Supplement for

A comprehensive study about the in-cloud processing of nitrate through coupled measurements of individual cloud residuals and cloud water

By Zhang et al.

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Introduction

Details including the analysis of air masses, meteorological conditions, and characteristics of individual particles over the sampling periods. Text describes the lifetime calculation for NOx and N₂O₅, and regression and random forest analysis of nitrate production. Tables provide the initial setup of model simulations for nitrate formation in aqueous phase (wet aerosol and cloud droplets). Figures mainly show the characteristics of individual particles, including representative mass spectra and the RPA ratios (nitrate/sulfate) for the identified particle types, distribution of nitrate RPA over cloud free, interstitial, and residual particles, and also the comparison of [NOx][O₃] and SA between cloud events and cloud-free periods.
The formation of nitrate from hydrolysis of N$_2$O$_5$ arises from the reactions between NO$_2$ and O$_3$ can be given as follows:

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  

(R1)

\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \]  

(R2)

Thus, NO$_x$ is converted to N$_2$O$_5$ at the following rate ($K_1 = 1.2 \times 10^{-13} \, \text{exp} \, (-2450/T)$, $T$ is the absolute temperature), and thus the lifetime of NO$_x$ can be calculated as:

\[ \tau_{\text{NO}_x} = \frac{1}{2K_1[O_3]} \]

During daytime, NO$_3$ rapidly photolyzes, but at night, NO$_3$ reacts with NO$_2$ to produce N$_2$O$_5$. The key reaction to produced condensed nitrate is the hydrolysis of N$_2$O$_5$ on aerosol or droplet surfaces:

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]  

(R3)

The reaction proceeds effectively on the surface of aerosol particles that contain water. When an N$_2$O$_5$ molecule strikes the surface of an aqueous particle, not every collision leads to reaction. A reaction efficiency or uptake coefficient $\gamma$ was introduced to account for the probability of reaction. Values of $\gamma$ for this reaction ranging from 0.06 to 0.1 have been reported. The the lifetime of N$_2$O$_5$ can be calculated as:

\[ \tau_{\text{N}_2\text{O}_5} = \left[ \frac{\gamma}{4 \left( \frac{8RT}{\pi m(N_2O_5)} \right)^{1/2} A_p} \right]^{-1} \]  

(Seinfeld and Pandis, 2006)

where ($\frac{8RT}{\pi m(N_2O_5)}$)$^{1/2}$ corresponds to the molecular mean speed of N$_2$O$_5$, $m(N_2O_5)$ is the molecular mass of N$_2$O$_5$, and $A_p$ is the aerosol/droplet surface area (SA) per unit volume (cm$^2$ cm$^{-3}$). The reaction occurs at a rate governed by that at which N$_2$O$_5$ molecules strike the aerosol surface area times the amount of surface area times the reaction efficiency.
Text S2 Regression and random forest analysis

As shown in Test S1, the formation of nitrate depends on the [NOx][O3], SA, and temperature as inputs, and thus could be roughly regressed as follows:

\[
\text{Nitrate} \sim \exp(-1/T) [O_3][NO_2] T^{1/2} A_p
\]

In the multiple linear model, the least-squares fit is used, and two of the most common measures of model fit are the residual standard error and the proportion of variance explained (R^2). It is noted that A_p (or SA) is not available and thus was not included in the regression for 2018 spring data.

Random forest analysis, is for nonlinear multiple regression, using trees as building blocks to construct powerful prediction models [Breiman, 2001]. The algorithm first creates multiple decision trees, where each tree is grown by using the bootstrap re-sampling method. The relative importance of the predictor variables can also be obtained, with “Mean Decrease Accuracy” presenting the capability of each independent variable in explaining the variability of SNRs.

Text S3 SPAMS

Individual particles are introduced into the SPAMS through a critical orifice. They are focused and accelerated to specific velocities, which can be determined by two continuous diode Nd:YAG laser beams (532 nm) placed downstream. Based on the measured velocities, a pulsed laser (266 nm) is subsequently triggered to desorp/ionize the particles. The generated positive and negative molecular fragments are recorded. The measured velocities are corresponding to \(d_{va}\), based on a calibration using polystyrene latex spheres.
(PSL, Duke Scientific Corp., Palo Alto) with predefined sizes (0.15-2.0 µm). Peak thresholds were set to record only those peaks with area greater than 5 units to distinguish peaks from the background noise (< 1 unit) in the mass spectra.
Table S1. The initial setup of model simulations for nitrate formation in aqueous phase (wet aerosol and cloud droplets)

In wet aerosol and cloud droplet the RH, LWC, and radius are different, in wet aerosol case: RH=85%, LWC1=1.0×10^{-5} g/m³, LWC2= 1.0×10^{-4} g/m³, radius of aerosol particles is 0.5 μm; in cloud droplet case: RH=99.99%, LWC1= 0.05 g/m³, LWC2= 0.15 g/m³, radius of aerosol particles is 8 μm, and photolysis rate was changed 100%, 50%, and 30%.

<table>
<thead>
<tr>
<th></th>
<th>Wet aerosol</th>
<th>Wet aerosol</th>
<th>Cloud 1#</th>
<th>Cloud 2#</th>
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<td>RH</td>
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<td>100%</td>
<td>100%</td>
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<td>10⁻⁴</td>
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<td>NO₂ (ppb)</td>
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<td>O₃ (ppb)</td>
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<td>photolysis rate (%)</td>
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<td>100</td>
<td>100; 50; 30</td>
<td>100; 50; 30</td>
</tr>
</tbody>
</table>
Figure S1. Temporal variations of T and RH, wind speed and direction, O$_3$/SO$_2$/NO$_x$, and mass concentration of PM$_{2.5}$ and visibility for 2018 spring (upper) and 2020 winter (bottom), respectively.
Figure S2. The HYSPLIT back trajectories (72 h) arriving at the sampling site (100 m above the sea level) at daytime (12:00 local time, left panel) and nighttime (00:00 local time, right panel) for 2018 spring (upper) and 2020 winter (bottom), respectively.
Figure S3. Representative mass spectra for the identified particle types. Each particle type is labeled according to the most significant chemical features in the mass spectra. In addition to the presence of secondary inorganic species (i.e., sulfate (-97[HSO₄]⁻), nitrate (-62[NO₃]⁻), and ammonium (18[NH₄]⁺)), the mass spectrum of the OC-rich particles is mainly contributed by OC markers (37[C₃H]⁺, 50[C₄H₂]⁺, 51[C₄H₃]⁺, 55[C₅H₇]⁻ and 63[C₅H₃]⁺); EC-rich by both EC ion peak clusters ([Cₙ]⁺⁻, n = 1, 2, 3, …); K-rich particles by intense potassium peak (39[K]⁺); Sea salt by 23[Na]⁺, 39[K]⁺, and chloride (-35[Cl]⁻ and -37[Cl]⁻); Amine-rich by [N(CH₃)₃]⁺ and [(C₂H₅)₂N(CH₃)]⁺; Dust by 27[Al]⁺ and 40[Ca]⁺; Metal-rich by 23[Na]⁺, 39[K]⁺, 56[Fe]⁺ and 206-208[Pb]⁺.
Figure S4. Distribution of RPA of nitrate, separated for cloud free, INT, and RES particles, in 2018 spring (upper) and 2020 winter (bottom).
Figure S5. Box-and-whisker plots of [NOx][O3] and SA (μm² cm⁻³) during cloud events and cloud-free periods in (a) 2018 spring and (b) 2020 winter, respectively.
Figure S6. The relative importance of predictors in the random forest analysis for the RPA of nitrate associated with the (a) cloud-free particles and (b) cloud residual particles, respectively, separated for daytime and nighttime during 2018 spring and 2020 winter. Used as an indicator for the relative contribution to the predicted variable, %IncMSE refers to the increased mean square-error when each independent variable is removed from the predictors.
Figure S7. The RPA ratios (nitrate/sulfate) varying on the seven single particle types are compared for mid-cloud and cloud dissipation periods (2h after cloud period) for 2018 spring, which is also similarly observed in 2020 winter. The RPA ratios during cloud dissipation periods generally follows those in the cloud RES particles during cloud stable periods. It suggests that the in-cloud produced nitrate remains after cloud evaporation. It is anticipated that the evaporation of the cloud droplets in the ambient atmosphere would lead to a level similar to the cloud RES nitrate, and perhaps more if the ambient relative humidity were higher or the temperature lower than that in the GCVI (Hayden et al., 2008). As the GCVI is a more severe and rapid approach to the
drying of cloud droplets than likely occurs in the atmosphere, the enhanced cloud
residual nitrate suggests that when the cloud evaporates, more particulate nitrate than
existed in the aerosol below cloud should be released into the air. If this process is
significant, an enhancement of nitrate (relative to sulfate) may be expected after cloud
evaporation.