

Reviewer comments in bold, author responses in plain text.

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, 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 form comparison. To help diagnose which halogen dominate, please supply each individual contribution (from Br, Cl and I) or tell clearly which halogen dominates the nitrate formation.

A detailed description of the reactive bromine (and iodine) chemistry in the version of the model used in this study can be found in Sherwen et al., ACP, 2016. We have not made any further modifications to the reactive halogen chemistry for this paper. There is no conflict between this work and Yang et al. (2005). Both Yang and Sherwen show that halogens have a large impact on NO_x levels in the remote marine atmosphere. However, NO_x levels and nitrate production in these regions are small regardless of the halogen chemistry, so halogens (XNO_3 hydrolysis) have a modest impact on global nitrate production, as shown here.

Sherwen et al. (2016) compared model results with and without reactive halogen chemistry. They found that the global, annual tropospheric NO_x burden decreased by 3.1% due to NO_x loss from the hydrolysis of XNO_3 . $ClNO_3$ and $BrNO_3$ hydrolysis were approximately equal contributors, while INO_3 was minor. I cannot find a similar value for the impact of reactive halogens on global, annual tropospheric NO_x in Yang et al. (2005) for direct comparison. Yang

et al. (2005) state that BrNO₃ hydrolysis accounts for up to 60-80% of NO_x loss at high latitudes, but it is much smaller (a few percent) at low latitudes. Figure 18 in Sherwen et al. (2018) suggests a similar spatial pattern, with NO_x reductions up to ~80% in the high latitudes, and much smaller impacts in the low latitudes. Based on this, the results from these two models do not seem inconsistent. The Sherwen et al. (2016) results are also consistent with previous studies (Long et al., 2014; von Glasow et al., 2004; Parrella et al., 2012; Schmidt et al., 2016).

Sherwen et al. (2016) found that the model underestimates the tropospheric BrO column in high latitudes, especially in the southern hemisphere (see Figure 9 from Sherwen et al. (2016)). This is mentioned in the manuscript as a possible explanation for why the model underestimates $\Delta^{17}\text{O}(\text{nitrate})$ at high latitudes.

In addition, the values shown in Figure 3 of the manuscript really puzzle me. The annual fraction of HNO₃ formation from the oxidation of NO_x in the troposphere below 1km altitude from the 'XNO₃+H₂O' is almost at same level as the 'NO₂+OH' and 'N₂O₅+H₂O' reactions. Why their global integration numbers are so different, e.g. by almost an order of magnitude, 6% vs 41%? Please explain it.

Figure 3 shows the *fractional* importance of nitrate production pathways. XNO₃ hydrolysis is a dominant nitrate production pathway relative to the other pathways over the remote oceans in the mid to high latitudes. However, NO_x emissions are pretty small in these regions, so that the contribution to total, global nitrate production in these remote oceanic regions is small. In the main (anthropogenic) NO_x source regions, the NO₂ + OH and N₂O₅ hydrolysis pathways dominate local nitrate production, resulting in these reactions being dominant globally.

Although previous studies have not specifically reported the importance of XNO₃ hydrolysis for nitrate production (they focus instead on the importance for NO_x loss), Sherwen et al. (2016) state that the rate of nitrate production from XNO₃ hydrolysis proceeds at a rate of 10% of NO_x loss through the NO₂ + OH pathway. This seems consistent with results from the present study that NO₂ + OH is 41% of global nitrate production near the surface and XNO₃ hydrolysis is about 6%. We have added the following sentence to section 3:

"Although XNO₃ hydrolysis is the dominant nitrate formation pathway over the remote oceans (Figure 3), its contribution to total, global nitrate production is relatively small due to small local NO_x sources in these regions."