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Two years of online measurement of fine particulate nitrate in the western Yangtze River Delta: influences of thermodynamics and N_2O_5 hydrolysis

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Supplement

1. The uncertainty of the calculation of N_2O_5 hydrolysis

The variation of N_2O_5 uptake coefficient and VOCs concentrations are the dominate sources of the uncertainty to calculate N_2O_5 hydrolysis. Here, a range of uptake coefficient from 0.01 to 0.05 (Brown et al., 2006; Brown et al., 2016; Wen et al., 2015; Osthoff et al., 2006) with the interval of 0.002 was deployed in the calculation to compare with the result in section 2.4. Since VOCs were not measured at SORPES station during 2014 – 2016, averaged nighttime values those were measured using a PTR-TOF_{1000} in the winter of 2017 were used in the calculation. Four species of isoprene, monoterpene, styrene and phenol, which have higher reaction rates with NO_3 radical (Osthoff et al., 2006) and higher concentrations at SORPES station. 10 percentiles, 25 percentiles, median ,75 percentiles and 90 percentiles of night VOCs concentrations in winter with the actual concentrations shown in table S1 have been selected as the input to calculate the uncertainties. The results are shown in Fig. S1. The largest uncertainty, which can be up to 70%, was from the variation of N_2O_5 uptake coefficient. The changes of VOCs concentrations can also cause about 30% uncertainty. More experiments are thus recommended to quantify the N_2O_5 uptake coefficient and in turn the contribution of N_2O_5 hydrolysis to nitrate formation.

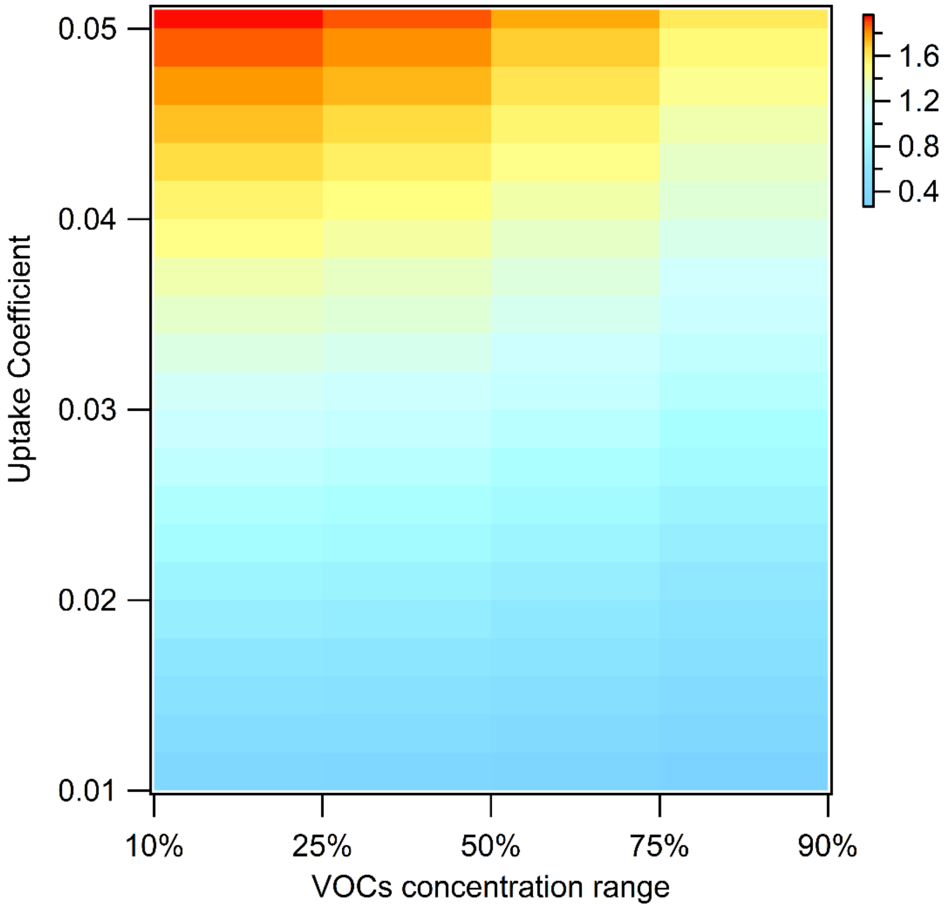

Figure S1 The uncertainty estimation for the calculation of nitrate from N_2O_5 hydrolysis. The calculated nitrate production from N_2O_5 hydrolysis in section 2.4 was set as the reference value. The figure is color-coded by the ratio of the calculated nitrate to this reference value with varied uptake coefficients and VOCs concentrations. The y axis presents N_2O_5 uptake coefficients from 0.01 to 0.05. The x axis presents the nighttime VOCs concentrations measured during the winter of 2017, which were listed in Table S1 and ranged from 10th percentiles to 90th percentiles.

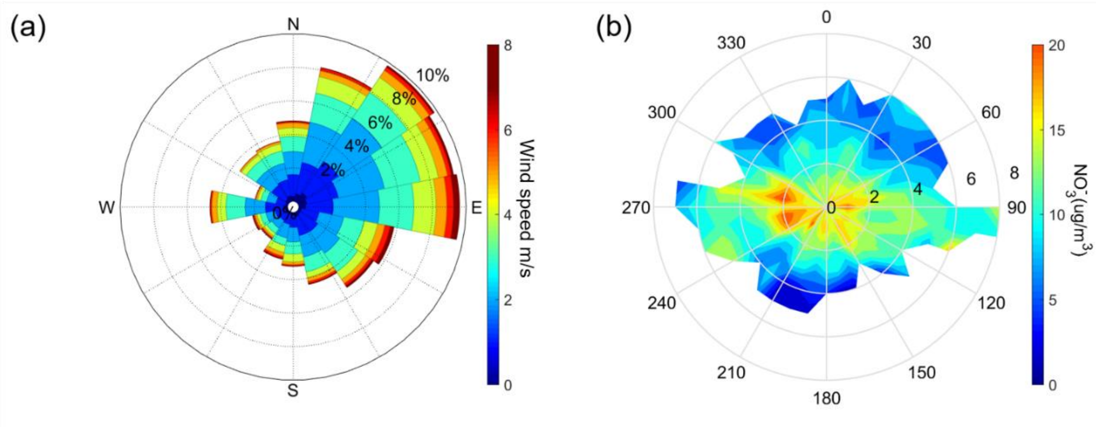

Figure S2 (a) Wind rose plot, color-coded by wind speed (m/s). **(b)**Wind rose plot, color-coded by the median nitrate mass concentrations at corresponding wind speed and wind direction.

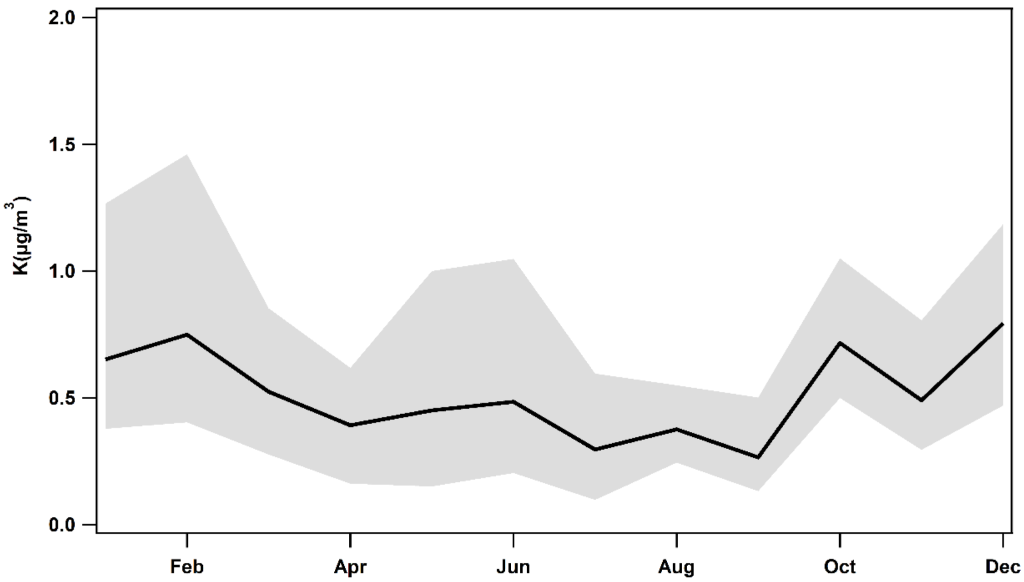

Figure S3 Monthly variation of potassium. Bold solid lines are the median values and thin solid lines represent percentiles of 75% and 25%.

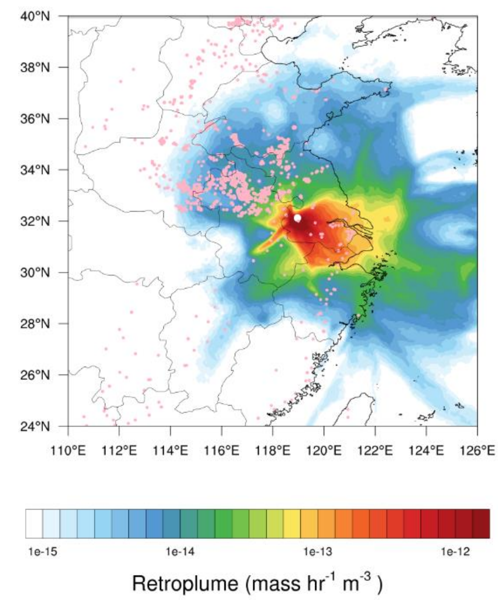

Figure S4 The averaged retroplumes (i.e., 100 m footprint) for the Top 25% nitrate concentrations in summer 2014 together with the fire spots during the same time. Pink points indicate the fire spots.

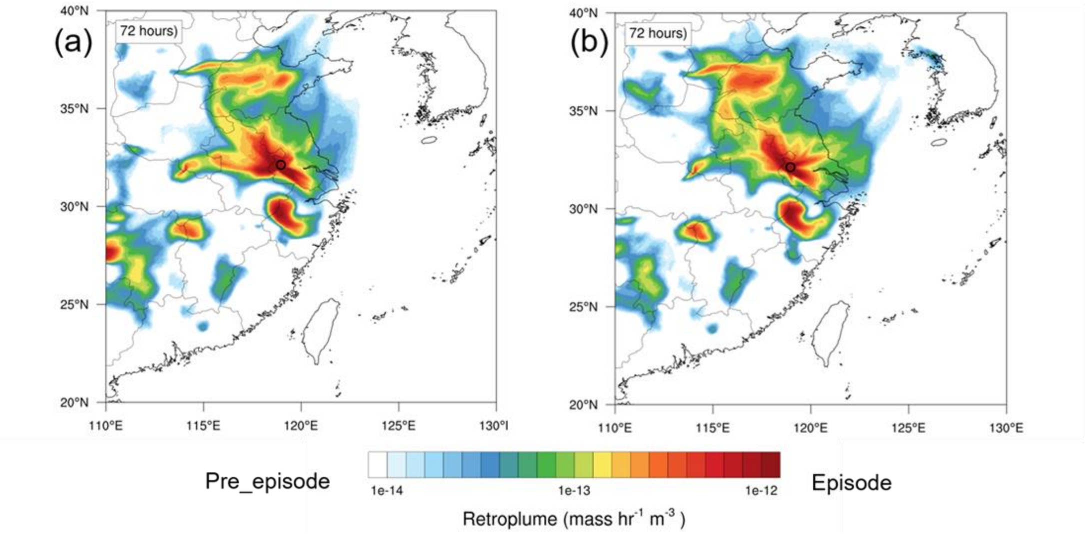

Figure S5 Averaged retroplume of air masses at Nanjing for the period of **(a)** pre-episode days and **(b)** episode days of nitrate pollution.

Table S1 The actual concentrations of VOCs different quantiles.

	Isoprene (ppb)	Monoterpene (ppb)	Phenol (ppb)	Styrene (ppb)
10%	0.07	0.04	0.05	0.06
25%	0.09	0.05	0.06	0.09
50%	0.14	0.06	0.08	0.14
75%	0.20	0.09	0.12	0.23
90%	0.28	0.14	0.16	0.34
average	0.16	0.09	0.10	0.18

Table S2 Average nitrate concentrations at different sites during winter and summer and the corresponding references.

Winer site	Measurement periods	NO_3^- (μg/m^3)	Provenance	**Summer site**	Measurement periods	NO_3^- (μg/m^3)	Provenance
Handan	2015	26.18	(Li et al., 2017)	Yucheng	2013/2014	18	(Wen et al., 2018)
Tianjing	2013	29.4	(Zou et al., 2018)	Beijing	2011	16.8	(Yang et al., 2017)
Beijing	2013	16.4	(Hu et al., 2017)	Jinan	2008	19.2	(Gao et al., 2011)
Tianjing	2003	25.5	(Cao et al., 2012)	Beijing	2005	13.7	(Pathak and Wu, 2009)
Beijing	2003	13.1	(Cao et al., 2012)	Beijing	2003	9.9	(Cao et al., 2012)
Nanjing	2014/2015	22.3	(This study)	Nanjing	2014/2015	11.8	(This study)
Shanghai	2013	22.5	(Zhang et al., 2015)	Shanghai	2005	7.1	(Pathak and Wu, 2009)
Linan	2013	15	(Zhang et al., 2015)	Hangzhou	2003	5.5	(Cao et al., 2012)
Shanghai	2003	17.5	(Cao et al., 2012)	Shanghai	2003	2.6	(Cao et al., 2012)
Hong Kong	2011/2012	3.3	(Griffith et al., 2015)	Hong Kong	2011/2012	1.1	(Griffith et al., 2015)
Hong Kong	2011	3.84	(Bian, et al., 2014)	Hong Kong	2011	0.53	(Bian, et al., 2014)
Zhongshan	2010	8.496	(Wang et al., 2012)	Shenzhen	2009	4.45	(He et al., 2011)
Guangzhou	2003	11.5	(Cao et al., 2012)	Guangzhou	2003	1.2	(Cao et al., 2012)

Table S3 The seasonal and annual average mass concentrations of $PM_{2.5}$, ammonium and other related gases at SORPES station from 2014.3 to 2016.2.

	NH_4^+ (μg/m^3)	$PM_{2.5}$ (μg/m^3)	NOx ppb	O_3 ppb	NH_3 (μg/m^3)	$NO_3/PM_{2.5}$
Jan.	14.8	93.8	46.7	12.1	5.0	23.7%
Feb.	12.9	78.6	28.3	22.8	6.2	26.3%
Mar.	11.0	67.7	28.5	24.0	5.3	26.4%
Apr.	9.3	58.9	23.0	31.6	5.8	24.5%
May	8.9	67.2	22.9	39.1	9.2	19.4%
Jun.	11.2	70.2	18.4	35.4	10.9	22.6%
Jul.	9.6	48.6	19.9	29.3	14.9	20.3%
Aug.	7.8	41.9	15.3	28.8	8.5	18.5%
Sept.	6.6	41.1	20.0	28.5	6.0	18.6%
Oct.	8.6	61.8	30.7	28.2	6.5	21.1%
Nov.	10.7	70.9	33.6	15.0	4.4	25.7%
Dec.	13.1	88.8	47.0	9.6	4.9	23.4%
Annual	10.5	65.8	27.9	24.8	7.4	22.6%

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