Table S1. Data for $NaNO_3$, Na_2SO_4 and 1:1 $NaNO_3/Na_2SO_4$ aerosol experiments shown in Figure 2 of the main text.

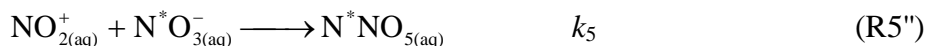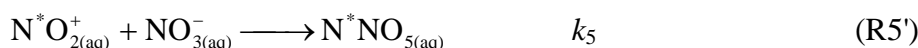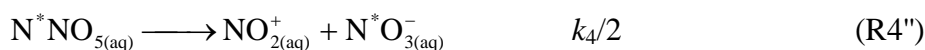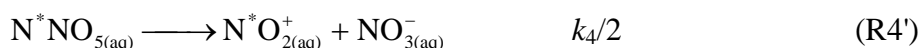| NaNO₃					
50% RH			70% RH		
Time (s)	$C^*_p(t) / C^*_p(t=0)$	std.dev.	Time (s)	$C^*_p(t) / C^*_p(t=0)$	std.dev.
0.75	1.78E-02	3.63E-03	0.75	4.17E-02	6.74E-03
1.26	2.73E-02	5.30E-03	1.25	6.40E-02	7.70E-03
1.76	2.83E-02	3.91E-03	1.75	8.61E-02	8.49E-03
2.27	3.62E-02	4.58E-03	2.25	1.07E-01	8.33E-03
2.77	5.25E-02	5.94E-03	2.76	1.17E-01	1.12E-02
3.28	6.12E-02	4.09E-03	3.26	1.48E-01	1.10E-02
3.78	6.80E-02	5.59E-03	3.76	1.68E-01	1.49E-02
Na₂SO₄					
51% RH			70% RH		
Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.	Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.
0.76	1.18E-03	2.65E-03	0.75	4.70E-03	3.48E-03
1.26	1.57E-03	1.61E-03	1.25	5.44E-03	4.31E-03
2.79	2.63E-03	2.61E-03	1.75	6.52E-03	3.32E-03
			2.25	8.86E-03	3.45E-03
			2.76	1.19E-02	3.36E-03
NaNO₃+Na₂SO₄					
51% RH			70% RH		
Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.	Time (s)	$[N_2O_5]_p(t) / [N_2O_5]_g(t=0)$	std.dev.
0.75	1.27E-02	2.14E-03	0.75	3.33E-02	4.19E-03
1.25	1.55E-02	3.26E-03	1.25	5.95E-02	8.93E-03
1.75	2.50E-02	3.65E-03	1.75	6.92E-02	1.13E-02
2.25	2.06E-02	3.47E-03	2.25	1.01E-01	1.21E-02
2.76	2.45E-02	3.99E-03	2.76	1.14E-01	8.94E-03
3.26	2.74E-02	3.47E-03			
3.76	3.92E-02	3.61E-03			

Description of box model calculations

The box model calculations are explicitly treating N_2O_5 chemistry in the aqueous phase for both labelled and non-labelled N_2O_5 molecules, as well as exchange of both with the gas phase. Diffusion is neglected in both phases. Labelling of reactions is done as in main text and as indicated in Figure 3a of the main text.

The following chemical reactions have been used to describe the aqueous phase chemistry of non-labelled N_2O_5:

$$N_2O_{5(aq)} \longrightarrow NO_{2(aq)}^+ + NO_{3(aq)}^- \qquad k_4 \qquad\qquad (R4)$$

$$NO_{2(aq)}^+ + NO_{3(aq)}^- \longrightarrow N_2O_{5(aq)} \qquad k_5 \qquad\qquad (R5)$$

$$NO_{2(aq)}^+ + H_2O_{(liq)} \longrightarrow NO_{3(aq)}^- + 2H_{(aq)}^+ \qquad k_7 \qquad\qquad (R7)$$

$$N_2O_{5(g)} \underset{\longleftarrow}{\overset{\longrightarrow}{}} N_2O_{5(aq)} \qquad k_{gbg}, k_{gbb}, k_{bgb}, k_{bgg} \qquad (R3)$$
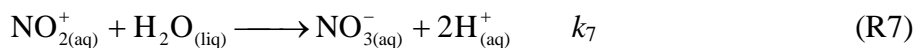
The chemical scheme for labelled N_2O_5 is analogous and assumes that the position of the labelled N^* atom within the N_2O_5 is not relevant, such that upon dissociation, labelled nitronium and labelled nitrate are formed at equal rates, but that otherwise the rate coefficients are the same as for the non-labelled species:

$$N^*NO_{5(aq)} \longrightarrow N^*O_{2(aq)}^+ + NO_{3(aq)}^- \qquad k_4/2 \qquad\qquad (R4')$$

$$N^*NO_{5(aq)} \longrightarrow NO_{2(aq)}^+ + N^*O_{3(aq)}^- \qquad k_4/2 \qquad\qquad (R4'')$$

$$N^*O_{2(aq)}^+ + NO_{3(aq)}^- \longrightarrow N^*NO_{5(aq)} \qquad k_5 \qquad\qquad (R5')$$

$$NO_{2(aq)}^+ + NO_{3(aq)}^- \longrightarrow NNO_{5(aq)} \qquad k_5 \qquad\qquad (R5)$$

$$NO_{2(aq)}^+ + N^*O_{3(aq)}^- \longrightarrow N^*NO_{5(aq)} \qquad k_5 \qquad\qquad (R5'')$$

$$N^*O_{2(aq)}^+ + H_2O_{(liq)} \longrightarrow N^*O_{3(aq)}^- + 2H_{(aq)}^+ \qquad k_7 \qquad\qquad (R7')$$

$$NO_{2(aq)}^+ + H_2O_{(liq)} \longrightarrow NO_{3(aq)}^- + 2H_{(aq)}^+ \qquad k_7 \qquad\qquad (R7)$$

$$\mathrm{N^*NO_{5(g)}} \xrightleftharpoons{} \mathrm{N^*NO_{5(aq)}} \qquad\qquad k_{gbg},\, k_{gbb},\, k_{bgb},\, k_{bgg} \qquad \text{(R3')}$$

$$\mathrm{N_2O_{5(g)}} \xrightleftharpoons{} \mathrm{N_2O_{5(aq)}} \qquad\qquad k_{gbg},\, k_{gbb},\, k_{bgb},\, k_{bgg} \qquad \text{(R3)}$$
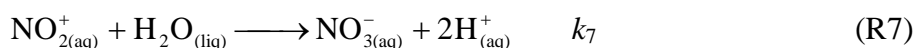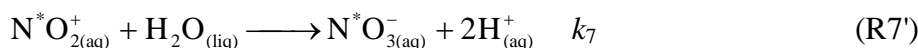
Due to the small fraction of labelled N, reactions among labelled species are not included in the scheme. The set of differential equations listed in Table S1 were used to solve for the evolution of all gas and aqueous phase species with time using Matlab.

The exchange rate coefficients to describe gas-aqueous and aqueous-gas transfer of N_2O_5 were obtained from the steady state condition given by Henry's law equilibrium, thus gas – aerosol equilibrium in absence of chemical reaction (assuming that the gas phase chemical reactions of N_2O_5 are in steady state on the time scale of gas – aerosol equilibration). The steady state of the gas phase N_2O_5 concentration in equilibrium with aqueous phase N_2O_5 is described by:

$$\frac{d[N_2O_5]_g}{dt} = k_{bg}[N_2O_5]_{aq}V_pN_{av} - \frac{\alpha_b\omega}{4}S_p[N_2O_5]_g = 0 \Rightarrow k_{bg} = \frac{\alpha_b\omega S_p}{4V_pN_{av}H'}$$

$$H' = \frac{[N_2O_5]_{aq}}{[N_2O_5]_g} = \frac{[N_2O_5]_{aq}}{N_{av}p_{N2O5}/RT} = H\frac{RT}{N_{av}}$$

k_{bg} is the first order rate coefficient for the release to the gas phase in units of s^{-1}, V_p is the total aqueous phase aerosol volume per volume of gas phase in liter cm^{-3}, S_p the total aerosol surface area per volume of gas phase in $cm^2\ cm^{-3}$, p_{N2O5} is the partial pressure of N_2O_5 in atm, R is the gas constant (8.314 J $mole^{-1}\ K^{-1}$), T is the temperature, H is the Henry's law constant in M atm^{-1}, H' is the ratio of the aqueous phase molarity of N_2O_5 to the gas phase concentration in molecule cm^{-3} and N_{av} is Avogadro's number (note that $[N_2O_5]_{aq}$ is in units of M, while $[N_2O_5]_g$ is in units of molecule cm^{-3}). The same result can also be obtained from considering steady state for the aqueous phase N_2O_5 concentration in an individual aerosol particle:

$$\frac{d[N_2O_5]_{aq}}{dt} = -k_{bg}[N_2O_5]_{aq} + \frac{\alpha_b\omega s_p}{4v_pN_{av}}[N_2O_5]_g = 0 \Rightarrow k_{bg} = \frac{\alpha_b\omega s_p}{4v_pN_{av}H'} \qquad \frac{s_p}{v_p} = \frac{S_p}{V_p}$$

Where v_p is the volume of an individual aerosol particle in liter, and s_p its surface area in cm^2. Thus, the rate coefficients describing the gas – aqueous phase exchange are:

$$k_{gbb} = \frac{\alpha_b \omega s_p}{4 v_p N_{av}} \qquad \left[\frac{\text{mole cm}^3}{\text{s liter molecule}} \right]$$

$$k_{gbg} = \frac{\alpha_b \omega S_p}{4} \qquad \left[\text{s}^{-1} \right]$$

$$k_{bgb} = \frac{\alpha_b \omega s_p}{4 v_p N_{av} H'} \qquad \left[\text{s}^{-1} \right]$$

$$k_{bgg} = \frac{\alpha_b \omega S_p}{4 H'} \qquad \left[\frac{\text{molecule liter}}{\text{s cm}^3 \text{ mole}} \right]$$

The apparent net uptake coefficient, γ and γ^*, can be derived from the effective loss rates of the gas phase N_2O_5 and N^*NO_5, respectively, obtained from the solutions to the differential equations, via:

$$\gamma = \left[-\frac{d[N_2O_5]_g}{dt} \right] \Big/ \left[\frac{\omega}{4} S_p [N_2O_5]_g \right] = \left[k_{bgg} [N_2O_5]_{aq} - k_{gbg} [N_2O_5]_g \right] \Big/ \left[\frac{\omega}{4} S_p [N_2O_5]_g \right]$$

$$\gamma^* = \left[-\frac{d[N^*NO_5]_g}{dt} \right] \Big/ \left[\frac{\omega}{4} S_p [N^*NO_5]_g \right] = \left[k_{bgg} [N^*NO_5]_{aq} - k_{gbg} [N^*NO_5]_g \right] \Big/ \left[\frac{\omega}{4} S_p [N^*NO_5]_g \right]$$

We note that due the fact that we neglect aqueous phase diffusion in the kinetics, these uptake coefficients are only representing estimates and should be compared with caution to the measured data. In principle they represent the uptake coefficients expected for small enough particles (smaller than those in the experiments) such that liquid phase diffusion would not play a role. While the apparent reacto-diffusive length based on the net hydrolysis kinetics is rather large, the true dissociation as suggested here is rather fast. Inclusion of diffusion would require an explicit depth resolving model, which was beyond the scope of this analysis. The purpose of the simulations here was to simulate the behavior of labelled and non-labelled N_2O_5 in the aqueous phase and especially the exchange of labelled nitrate with the non-labelled nitrate pool for the case of $NaNO_3$.

For the simulations of the $NaNO_3$ and mixed Na_2SO_4 / $NaNO_3$ cases, we used the parameters for the kinetics as compiled by Mentel et al. (1999). The aerosol composition was derived from the E-AIM model as described in the main text and listed there in Table 1. Mentel et al. (1999) assumed the solubility of N_2O_5 to be 5 M atm^{-1} (2 M atm^{-1} in the IUPAC recommended parameterization). As mentioned in the main text and in the other recent studies (Bertram and Thornton, 2009), in view of the fact that the concentration of nitronium has never been measured, the solubility and also the other rate coefficients determining its

concentration are not well constrained. Mentel et al. set the dissociation rate coefficient, k_1, to 5×10^6 s^{-1}, the rate coefficient for the recombination, k_2, to 2.4×10^{10} M^{-1} s^{-1}, and the first rate coefficient for the reaction of nitronium with water, $k_3 \times [H_2O]_{aq}$, to $\times 10^9$ s^{-1} (note that the values given in Mentel et al.'s Table 2 are on a molality unit basis). This set of parameters that led to agreement with their own data and also nicely explain the data with labelled N_2O_5 presented in this study in the main text without further adjustments.

For the simulations of the Na_2SO_4 case, the dissociation and recombination rate coefficients were kept constant, but the rate of reaction of nitronium with water, $k_3 \times [H_2O]_{aq}$, was reduced by one order of magnitude to $\times 10^9$ s^{-1}, to obtain net uptake coefficients in agreement with the measurement. As mentioned and discussed in the main text, reducing the dissociation rate would have a similar effect. However, the parallel behavior of labelled and non-labelled N_2O_5 for the Na_2SO_4 aerosol is not affected by that.

References

Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, 2009.

Mentel, T. F., Sohn, M., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, Phys. Chem. Chem. Phys., 1, 5451-5457, 1999.

Table S2: Differential equations. $[N_2O_5]_{aq}$ is in units of M, while $[N_2O_5]_g$ is in units of molecule cm^{-3}. The rate coefficients are explained in more detail on the previous pages.

$\dfrac{d[N_2O_5]_{aq}}{dt} = -k_1[N_2O_5]_{aq} + k_2[NO_2^+]_{aq}[NO_3^-]_{aq} - k_{bgb}[N_2O_5]_{aq} + k_{gbb}[N_2O_5]_g$	D1
$\dfrac{d[N^*NO_5]_{aq}}{dt} = -k_1[N^*NO_5]_{aq} + k_2[N^*O_2^+]_{aq}[NO_3^-]_{aq} + k_2[NO_2^+]_{aq}[N^*O_3^-]_{aq} - k_{bgb}[N^*NO_5]_{aq} + k_{gbb}[N^*NO_5]_g$	D2
$\dfrac{d[NO_2^+]_{aq}}{dt} = k_1[N_2O_5]_{aq} + \dfrac{k_1}{2}[N^*NO_5]_{aq} - k_2[NO_2^+]_{aq}[NO_3^-]_{aq} - k_2[NO_2^+]_{aq}[N^*O_3^-]_{aq} - k_3[NO_2^+]_{aq}[H_2O]_{aq}$	D3
$\dfrac{d[N^*O_2^+]_{aq}}{dt} = \dfrac{k_1}{2}[N^*NO_5]_{aq} - k_2[N^*O_2^+]_{aq}[NO_3^-]_{aq} - k_3[N^*O_2^+]_{aq}[H_2O]_{aq}$	D4
$\dfrac{d[NO_3^-]_{aq}}{dt} = k_1[N_2O_5]_{aq} + \dfrac{k_1}{2}[N^*NO_5]_{aq} - k_2[NO_2^+]_{aq}[NO_3^-]_{aq} - k_2[N^*O_2^+]_{aq}[NO_3^-]_{aq} + k_3[NO_2^+]_{aq}[H_2O]$	D5
$\dfrac{d[N^*O_3^-]_{aq}}{dt} = \dfrac{k_1}{2}[N^*NO_5]_{aq} - k_2[NO_2^+]_{aq}[N^*O_3^-]_{aq} + k_3[N^*O_2^+]_{aq}[H_2O]_{aq}$	D6
$\dfrac{d[H_2O]_{aq}}{dt} = -k_3[N^*O_2^+]_{aq}[H_2O]_{aq} - k_3[NO_2^+]_{aq}[H_2O]_{aq}$	D7
$\dfrac{d[H^+]_{aq}}{dt} = 2k_3[N^*O_2^+]_{aq}[H_2O]_{aq} + 2k_3[NO_2^+]_{aq}[H_2O]_{aq}$	D8
$\dfrac{d[N_2O_5]_g}{dt} = k_{bgg}[N_2O_5]_{aq} - k_{gbg}[N_2O_5]_g$	D9
$\dfrac{d[N^*NO_5]_g}{dt} = k_{bgg}[N^*NO_5]_{aq} - k_{gbg}[N^*NO_5]_g$	D10