European Commission's 7th Framework Programme
Grant Agreement No. **226520**

Project acronym: **COMBINE**

Project full title: **Comprehensive Modelling of the Earth System for Better Climate Prediction and Projection**

Instrument: Collaborative Project & Large-scale Integrating Project

Theme 6: *Environment* Area 6.1.1.4: *Future Climate*

ENV.2008.1.1.4.1: *New components in Earth System modelling for better climate projections*

Start date of project: 1 May 2009 Duration: 48 Months

Deliverable reference number and title:

D2.3: Report on heterogeneous processes on aerosol and cloud droplet surface

Lead work package for this deliverable: WP2

Organization name of lead contractor for this deliverable: CNRS

Due date of deliverable: Month 18
Actual submission date: Month 32

Project co-funded by the European Commission within the Seven Framework Programme (2007-2013)		
Dissemination Level PU		
PU	Public	PU
PP	Restricted to other programme participants (including the Commission Services)	
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D2.3 Report on heterogeneous processes on aerosol and cloud droplet surface

We investigated the influence of heterogeneous chemistry on aerosol and cloud droplet on the chemistry of the troposphere.

Aerosol surfaces are the site for irreversible or reversible uptake of chemically reactive species and particular attention is brought on how they affect the ozone cycle. Of the many species that play a role in determining O_3 tropospheric concentrations, several important ones are rapidly taken up at the surface of aerosols (Jacob et al., 2000). This work describes the effect of the most relevant one for the O_3 cycle, the reaction of HNO_3, which causes the largest decrease in O_3 concentrations when it undergoes heterogeneous reactions, particularly on mineral dust (Dentener et al., 1996, Bauer et al., 2004; Fairlie et al., 2010; Crowley et al., 2010).

Recent laboratory studies have lead to significant advances in the description of uptake of trace-gases by aerosol surfaces. Several publications have identified that environmental factors (such as relative humidity and HNO_3 concentrations) play an important rôle on HNO_3 uptake by dust. In addition, new findings have documented how photolytically-induced reactions might affect atmospheric composition through the interactions of SO_2, O_3 or NO_x with aerosols surfaces . We focus in this report on the effect of these processes on O_3 and on nitrogen oxides concentrations. Furthermore, we also investigate how OH concentrations are affected by these newly identified réactions. Global experiments were carried out with the GCM LMDz coupled to the INCA module (Interactions between Chemistry and Aerosols). The uptake coefficient γ values for HNO_3, O_3, N_2O_5, NO_2, NO_3, SO_2, OH and HO_2, are based on the 'most-likely' values published in an extensive review by Crowley et al. (2010).

1. Uptake of O3, HNO3, NO2, N2O5, NO2 and OH in the presence of aerosols

Table 1 presents the percentage of tropospheric O_3 loss that can be explained by the individual contributions of the different gas species that are adsorbed onto dust particles (see *Table 1 & Figure 1*). In case of O_3, uptake of HNO_3 by dust turns out to be a major factor in decreasing the O_3 concentration as indicated by the earlier work of Bauer et al. (2004). This study concludes that O_3 concentration reduction from the HNO_3 uptake is -10.4% (to be compared with -4.4% in *Bauer et al., 2004*). We included the dependence of the O_3 uptake coefficient on the O_3 concentrations. This relation

leads to a significant impact in O_3 reduction, when compared to an uptake independent of these concentrations as in Bauer et al. (2004). The direct O_3 uptake causes a 3.5% decrease in trospospheric O_3 concentrations compared to -0.5% in the absence of such relationship (Bauer et al., 2004).

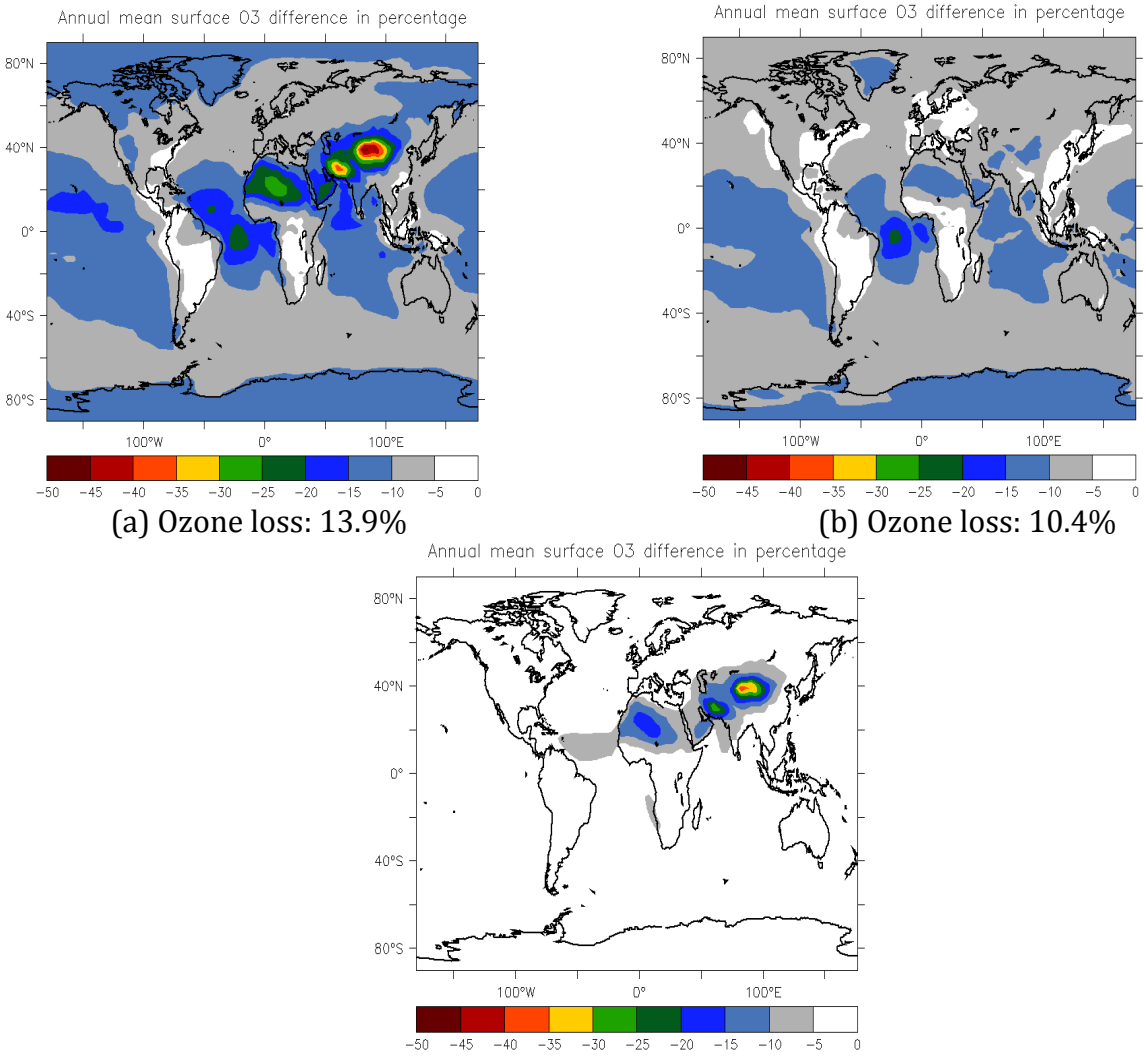
Table 1. *Percentage difference in Ozone Concentrations (HET-CRT) in the Troposphere due to the Uptake of All Gases on the Dust Surface and the Uptake of the Single Gases HNO_3, O_3, N_2O_5, and NO_3 respectively.*

	All	HNO_3	O_3	N_2O_5	NO_3
Bauer et al., 2004	-5.4	-4.4	-0.5	-0.7	-0.4
This study	-13.9	-10.4	-3.5	-1.5	-0.009

Table 2 shows the percentage difference in each species (O_3 and other species) when heterogeneous reactions are taking place. These numbers are compared with the ones obtained by Bauer et al. (2004) and this study. With newly updated heterogeneous uptake coefficients in LMDz-INCA model, we found that, globally speaking, dust aerosol uptake can be responsible for 13.9 % decrease of O_3 mixing ratio in the troposphere whereas 5.4% decrease was proposed by the earlier work of Bauer et al. (2004). In Asia, the O_3 depletion due to the uptake of dust aerosols is more significant than in Europe as the result of vast dust source areas located in Western and Northern China and a high frequency of dust storm occurrences in this region. The global losses of 1.8% and 13.6% in the troposphere are generated by LMDz-INCA model for NO_2 and NO_3 respectively due to the effect of dust aerosol uptake as opposed to the values of 1.4% and 17.7% proposed by Bauer et al. (2004).

Table 2. *Percentage difference in tropospheric concentrations (HET-CRT) when all gases are taken up on dust surfaces.*

	O_3	HNO_3	NO_2	N_2O_5	NO_3	OH
This study	-13.9	-72.7	-1.8	-3.7	-13.6	-16.3
Bauer et al., 2004	-5.4	-35.3	-1.4	-10.6	-17.7	-6.6



(a) Ozone loss: 13.9%

(b) Ozone loss: 10.4%

(c) Ozone Loss: 3.5%

Figure 1. *(a) Yearly averaged loss of O_3 (in percent, at the surface) when all species (HNO3, O3, NO2, N2O5, NO3 and OH) are allowed to be taken up by dust surfaces; (b) Loss of O3 due to the uptake of HNO3 only (this result was obtained by difference of 2 simulations: one with all heterogeneous reactions taking place (HET) and a second one with all heterogeneous reactions but the one with HNO3 taking place); (c) Loss of O3 due to the direct reaction of O3 with dust surfaces (this result was obtained by difference of 2 simulations: the first one with all heterogeneous reactions taking place (HET) and a second one with all heterogeneous reactions but the one with O3 taking place).*

We documented the changes of NO_x for each experiment, as NO_x is an important precursor for O_3. Nitric acid uptake is accompanied by a decrease in tropospheric NO_x concentrations as HNO3 constitutes a reservoir for NO_2 (*Figure 2b*). In contrast, the uptakes of either O_3 or HO_2 by dust will increase NO_x concentrations (*Figures 2c & d*). The overall effect of the three reactions leads to a NO_x decrease except at high elevations over the Tibetan Plateau (*Figure 2a*). Based on the work of Ndour et al. [2009] with an uptake value of 1.2e-8, the direct uptake of NO_2 on dust has a small impact on NO_x levels.

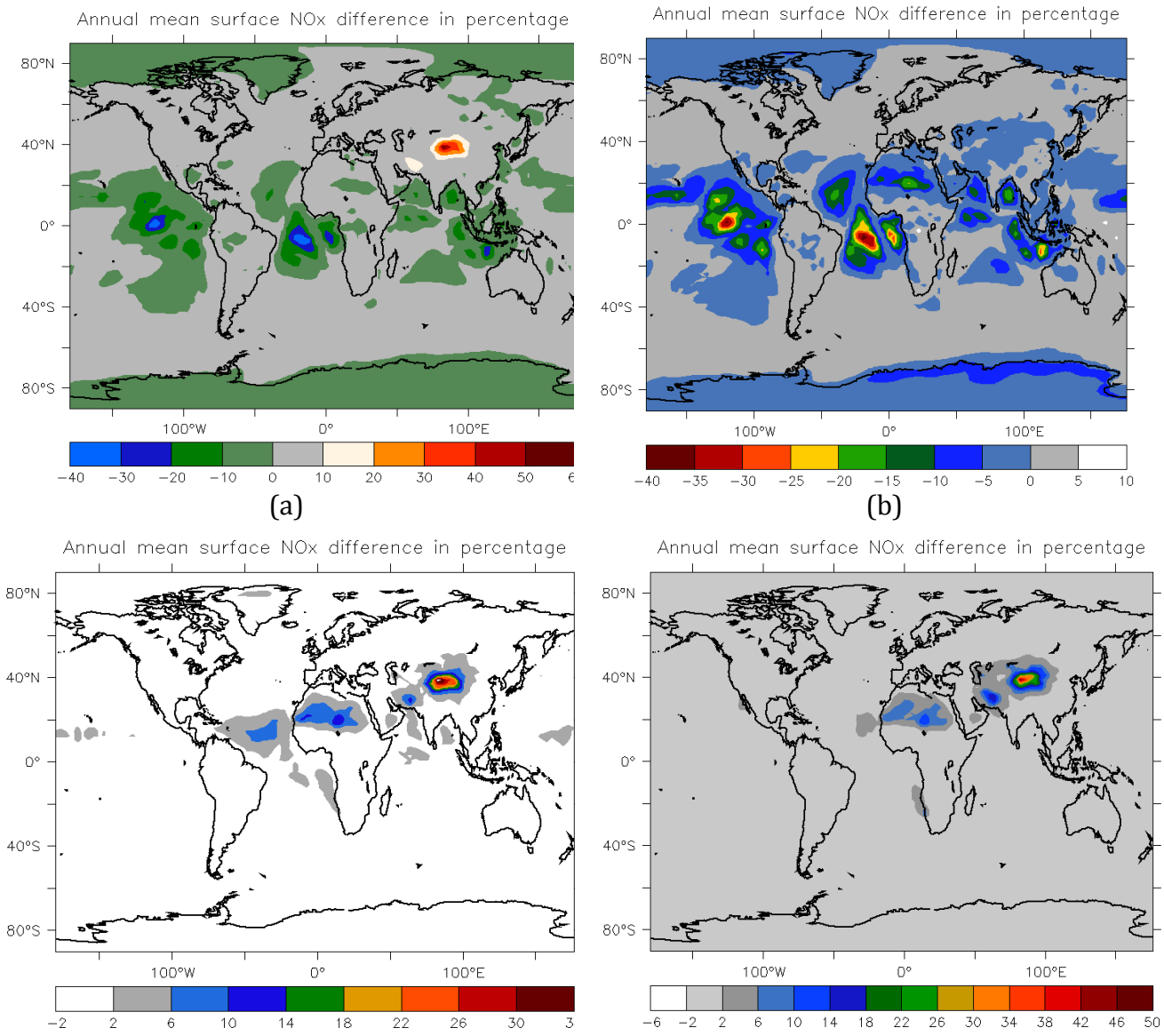
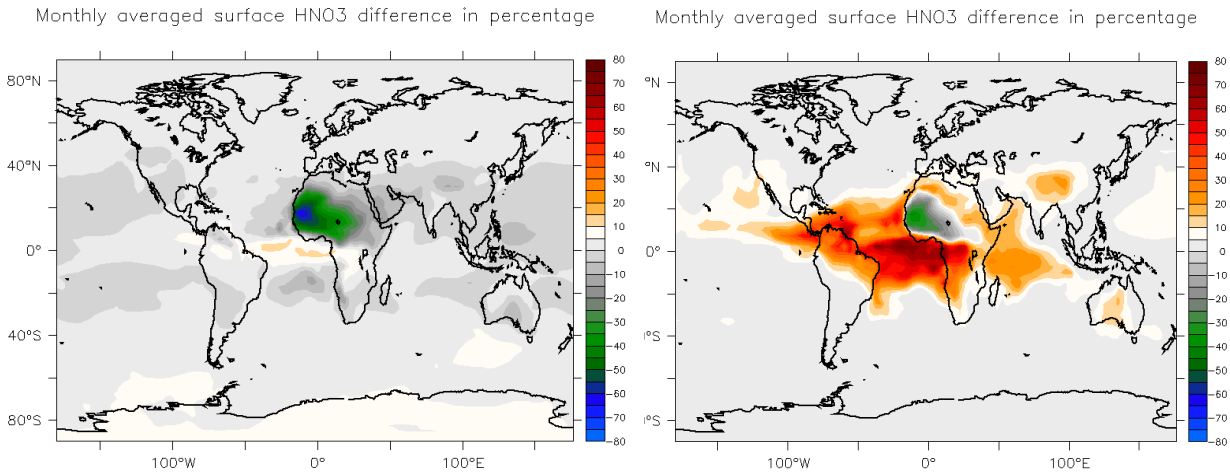


Figure 2. *Percentage difference of surface NOx between different model runs: (a) the difference between the control run (CTR) without any heterogeneous uptakes and the heterogeneous uptake run (HET) with all heterogeneous uptakes being switched on; (b) the difference between the HET run and the model run with HNO3 uptake being turned off; (c) the difference between the HET run and the model run with O3 uptake being turned off; (d) the difference between the HET run and the model run with HO2 uptake turned off.*

3 Introducing the environmental variables to compute the uptake coefficients of HNO3: influence on model results

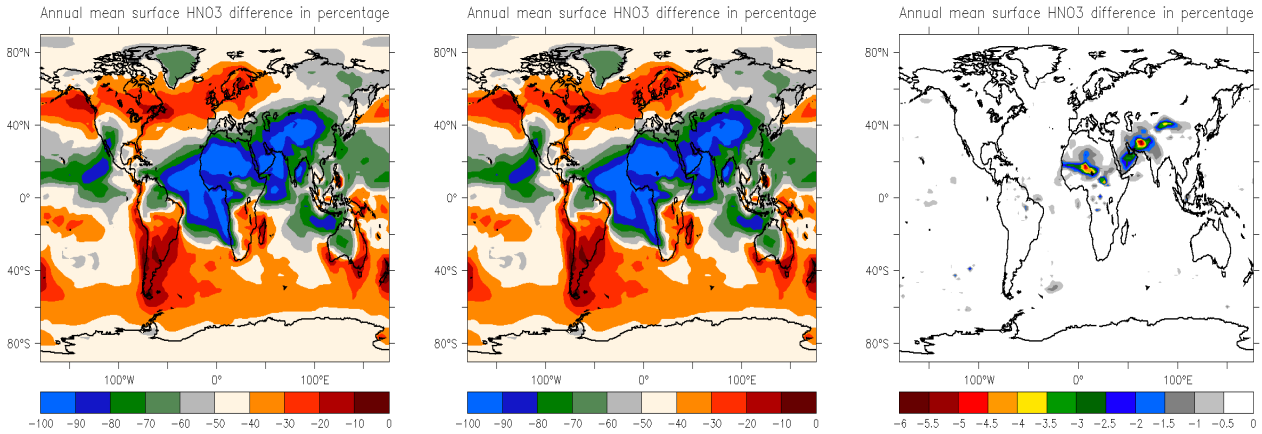
Based on laboratory experiments, different groups have published different parameterizations for uptake coefficient γ, which varies from a constant value to humidity dependent value. We adopted the dependence of HNO_3 uptake coefficient γ on both humidity and concentration of HNO_3 (molecule/cm3) ([Vlasenko et al., 2009]; [Crowley et al., 2010]) in this experiment, of which results were compared with the case where the constant value of γ=0.1 was used. It has been found that using the constant value for the uptake coefficient can potentially overestimate the removal of HNO3 in dust source areas due to the high values of γ. However, removal of HNO_3 can be potentially underestimated over oceans where the humidity is high and the uptake coefficient γ can be subsequently increased when the dependence of γ on humidity is taken into account (Figure 3a). Moreover, considering the dependence of γ on concentration of HNO_3 will increase the underestimation of uptake removal in humid regions and decrease the overestimation in dry regions (Figure 3b).



(a) (b)

Figure 3. *The comparisons of surface HNO_3 mixing ratio for different model runs: (a) the difference in percentage between the run where the uptake coefficient is fixed in the value γ=0.1 and the run where the uptake coefficient γ is humidity dependent (fixed case subtracted by humidity dependant case); (b) the difference in percentage between the run where the uptake coefficient is fixed in the value γ=0.1 and the run where the uptake coefficient γ is both humidity and HNO3 concentration dependant (fixed case subtracted by humidity and HNO3 concentration dependent case).*

In case of HNO_3, it has been found that direct uptake of HNO_3 by dust aerosol is mainly responsible for the HNO_3 decrease, and O_3 uptake also plays a role in reducing HNO_3 concentration up to 6% in some areas.



(a) (HET-CTR)/CTR (b) HNO_3 uptake deactivated (c) O_3 uptake deactivated

Figure 4. *Percentage difference of surface HNO_3 between different model runs: (a) the difference between the control run (CTR) without any heterogeneous uptakes and the heterogeneous uptake run (HET) with all heterogeneous uptakes being switched on; (b) the difference between the HET run and the model run with HNO_3 uptake being turned off; (c) the difference between the HET run and the model run with O_3 uptake being turned off.*

4. Impacts of photolytic uptake on the model results

The uptakes of NO_2 and O_3 by dust aerosol have been shown by the group of Christian George in IRCELYON to be highly stimulated by photolysis in experiments using fluorescence lights. We implemented this effect using the photolytic uptake coefficients data provided by this group. The photolytic uptake coefficients were normalized to the measured average irradiance I according to:

$$\Gamma_{phot} = \frac{\gamma_{BET}}{I}$$

where the photochemical uptake coefficient Γ_{phot} has units of $(mW\ cm^{-2})^{-1}$ and I is the total integrated light intensity below 400 nm (could be extended to 410, 420, 430, 440 nm) in $mW\ cm^{-2}$. The values of the photochemical uptake coefficient, Γ_{phot}, obtained and proposed by IRCELYON are 1.48×10^{-5} and 2×10^{-5} for NO_2 and O_3 respectively. In order to get the real uptake values to be used in the model simulation, we multiplied those values with the solar irradiance calculated in our model and get the diurnal cycle of photolytic uptake coefficients for NO_2 and O_3.

When the photolytic effect was considered for NO_2 uptake by dust particles, insignificant impacts were found in our study, and the NO_2 uptake does not seem to have noticeable influences on some key gas species in the troposphere such as O_3, NO_x, HNO_3 and OH.

However, simulated photolytic uptake of O_3 on dust particles show significant impacts as seen from Figure 5 through Figure 8. Figure 5b illustrated the change in surface O_3 due to these photolytically activated processes. Near-surface level the uptake of O_3 by dust can be increased by 10-15% as compared to the case where the uptake coefficient of O_3 was only calculated as a function of O_3 concentration as proposed by Crowley et al. (2010). Based on the earlier results shown by this study, we found that the O_3 uptake can greatly impact the atmospheric concentration of O_3, NO_x and OH particularly. In order to further understand if this phenomenon can be further affected by the photolytic uptake of O_3, particularly in vertical distribution, zonally averaged vertical profiles for O_3, NO_x and OH were plotted in Figure 6 to Figure 8. Compared to the case where O_3 uptake coefficient was parameterized by utilizing O_3 concentration (Fig. 6a, Fig. 7a and Fig. 8a), the experiments with photochemically parameterized O_3 uptake coefficient (Fig. 6b, Fig. 7b and Fig. 8b) exhibited more evident decreasing effect on O_3 concentration, increasing effect on NO_x concentration as well as decreasing and increasing effects on OH for altitudes lower and higher than 400mb respectively, as the result of heterogeneous uptake of O_3 by dust aerosols.

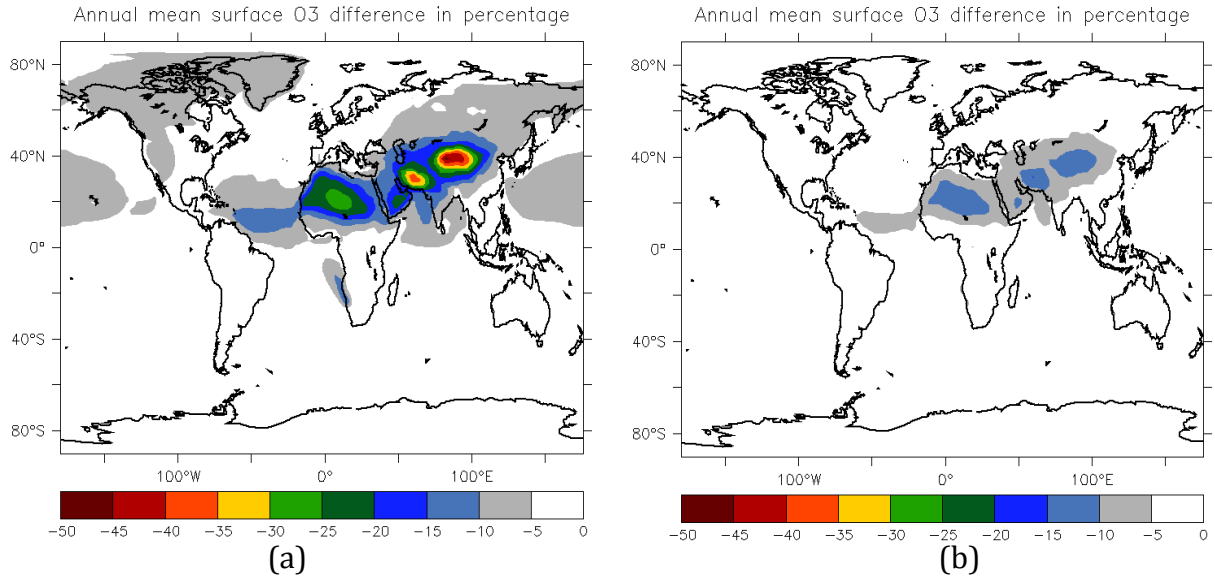


Figure 5. Percentage difference of O_3 surface concentration between different model runs: (a) the difference between the run where all heterogeneous uptakes are included with O3 uptake coefficient being photochemically calculated and the run where O_3 uptake was turned off; (b) the difference between the run where all heterogeneous uptakes are included with O_3 uptake coefficient being photochemically calculated and the run where O_3 uptake coefficient was calculated as the function of O_3 concentration as in the control run.

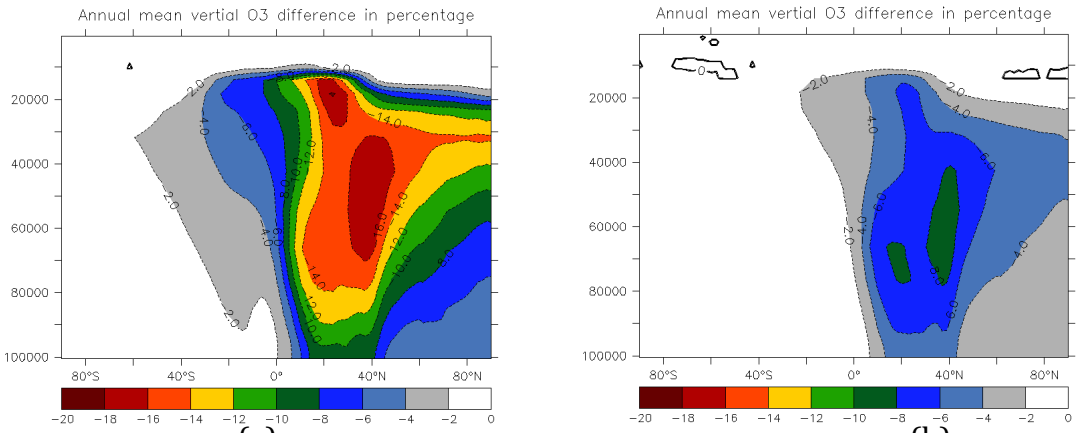


Figure 6. Percentage difference of O_3 vertical profiles due to: a) the photolytically-induced reaction of O_3 obtained as the difference of the run with heterogeneous reactions (HET) and the run where uptake coefficient of O_3 induced by photolysis is calculated; b), the direct O_3 uptake on dust surface obtained as the different in reaction of O_3 from the control run (CTR) and the run where uptake coefficient of O_3 is concentration dependent.

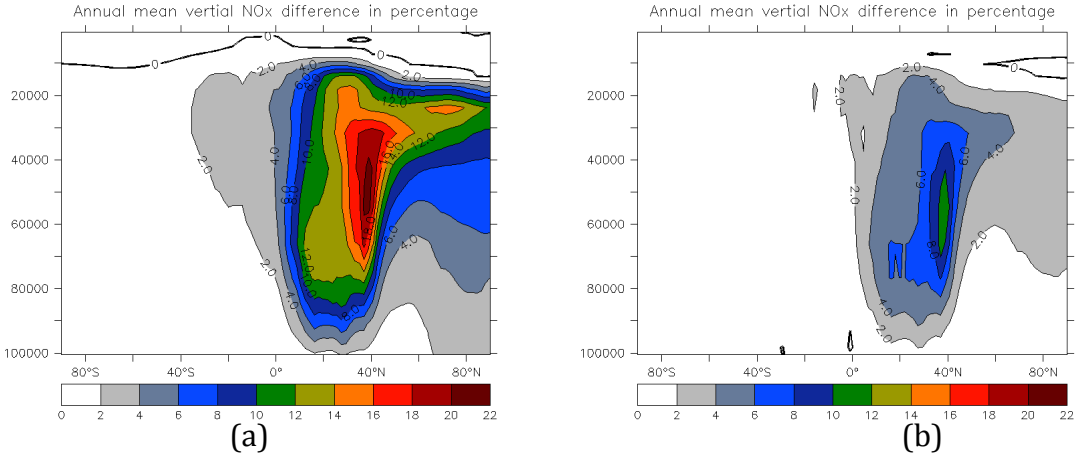


Figure 7. Percentage difference in NOx vertical profiles due to: a) the photolytically-induced reaction of O_3 obtained as the difference of the run with heterogeneous reactions (HET) and the run where uptake coefficient of O_3 induced by photolysis is calculated; b) the direct O_3 uptake on dust surface obtained as the different in reaction of O_3 from the control run (CTR) and the run where uptake coefficient of O_3 is concentration dependent.

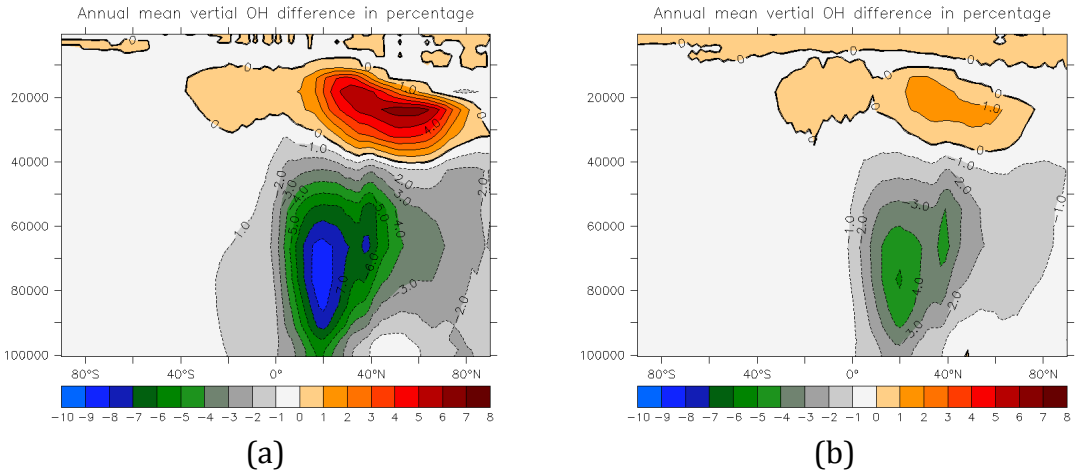


Figure 8. Percentage difference in OH vertical profiles due to: a) the photolytically-induced reaction of O_3 obtained as the difference of the run with heterogeneous reactions (HET) and the run where uptake coefficient of O_3 induced by photolysis is calculated; b), the direct O_3 uptake on dust surface obtained as the

different in reaction of O_3 from the control run (CTR) and the run where uptake coefficient of O_3 is concentration dependent.

5. References

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