

Supporting Information

Constraints on aerosol nitrate photolysis as a potential source of HONO and NO_x

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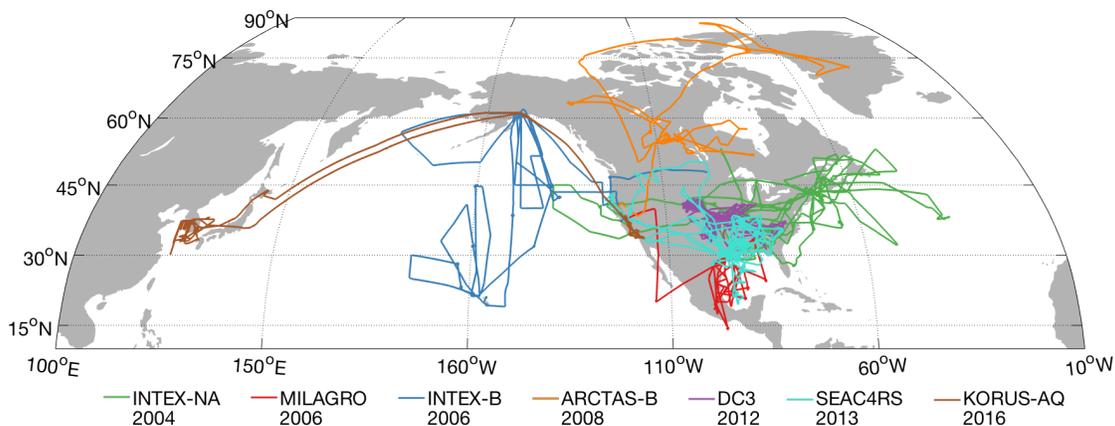


Figure S1: Map of all measurements taken on all 7 campaigns used in the extended analysis. The first phase of ARCTAS deployment (ARCTAS-A) was not included because conditions in the springtime Arctic (low light, high halogens) make it difficult to compare against other spring/summertime measurements.

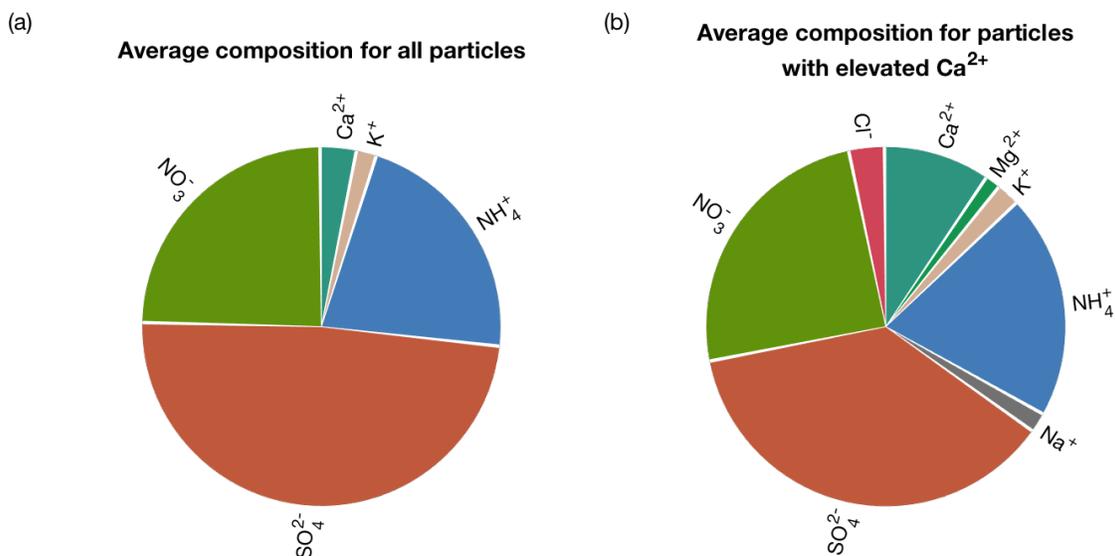


Figure S2: Average inorganic mass composition measured by SAGA in the boundary layer over the Yellow Sea for all filter samples (Panel a) and samples with over 5% mass composed of Ca^{2+} ions (Panel b).

Back trajectory centers of boundary layer observations over the Yellow Sea

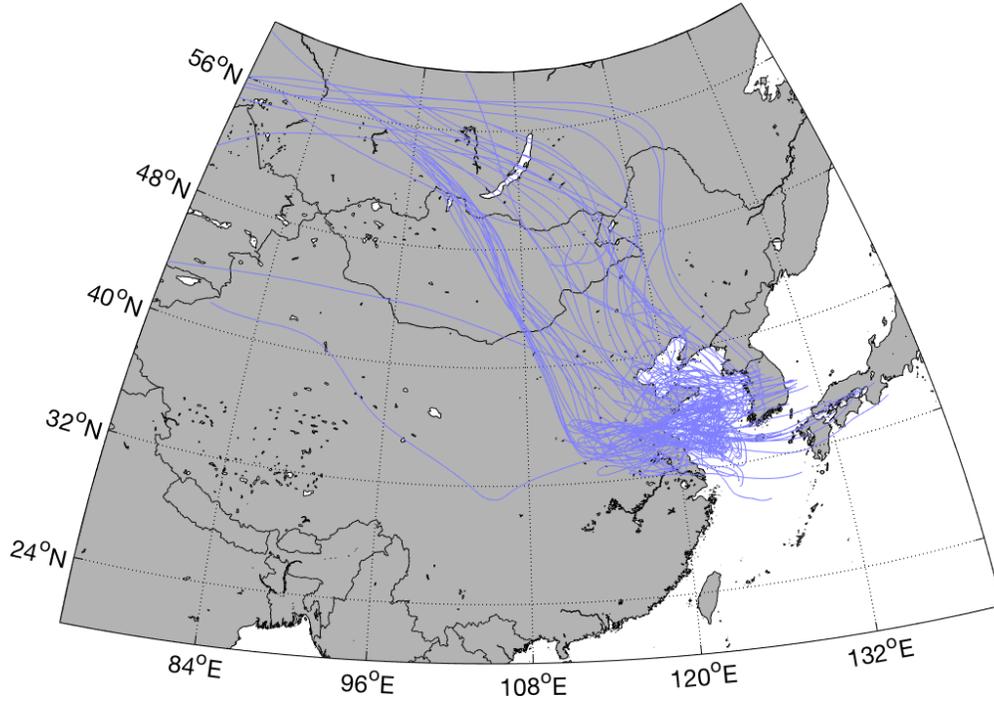


Figure S3: Back trajectories of air masses sampled by the DC-8 in the boundary layer over the Yellow Sea calculated using FLEXPART driven by NCEP GFS analyses.

Back trajectory centers of free troposphere observations over the Yellow Sea

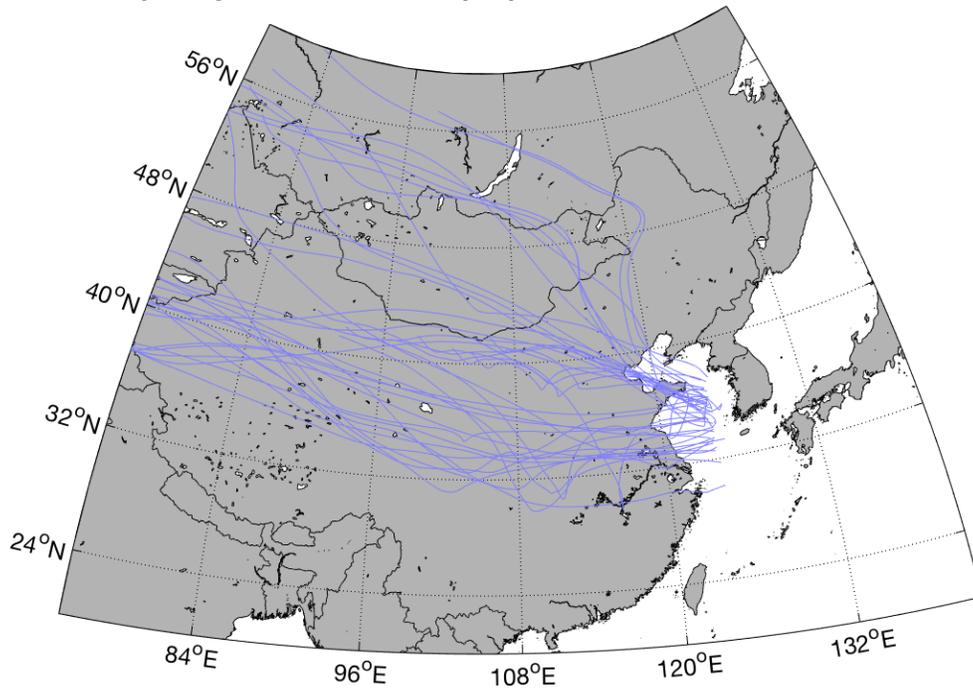


Figure S4: Back trajectories of air masses sampled by the DC-8 in the free troposphere over the Yellow Sea calculated using FLEXPART driven by NCEP GFS analyses.

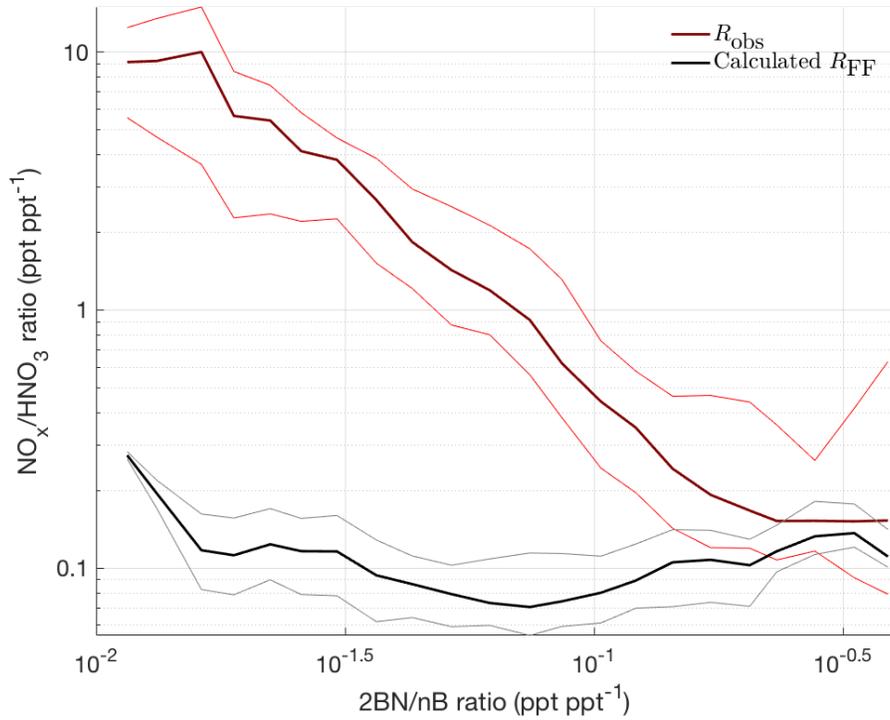


Figure S5: Evolution of the observed NO_x/HNO_3 ratio (red) and the calculated far-field ratio (black) as a function of the 2-Butyl Nitrate to n -butane ratio for all boundary-layer observations during KORUS-AQ. For both quantities, the thick line shows the binned median, and the thin lines show the binned inter-quartile range. R_{FF} is calculated assuming $EF = 10$ and using the best-guess estimates from Table S1.

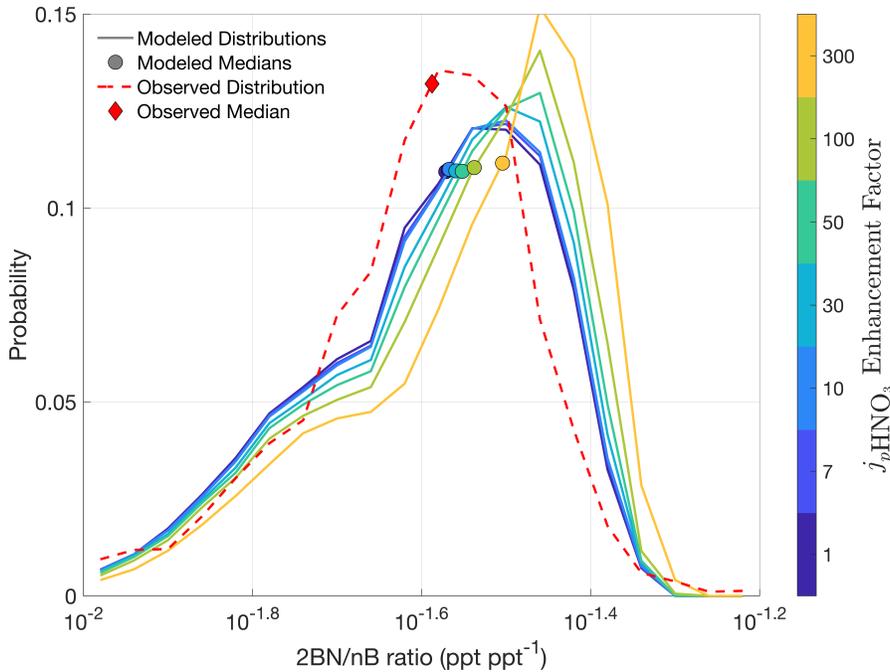


Figure S6: Modeled and observed distribution of 2BN/ n B ratios over the Yellow Sea. The modeled distribution includes all daytime model points between 0 and 3 days after model initialization.

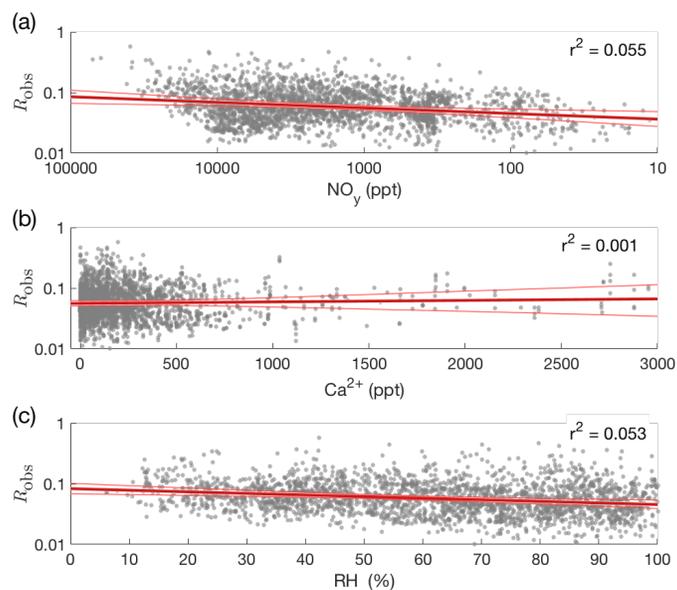


Figure S7: R_{obs} in highly-aged air masses as a function of total NO_y (Panel a), Ca^{2+} (Panel b), and relative humidity (Panel c). Note the reversed x-axis in Panel a, so that moving to the right on all panels is expected to correspond to an increase in nitrate photolysis rate and therefore an increase in R_{obs} . The thick red line represents a linear fit to all data points; the thin red lines show the error in the fit calculated by bootstrap sampling.

Table S1: Parameters used in the calculation of R_{FF} .

Parameter	Low-End	Best-Guess	High-End
Cl_Y (ppt)	7.0	18	36
Br_Y (ppt)	2.5	3.5	7.0
I_Y (ppt)	2.5	5.5	11
γ_{ClONO_2}	0.01	0.10	0.30
γ_{BrONO_2}	0.02	0.10	0.80
γ_{IONO_2}	0.02	0.10	0.80
γ_{RONO_2}	0.001	0.002	0.010
$\text{MW}_{\text{RONO}_2}$ (kg)	0.120	0.120	0.120
$v_{\text{dep,HNO}_3}$ (cm s^{-1}) ^a	1	2	4

^a Gas-phase only, daytime average.Table S2: Parameters used for modeling of plumes over the Yellow Sea. Median values were chosen to match best-guess estimates in the calculation of R_{FF} . The 5th and 95th percentiles were set to best match the low-end and high-end estimates using either a normal or a log-normal distribution.

Parameter	Median Value	5 th –95 th percentiles
Pressure (mbar)	960	880–990
Temperature (K)	291	287–296
RelativeHumidity (%)	47	21–80
Altitude (km)	0.46	0.16–1.2
Latitude ($^{\circ}\text{N}$)	20	10–30
HNO_3 Gas-Phase Fraction	0.51	0.12–0.88
Aerosol Surface Area ($\mu\text{m}^2 \text{cm}^{-3}$)	38	10–134
k_{dil} (s^{-1})	1.7e-05	1.1e-05–2.3e-05
$v_{\text{dep,HNO}_3}$ (cm s^{-1}) ^a	2.0	1.1–4.0
γ_{ClONO_2}	0.10	0.017–0.60
γ_{BrONO_2}	0.10	0.015–0.68
γ_{IONO_2}	0.10	0.015–0.68
γ_{RONO_2}	0.005	0.003–0.009
$\gamma_{\text{N}_2\text{O}_5}$	0.014	0.007–0.039
Br_Y (ppt)	3.5	2.0–6.0
Cl_Y (ppt)	18	7.7–42
I_Y (ppt)	5.5	2.5–12

^a Gas-phase only, daytime average.

Table S3: Initial concentrations used for modeling of plumes over the Yellow Sea.

Species	Median Concentration	5 th –95 th percentiles
O ₃ (ppb)	33	6–77
NO (ppb)	18	4–56
NO ₂ (ppb)	15	3–42
HNO ₃ (ppb)	4.6	1.1–13
PAN (ppb)	2.1	0.7–5.1
Methane (ppb)	2050	1920–2240
CO (ppb)	320	180–540
Ethane (ppb)	3.5	2.0–7.2
Ethene (ppb)	1.1	0.34–19
Propane (ppb)	2.9	1.1–15
Propene (ppb)	0.21	0.05–5.5
n-Butane (ppb)	1.5	0.5–5.6
2-Butyl Nitrate (ppb)	0.026	0.011–0.072
n-Pentane (ppb)	0.69	0.18–2.7
n-Hexane (ppb)	0.37	0.07–5.7
Toluene (ppb)	1.8	0.32–6.3
m-Xylene (ppb)	0.55	0.14–2.4
Isoprene (ppb)	0.3	0.04–0.6
α -Pinene (ppb)	0.016	0.004–0.054
Methanol (ppb)	19	8–42
Acetaldehyde (ppb)	2.5	0.7–7.1
Formaldehyde (ppb)	4.6	1.8–14
Additional VOCR (s ⁻¹)	1.4	1.4–1.4

Table S4: Background concentrations used for modeling of plumes over the Yellow Sea.

Species	Median Concentration	5 th –95 th percentiles
O ₃ (ppb)	99	79–120
NO _x (ppb) ^a	0.14	0.07–0.20
HNO ₃ (ppb)	2.6	1.3–3.4
PAN (ppb)	0.6	0.3–1.4
Methane (ppb)	1960	1930–2020
CO (ppb)	194	147–309
Ethane (ppb)	2.78	2.12–3.18
Ethene (ppb)	0.013	0.006–0.019
Propane (ppb)	0.80	0.44–1.0
Propene (ppb)	0.017	0.015–0.019
n-Butane (ppb)	0.096	0.07–0.265
2-Butyl Nitrate (ppb)	0.025	0.016–0.029
n-Pentane (ppb)	0.02	0.008–0.07
n-Hexane (ppb)	0.01	0.004–0.05
Toluene (ppb)	0.005	0.002–0.17
m-Xylene (ppb)	0.012	0.006–0.015
Isoprene (ppb)	0.01	0.002–0.04
α-Pinene (ppb)	0	0–0
Methanol (ppb)	6.7	5.0–11.2
Acetaldehyde (ppb)	0.33	0.25–1.2
Formaldehyde (ppb)	0.506	0.35–3.1

^a The partitioning of background NO_x between NO and NO₂ was assumed to match the instantaneous partitioning in the model.

Eigenvector analysis of NO_x , HNO_3 , and PAN

Equations S1–S12 give explicit formulas for the effective first-order rate constants used in the eigenvector analysis. Values for all rate constants were taken from the IUPAC chemical kinetics database (Atkinson et al., 2006), except for $k_{\text{OH}+\text{NO}_2}$ which used the results of Dulitz et al. (2018). Formulas for k_{assoc} and k_{dissoc} were taken from LaFranchi et al. (2009). Species marked in bold in the equations were not measured, and concentrations taken from a chemical box model were used instead. S_a is the aerosol surface area concentration, MW_X is the molecular weight of X , and R in Eq. S9 is the gas constant.

$$k_{\text{forward}} = \frac{1}{[\text{NO}_x]} \left(k_{\text{OH}+\text{NO}_2} [\text{OH}] [\text{NO}_2] + [\text{RONO}_2] \frac{\bar{v}_{\text{RONO}_2} \cdot \gamma_{\text{RONO}_2} S_a}{4} + [\mathbf{XONO}_2] \frac{\bar{v}_{\text{XONO}_2} \cdot \gamma_{\text{XONO}_2} S_a}{4} + [\mathbf{N}_2\mathbf{O}_5] \frac{\bar{v}_{\text{N}_2\mathbf{O}_5} \cdot \gamma_{\text{N}_2\mathbf{O}_5} S_a}{4} \right) \quad (\text{S1})$$

$$k_{\text{backward}} = k_{\text{OH}+\text{HNO}_3} [\text{OH}] f_g + j_{g\text{HNO}_3} f_g + j_{g\text{HNO}_3} EF (1 - f_g) \quad (\text{S2})$$

$$k_{\text{removal}} = \frac{1}{[\text{NO}_x]} \left(\sum_i k_{\text{R}_i\text{O}_2+\text{NO}} [\mathbf{R}_i\mathbf{O}_2] [\text{NO}] \alpha_i \right) \quad (\text{S3})$$

$$k_{\text{dep}} = \frac{v_{\text{dep}}}{\text{BLH}} f_g \quad (\text{S4})$$

$$k_{\text{assoc}} = \frac{1}{[\text{NO}_x]} (k_{\text{CH}_3\text{CHO}+\text{OH}} [\text{CH}_3\text{CHO}] [\text{OH}] + j_{\text{Acetone}} [\text{Acetone}]) \beta \quad (\text{S5})$$

$$k_{\text{dissoc}} = (k_{\text{PAN}} + j_{\text{PAN}}) \cdot (1 - \beta) \quad (\text{S6})$$

$$f_g = \frac{[\text{gHNO}_3]}{[\text{gHNO}_3] + [\text{pHNO}_3]} \quad (\text{S7})$$

$$\beta = \frac{k_{\text{R(O)O}_2+\text{NO}_2} [\text{NO}_2]}{k_{\text{R(O)O}_2+\text{NO}_2} [\text{NO}_2] + k_{\text{R(O)O}_2+\text{NO}} [\text{NO}] + k_{\text{R(O)O}_2+\text{HO}_2} [\text{HO}_2]} \quad (\text{S8})$$

$$\bar{v}_X = \sqrt{\frac{8RT}{\pi \cdot \text{MW}_X}} \quad (\text{S9})$$

$$\frac{d[\text{NO}_x]}{dt} = -k_{\text{forward}} [\text{NO}_x] + k_{\text{backward}} [\text{HNO}_3] - k_{\text{removal}} [\text{NO}_x] - k_{\text{assoc}} [\text{NO}_x] + k_{\text{dissoc}} [\text{PAN}] \quad (\text{S10})$$

$$\frac{d[\text{HNO}_3]}{dt} = k_{\text{forward}} [\text{NO}_x] - k_{\text{backward}} [\text{HNO}_3] - k_{\text{dep}} [\text{HNO}_3] \quad (\text{S11})$$

$$\frac{d[\text{PAN}]}{dt} = k_{\text{assoc}} [\text{NO}_x] - k_{\text{dissoc}} [\text{PAN}] \quad (\text{S12})$$

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