Atmospheric gas phase oxidants can be transferred into the aqueous-phase where their concentrations are decreasing or increasing due to aqueous phase chemistry, and then they are transferred back to the gas-phase. These processes are affecting the oxidation capacity of the atmosphere. The main atmospheric reservoirs of liquid water in the troposphere are cloud droplets and wet aerosols. Radical reactions in the liquid water content (LWC), involve a variety of atmospheric oxidants. Box-modeling studies (e.g. Herrmann et al. 2005) supported that in the aqueous phase the most important radical sources, with decreasing order, are i) the Fenton reaction between Fe²⁺ and H₂O₂, ii) the photolytic decomposition of H₂O₂ and (iii) the uptake of gas-phase OH radical into the droplets out of the total source of OH in the droplets. In the present study, the importance of aqueous-phase chemistry for HO_x budget is investigated, on the regional and global scales.

2 Model Description

Table 1. HO_x reactions taking into account by the model.

Aqueous Phase HO _x Reactions		
O ₃ + <i>hν</i> (+ H ₂ O)	→	H ₂ O ₂ + O ₂
H ₂ O ₂ + <i>hν</i>	→	2OH
NO ₃ ⁻ + <i>hν</i> (+ H ⁺)	→	NO ₂ + OH
HO ₂ + HO ₂	→	H ₂ O ₂ + O ₂
HO ₂ + O ₂ ⁻ (+ H ⁺)	→	H ₂ O ₂ + O ₂
O ₃ + O ₂ ⁻ (+ H ⁺)	→	OH + 2O ₂
O ₃ + OH	→	HO ₂ + O ₂
HO ₂ + OH	→	O ₂ + H ₂ O
OH + OH	→	H ₂ O ₂
H ₂ O ₂ + OH	→	HO ₂ + H ₂ O
NO ₃ ⁻ + OH	→	NO ₃ ⁻ + OH
NO ₃ + <i>hν</i>	→	NO ₂ + O ₃
¹ Fe(III) + <i>hν</i>	→	Fe(II) + OH
¹ Fe(III) + HO ₂	→	Fe(II) + O ₂ + H ₂ O
Fe(II) + H ₂ O ₂	→	Fe(III) + OH
Fe(II) + HO ₂ + H ₂ O	→	Fe(III) + H ₂ O ₂
Fe(II) + OH	→	Fe(III)
Fe(II) + O ₃ + H ₂ O	→	Fe(III) + OH + O ₂

¹Ferric cation (Fe(III)) can be present in the aqueous phase in the forms of Fe³⁺, Fe(OH)²⁺ and Fe(OH)₂⁺ depending on the pH of the solution

For the present study the 3D global chemistry-transport model TM4-ECPL (Myriokefalitakis et al. 2011 and references therein) is used to quantify the impact of aqueous-phase chemistry on the oxidation capacity of the troposphere. TM4-ECPL simulates O_3 chemistry, including non-methane volatile organic compounds together with all major (primary and secondary) aerosol components.

TM4-ECPL accounts for aqueous-phase reactions (Table 1) in cloud and aerosol water that affects both gas phase chemistry and secondary organic aerosol (SOA) formation. Cloud information and meteorology in TM4-ECPL is driven by ECMWF (European Center for Medium-Range Weather Forecasts) Interim re-analysis (ERA-Interim) and aerosol water is calculated online by the ISORROPIA II thermodynamic equilibrium model (Fountoukis and Nenes 2007).

2.1 Simulations

The base case simulation (BASE) takes into account cloud aqueous phase chemistry as described in Myriokefalitakis et al. (2011). Two additional global simulations have been performed for the investigation of the effect of aqueous-phase chemistry on OH tropospheric levels; one neglecting the effect of aqueous phase chemistry in clouds (Simulation NoAqChem) and one by taking into account also Iron (Transition Metal Ion - TMI) chemistry (Simulation TMI). The latter simulation will show the effect of Fenton reactions both in cloud and aerosol water.

2.2 Results

Figure 1 shows the global tropospheric mean (and standard deviation) of OH concentrations as calculated by TM4-ECPL (BASE) and compares it to other model results as presented by Bloss et al. (2005).



Fig. 1. Global mean annual tropospheric OH, calculated by the TM4-ECPL model (red line) and values (error bars show the standard deviation of monthly mean values from the annual mean) determined by observational and computational studies (black lines) as adopted by Bloss et al. (2005)

Figure 2 shows the simulated surface annual mean and zonal distribution of OH in the troposphere for both January and July 2008. The OH concentration results in a methane lifetime ~ 7.46 yr within the troposphere. This value is obtained by dividing the global mean burden of methane (~ 4847 Tg) by the sum of the methane loss due to OH oxidation in the troposphere (~ 560 Tg yr^{-1}) and losses due to soil oxidation and by methane oxidation in the stratosphere (~ 70 Tg yr^{-1} ; Stevenson et al. 2006, Huijnen et al. 2010). Note that the calculated methane lifetime is within the range of the mean value of 8.67 ± 1.32 yr calculated based on the results of 26 models that participated in Stevenson et al. (2006). The calculated tropospheric OH production terms for the BASE simulation supports that O_3 photolysis in the presence of water vapour produces ~ 2239 Tg OH yr^{-1} .

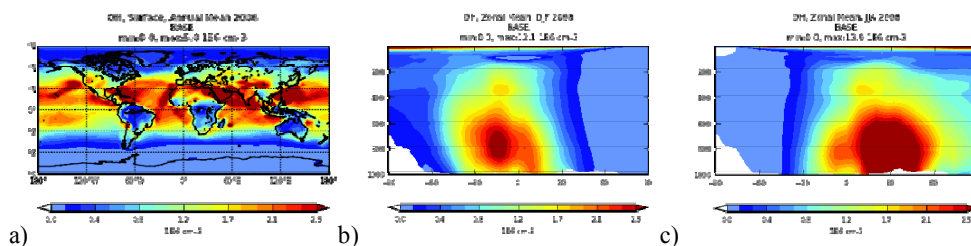


Fig. 2. a) Surface annual mean OH concentrations b) Zonal monthly mean OH concentrations for DJF (December, January, February mean) and c) JJA (June, July, August mean) 2008 as simulated by TM4-ECPL model. OH concentrations are in 10^6 molecules cm^{-3} .

Most of this amount ($\sim 78\%$) is produced in the tropics, while NH extra-tropics ($\sim 12\%$) have a larger contribution than the SH extra-tropics ($\sim 7\%$). The radical recycling terms ($\text{NO} + \text{HO}_2$ and $\text{O}_3 + \text{HO}_2$) contribute by another $\sim 687 \text{ Tg yr}^{-1}$ and $\sim 1961 \text{ Tg yr}^{-1}$ respectively and the smaller primary and recycling terms by $\sim 466 \text{ Tg yr}^{-1}$. The OH loss budget is dominated by the oxidation of CO ($\sim 30\%$) and CH_4 ($\sim 10\%$), with the remaining by reactions with many other minor trace gases. The model calculates (BASE) a mean tropospheric OH radical lifetime of less than a minute ($\sim 44 \text{ sec}$).

The calculated OH radical concentrations are also compared with observations: the MINOS campaign (Finokalia, Greece, August 2001) and the NAMBLEX campaign (Mace Head, Ireland, July–September 2002).

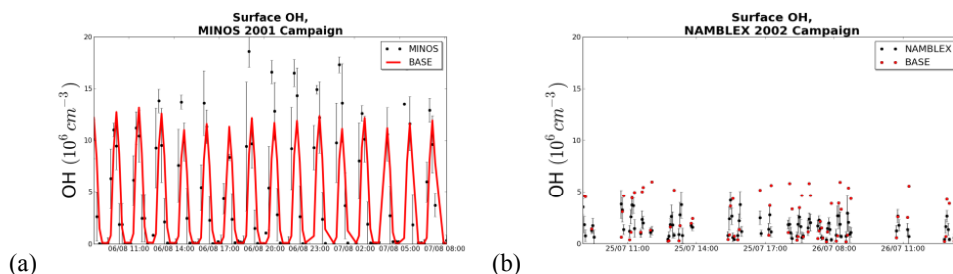


Fig. 3. OH comparison of TM4-ECPL BASE simulation (red line) for a) for MINOS campaign in Finokalia, Greece and b) NAMBLEX campaign at Mace Head, Ireland

The global model satisfactorily simulates the daily variability of OH radical in both stations (Fig. 3). However, in the case of MINOS campaign, the model underestimates OH maxima in contrast to NAMBLEX observations, where the model tends to overestimate the maximum daily OH concentrations. These differences can be attributed to the coarse spatial and temporal resolution of the global model. In particular, TM4-ECPL tends to underestimate OH observations by about $\sim 23\%$.

3 Discussion

Figure 4 presents annual mean model results for the three simulations performed for this study. According to model calculations, wet aerosol aqueous-phase chemistry affects OH concentrations near the surface close to emission sources and on the other hand, cloud aqueous phase chemistry maximizes its effect on OH concentrations at $\sim 800\text{--}400 \text{ hPa}$ over the mid-latitude and in tropical convective systems. The model calculates higher OH surface concentrations (Fig. 4a) above oceans ($\sim 4\%$ on average) when aqueous-phase chemistry is taken into account. This is attributed to the relatively high aerosol water concentrations calculated by the thermodynamic model over the oceans, related to high sea-salt concentrations.

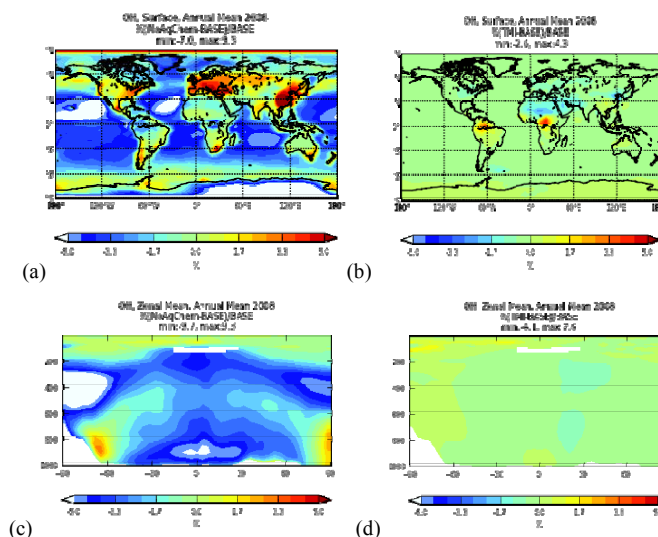


Figure 4. Percentage differences of annual mean OH surface concentrations calculated by TM4-ECPL for 2008 when the model is taking into account aqueous-phase chemistry and iron chemistry a, b) surface and c, d) zonal mean; a, c) NoAqChem-BASE, and b, d) TMI-BASE.

Over land, the implementation of aqueous-phase chemistry in the model presents a different pattern concerning the OH burden. It can be seen that the OH surface mixing ratios are increased in the tropics because of the uptake on cloud droplets that dominates the global budget term for HOx transformation by aerosol scavenging. Especially around the equator, the model calculates an enhanced aqueous-to-gas transfer of OH radicals attributed to the highest temperatures. On the other hand, when aqueous-phase chemistry is taking into account, a decrease of ~5% is calculated over the major polluted regions mainly in the Northern Hemisphere (i.e. Europe, US and China). At the northern and southern mid-latitudes, where instances of complete cloud coverage are frequent, and over regions with a strong contribution due to aerosol particles, a decrease in OH mixing ratios is also calculated (~ 5 %).

4 Conclusions

A CTM (TM4-ECPL) aqueous-phase chemistry parameterization is further extended to take into account the effect of (iron) Fenton reactions. TM4-ECPL satisfactorily simulates the daily variability of OH radical at remote sites, although it underestimates ~ 23% the observed OH concentrations. The discrepancy between model and observations can be also attributed to the coarse spatial and temporal resolution of the model. When the aqueous-phase chemical scheme with the Fenton reactions ($\text{Fe}^{2+}/\text{Fe}^{3+}$) is taken into account, the model calculates:

- an increase of OH surface concentrations above oceans (~4% on average) related to high aerosol water due to high sea-salt concentrations, and
- a decrease of ~5% over the major polluted regions mainly in the Northern Hemisphere.

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