Atmos. Chem. Phys. Discuss., 11, C3392–C3396, 2011
www.atmos-chem-phys-discuss.net/11/C3392/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "The HNO_3 forming branch of the HO_2 +NO$reaction : pre - industrial - to - present trends in atmospheric species and radiative forcings"b

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Received and published: 16 May 2011

As pointed out correctly in the text, the results of Butkovskaya et al. (2005) indicated that the abundance of water vapour increases the importance of the HNO_3-forming channel in the reaction of HO_2 with NO. However, the assertion that "there is no parameterisation of this effect which would be suitable for incorporation into an atmospheric model" is incorrect. Butkovskaya et al. (2009) presented a new experimental study where the effect of H_2O has been determined at 298 K. A rate constant of $6 \cdot 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} was derived for the reaction involving the $HO_2 \cdot H_2O$ complex. The complexed fraction of the hydroperoxyl radical HO_2 can be estimated from the esti-

mated equilibrium constant of $HO_2 + H_2O \leftrightarrow HO_2 \cdot H_2O$: see e.g. Kanno et al. (2005) (and references therein) : $1.57 \cdot 10^{-24}$ exp(3775/T) molec. cm^3. In Tropical regions, near the surface, the complexed fraction reaches about up to about 25%. In these conditions, the total rate of the HNO_3-forming channel is increased from ca. $0.45 \cdot 10^{-13}$ without H_2O-assistance to 1.6-1.9 $\cdot 10^{-13}$ molec.$^{-1}$ cm^3 when H_2O-assistance is taken into account.

We performed 3 simulations with the global chemistry-transport model IMAGESv2 (see e.g. Stavrakou et al., 2009 for a description of the CTM):

- A : without the reaction $HO_2 + NO \rightarrow HNO_3$
- B : with the reaction $HO_2 + NO \rightarrow HNO_3$, without H_2O-assistance
- C : id. with H_2O-assistance

The impact of the reaction on NOx concentrations is displayed in Fig. 1 below. The calculated effect of the reaction without water-assistance is consistent with the modelling results shown in this study with the Oslo CTM. The effect of water-assistance is large in tropical regions, where water vapour is abundant. The lifetime of methane is increased from 7.7 years in run A to 8.8 in run B and 9.8 years in run C. Water-assistance has also a large impact of surface ozone mixing ratio (up to ca. 30% e.g. over Amazonia).

It is worth noting that the vertically integrated columns of NO_2 (with averaging kernels of satellite instruments such as GOME) are substantially decreased as a result of the reaction (see Fig. 2). Therefore, the top-down estimation of NOx emissions based on satellite (e.g. GOME, OMI etc.) should be greatly affected by the implementation of this reaction. In particular, tropical emissions (especially soil NO emissions) will need to be increased by 10-30%.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14801, 2011.

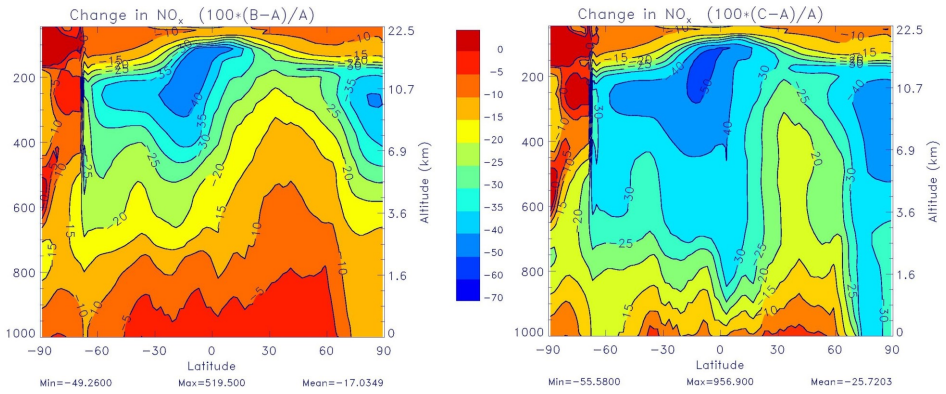

Fig. 1. Effect of HNO3-forming channel of HO2+NO reaction on zonally average NOx (in %) without H2O-assistance (left) and with H2O-assistance (right), for the month of July.

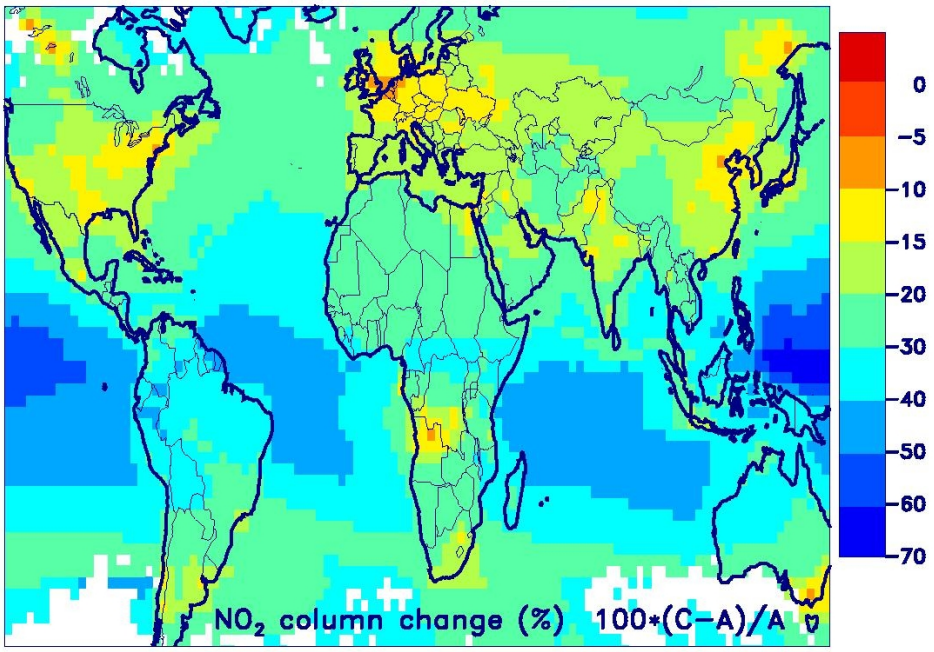

Fig. 2. Effect of HNO3-forming channel of HO2+NO reaction on vertically integrated NO2 column for the month of July. The impact of the averaging kernel of the instrument (GOME) is taken into account.