

A specific comment to Alexander et al.'s manuscript 'Global inorganic nitrate production mechanisms: Comparison of a global model with nitrate isotope observations'

Certainly this is a comprehensive modelling study on global inorganic nitrate production mechanisms with a major aim of investigating how they affect global oxygen isotopic composition of nitrate. A state-of-the-art model (GEOS-Chem) is used in this study. Here what I want to address is the role of reactive halogens (BrO, ClO or IO) on the formation of nitrate. As mentioned in the manuscript, the hydrolysis of halogen nitrates (XNO_3 , where $X=Br, Cl, \text{ or } I$) is an important pathway for the inorganic nitrate formation, particularly in marine boundary layer, where open ocean sea spray serves as a large source of inorganic halogens. Basing on their modelling integrations, the authors conclude that halogens is not important and only accounts for ~6% of the global (<1 km) nitrate production. The dominant processes are reaction of NO_2+OH and hydrolysis of dinitrogen pentoxide (N_2O_5), each accounting for 41% of the production respectively.

However, in an early tropospheric global model (p-TOMCAT) bromine study (Yang et al., 2005, Figure 12c), what they derived is just opposite: A month-long integration (March) shows that $BrNO_3$ hydrolysis reaction can cause a net reduction of lower tropospheric NO_x ($=NO+NO_2$) by 40-80% at latitudes $>50S$ in the Southern Hemisphere and by 20-60% at latitudes $>70N$ in the Northern Hemisphere, though the reduction in the tropical regions is very small (<1%) (due to very lower BrO simulated and relatively higher OH concentrations). Note that this modelling work did include any sea ice sourced bromine source (an additional bromine source to the polar troposphere apart from sea spray and short-lived halocarbons). Thus the actual contribution from halogens could be even higher than the result shown in the paper. Then my question is why these two global models give such a big different result of the bromine-related NO_x reduction (or HNO_3 production)? Please discuss about it and supply more information such as surface layer BrO from the GEOS-Chem model for comparison. To help diagnose which halogen dominates, please supply each individual contribution (from Br, Cl and I) or tell clearly which halogen dominates the nitrate formation.

In addition, the values shown in Figure 3 of the manuscript really puzzle me. The annual fraction of HNO_3 formation from the oxidation of NO_x in the troposphere below 1km altitude from the ' XNO_3+H_2O ' is almost at same level as the ' NO_2+OH ' and ' $N_2O_5+H_2O$ ' reactions. Why their global integration numbers are so different, e.g. by almost an order of magnitude, 6% vs 41%? Please explain it.

Reference:

Yang, X., R. A. Cox, N. J. Warwick, J. A. Pyle, G. D. Carver, F. M. O'Connor and N. H. Savage, Tropospheric bromine chemistry and its impacts on ozone: A model study. *J. Geophys. Res.*, 110, D23311, doi:10.1029/2005JD006244, 2005