



Release of ClNO₂ from tropospheric aerosol and its impact on tropospheric oxidation

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Nitrogen oxides play a central role in the chemistry of the atmosphere, affecting levels of both ozone and OH. Heterogeneous removal of the NO_x reservoir, N₂O₅, onto aerosol particles can be a major loss route for NO_x with modelling work by Tie et al. (2003) suggesting that, at high latitudes, N₂O₅ hydrolysis can reduce NO_x levels by as much as 90 %. The reactivity of the aerosol towards N₂O₅ has been shown to be a complex function of ambient temperature and RH as well as aerosol composition.

More recently, Thornton and co-workers demonstrated that the presence of chloride ions in the aerosol can release of nitryl chloride, ClNO₂, following uptake of N₂O₅. The night-time chemistry leads to a build-up of nitryl chloride, which can subsequently be photolysed to yield chlorine radicals, an atmospheric oxidant, and NO₂, regenerating NO_x. The yield of ClNO₂ depends on particulate levels of chloride and nitrate, as well as factors controlling initial N₂O₅ uptake.

Recent field measurements (Thornton, 2009; Tang, 2012) have shown the presence of ClNO₂ in mid-continental air over both the US and Europe, demonstrating the widespread interaction between halogen and NO_x chemistry. Night-time levels of ClNO₂ in excess of 500 pptv have been found.

For this work, we will use box models to investigate the aerosol processes controlling both N₂O₅ uptake and ClNO₂ production as a function of particle composition and ambient RH and temperature. The yield of ClNO₂ and subsequent oxidation chemistry will be investigated.

A parameterised yield of ClNO₂ from N₂O₅ uptake will be prepared suitable for use in global modelling studies. The performance of the parameterisation within the UK Met Office Unified Model Chemistry and Aerosol model UKCA/MODE will be examined and the effect of the halogen chemistry on levels of e.g. ozone and particulate nitrate will be investigated. Comparison with field measurements e.g. Tang et al. will also be made, and the impact of ClNO₂ release on oxidative chemistry in the troposphere quantified.