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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The fate of NO_x emissions due to nocturnal oxidation at high latitudes: 1-D simulations and sensitivity experiments" *by* P. L. Joyce et al.

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We thank Anonymous Referee #2 for constructive comments on the manuscript. The reviewer wished to see the following modifications:

1) Expand background referencing on prior work on N2O5 heterogenous hydrolysis and discuss further measurements of N2O5 and production of ClNO2. We have done this towards the end of the introduction and in section 2.1, where the parameterization of Bertram and Thornton (2009) is discussed.

Specifically, in section 1, p7388, we added the following paragraph. Other methods for

parameterizing gamma have been developed. Chang et al., (2011) wrote an excellent review article on N2O5 heterogeneous hydrolysis that describes various models for gamma, comparison to ambient measurements, and size and chemical composition effects on gamma. The nitrate effect and production of nitryl chloride are well documented by Chang et al. (2011) and cited references, as well as the effect of organic aerosol particle components, which generally is indicated to reduce gamma, as described below. Evans et al., (2005) parameterized gamma based upon aerosol particle type, and for some types gamma was a function of temperature and relative humidity and performed global model simulations resulting in a global mean gamma of 0.02, which is lower than Dentener and Crutzen (1993), but often larger than predicted by Bertram and Thornton (2009)'s model. Anttila et al., (2006) described a resistor model for how organic coatings on inorganic-core / organic shell aerosol particles could slow heterogeneous hydrolysis and Riemer et al., (2009) found that inclusion of these coatings slowed nitrate formation in a modeling study. Gaston et al., (2013) performed laboratory studies of the reduction of gamma due to addition of organic to ammonium bisulfate aerosol particles. They found that low O:C ratio (atomic O:C ratio < 0.5) suppressed gamma, while more highly oxygenated (O:C ratio > 0.8) species had little effect on gamma. Ambient observations of gamma N2O5 (Bertram et al., 2009, Riedel et al., 2012, Ryder et al., 2014) or modeling of ambient levels of N2O5 where gamma is varied in the model to constrain its value (Brown et al., 2009, Wagner et al., 2013) have generally found that field measured gamma values are lower by factors of 2 or larger than the Bertram and Thornton (2009) parameterization. More recent of these studies have indicated that the inclusion of organic aerosol information and particle mixing state improved the agreement between modeled and observed gamma, but overprediction by $\sim$2 times still exists in polluted airmasses (Ryder et al., 2014). Only one study of gamma during wintertime has been reported upon by Wagner et al, (2013). This study supports the nitrate effect, but finds that the wintertime observed gamma is often larger than that of the Bertram and Thornton (2009) model.

2) Discuss aerosol particle size effects. We added text to section 2.1 to discuss the

aerosol particle size distribution and the dominance of the submicron aerosol particles in the surface area distribution. The discussion was also enhanced to discuss how uncertainties in the reactive uptake model may affect the results. However, because we lack detail on organic properties and aerosol particle mixing state, we cannot correct for how organic coatings may modify gamma. Additionally, in the model description section (2.1), we added details on why Bertram and Thornton's 2009 parameterization was chosen.

3) Discuss the poor performance of heterogenous hydrolysis uptake coefficient models (e.g. the selected Bertram and Thornton (2009) model) in prior work and its relevance to this work. We did this by expanding the introduction section (see above) on past work and then discussing these impacts in the discussion.

Specifically, section 4.3 (Aerosol emission rate) was modified to discuss how possible effects of improper calculation of gamma. The following text was added: As discussed in the introduction, the gamma calculation model (Bertram and Thornton 2009) may overestimate gamma, particularly in the case where organic aerosol coats the surface. Because the rate of N2O5 heterogeneous hydrolysis is dependent upon both the aersosol particle surface area and gamma, the effect of increasing gamma is likely to be similar to increased aerosol emission. Therefore, we would expect that if the actual gamma is lower than calculated by Bertram and Thornton (2009), as has been observed in the presence of organic coatings (Bertram et al., 2009, Riedel et al., 2012, Ryder et al., 2014), the aerosol reacted fraction would decrease. Alternatively, if the actual gamma is larger than modeled, as has been observed at times during the wintertime study of Wagner et al., (2013), the aerosol reacted fraction would be expected to increase.

The discussion in section 5.4 (Model limitations) was also modified to discuss uncertainties in gamma calculation. We added a final paragraph with the following text. Field observations have shown that the gamma parameterization of Bertram and Thornton (2009) often results in gamma values larger than observed in the field, which has been

associated with organic aerosol content (Bertram et al., 2009, Riedel et al., 2012, Ryder et al., 2014). We had no observational constraints on the properties of the organic matter in the aerosol particles (e.g. internal/external mixing state, O:C ratio, etc.), so we could not enhance the gamma calculation model. However, gamma observed under wintertime conditions in the study of Wagner et al., (2013) was comparable to and sometimes exceeded the calculation method used here, possibly indicating that the Bertram and Thornton (2009) model is reasonably accurate under the conditions simulated here. The significant uncertainties that exist in proper calculation of gamma need further study, and the study we report here indicates that airborne observations of N2O5 should be particularly sensitive to gamma and aerosol particle properties.

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