Electronic Supplementary Material to RO_x Budgets and O_3 Formation during Summertime at Xianghe Suburban Site in the North China Plain*

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Descriptions of instruments

O_3, NO_x, and CO measurements

An O_3 calibrator (49C PS) was used to calibrate the O_3 analyzers. The calibrator is traceable to the National Institute of Standards and Technology in the USA. The analyzers of NO_x and CO were calibrated using a 52 ppmv NO standard gas and a 5000 ppmv CO standard gas (Scott-Marin gases, Riverside, CA, USA), respectively. In addition, the CO analyzer was zeroed every two hours using an internal catalytic converter (Ji et al., 2014). Scheduled quality control procedures included daily zero and span checks, biweekly precision checks, quarterly multiple-point calibrations, and data validations.

VOC measurements

Ambient VOC samples were analyzed continuously using a gas chromatography instrument (GC, 7820A, Agilent Technologies, Santa Clara, CA, USA) equipped with a mass spectrometer (MS) and flame ionization detector (FID) (5977E, Agilent Technology, Santa Clara, CA, USA) with a time resolution of 1 h. A complete analysis cycle for ambient VOC measurements by the online GC-MS/FID system includes five stages: preparation, sampling and pre-concentration, injection/GC analysis, idle/GC analysis, and back purge/GC analysis (Wang et al., 2014). Briefly, samples are collected into GC–MS/FID every 1 h for a duration of 5 min at a flow of 60 mL min^{-1}. Both the CO_2 and H_2O were removed in an electronic cryogenic pre-concentrator (TH300, Wuhan Tianhong Environmental protection industry co., LTD, Wuhan, China) before VOC analysis. The air was then thermally desorbed at 100°C and transferred for analysis. Dual columns and detectors were applied for the simultaneous analysis of C2-C12 hydrocarbons. C2-C5 hydrocarbons were separated on a PLOT-Al_2O_3 column (15 m × 0.32 mm ID × 3 μm, J&W Scientific, USA) and were measured by the FID channel. Other compounds were separated on a semipolar column (DB624, 60 m × 0.25 mm ID × 1.4 μm, J&W Scientific, USA) and were quantified using a quadrupole MS detector.

The system was calibrated at multiple concentrations in the range of 0.8–8 ppbv with gas standard of a mixture of 57 PAMS (provided by Spectra Gases Inc., USA). Daily calibrations were performed, and the variations of target species responses were required to be within ± 20% from the calibration curve. R^2 values for calibration curves ranged from 0.941 (n-dodecane) to 1.000 for VOCs, indicating that integral areas of peaks were proportional to the concentrations of target compounds.

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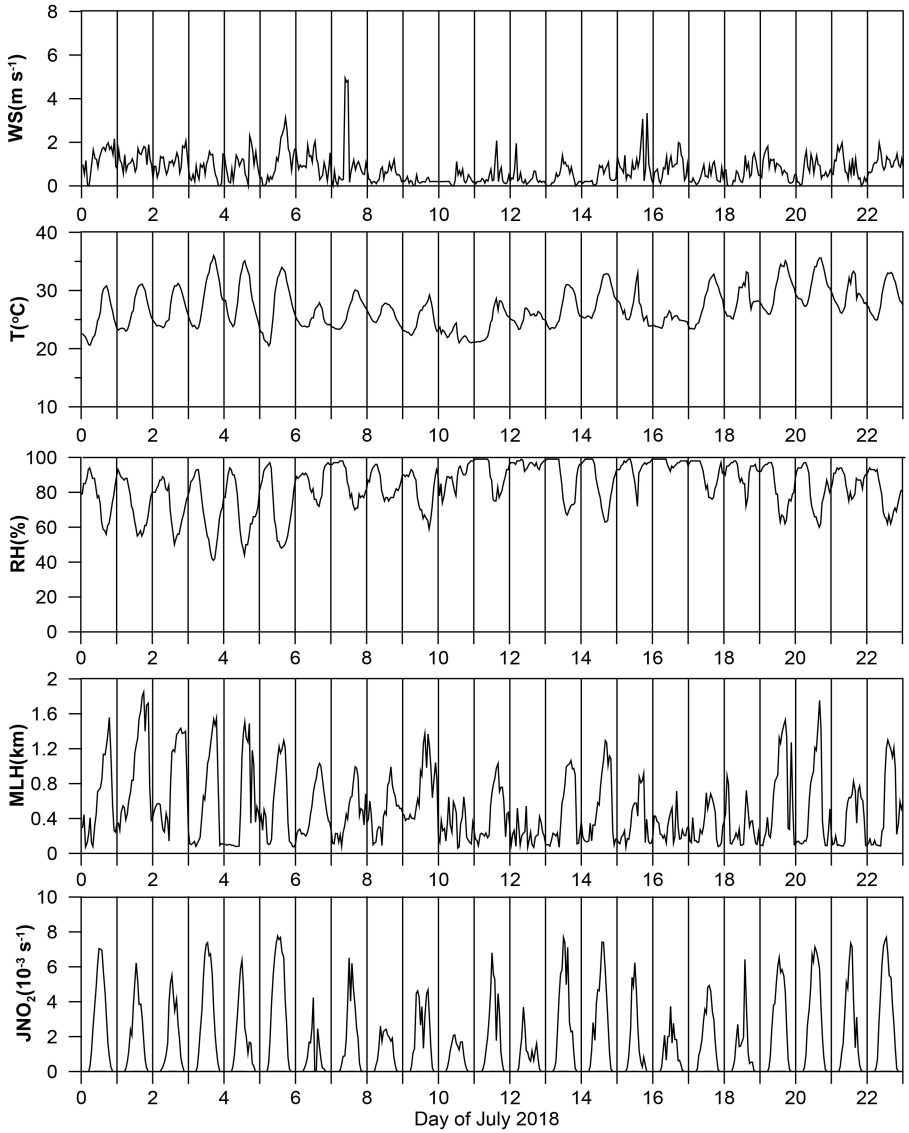

Fig. S1. The time series of measured wind speed (WS), temperature (T), relative humidity (RH), mixing layer height (MLH), and NO_2 photolysis frequency (JNO_2) at the Xianghe site.

Table S1. Overview of trace gas measurements at the Xianghe site.

Species	Instrument of Techniques	Time resolution	Detection limit	Accuracy
NO_x	Thermo 42i	30 min	0.05 ppbv	0.4 ppb
O_3	Thermo 49i	5 min	1 ppbv	1 ppb
CO	Thermo 48i	5 min	0.04 ppmv	0.1 ppm
HONO	LOPAP	1 min	10 pptv	10%
VOCs	GC-MS/FID	60 min	1–39 pptv	2%–17%

HONO measurements

HONO was measured using a custom-made HONO analyzer, and the principle of which is similar to long path absorption photometer (LOPAP)(Kleffmann et al., 2002). HONO is quickly collected by a two-channel glass stripping coil with an absorption solution (0.06 M sulfanilamide in 1 M HCl) to form a stable diazonium salt which then reacts with a dye solution [0.8 mM N-(1-naphthyl) ethylene diamine dihydrochloride]. Then an azo dye is formed and finally pumped into a 50 cm liquid waveguide capillary cell (LWCC). A subsequent detection is performed by an optical absorption spectrometer (SD2000, Ocean Optics USA). The final HONO concentration is the difference of signals between the two channels. The

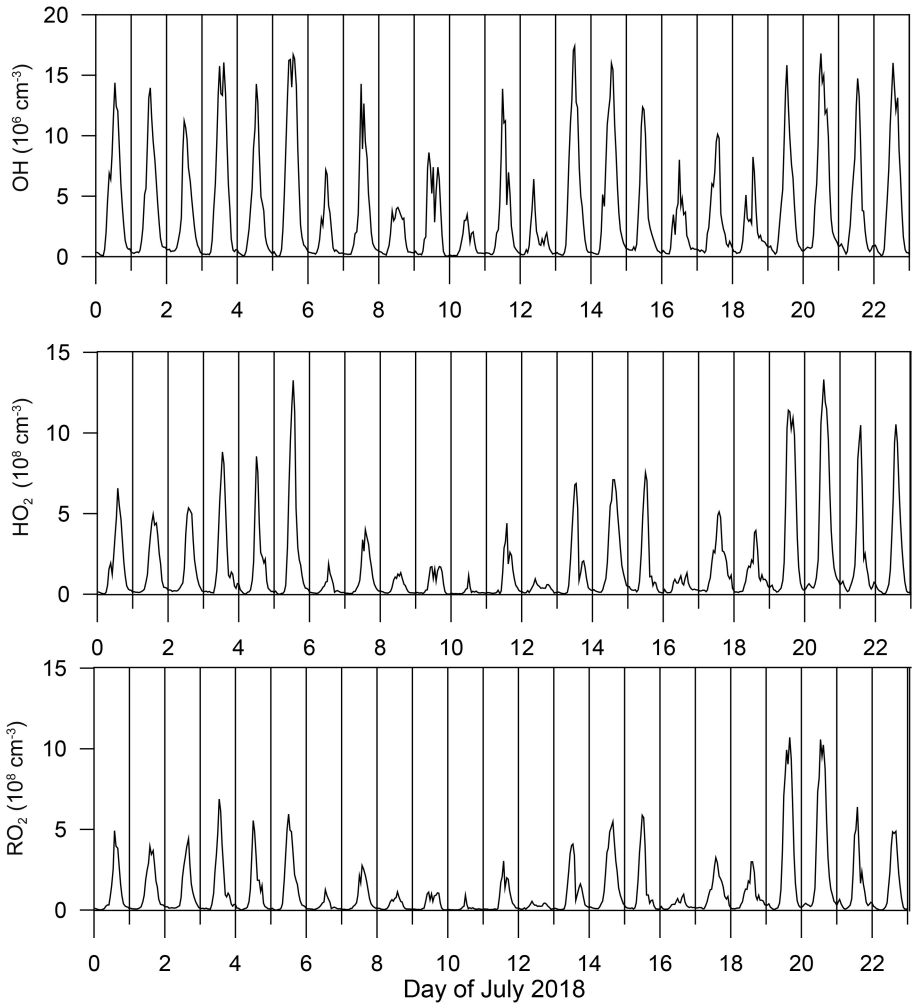

Fig. S2. Simulated time series concentrations of OH, HO_2, and RO_2 at the Xianghe site.

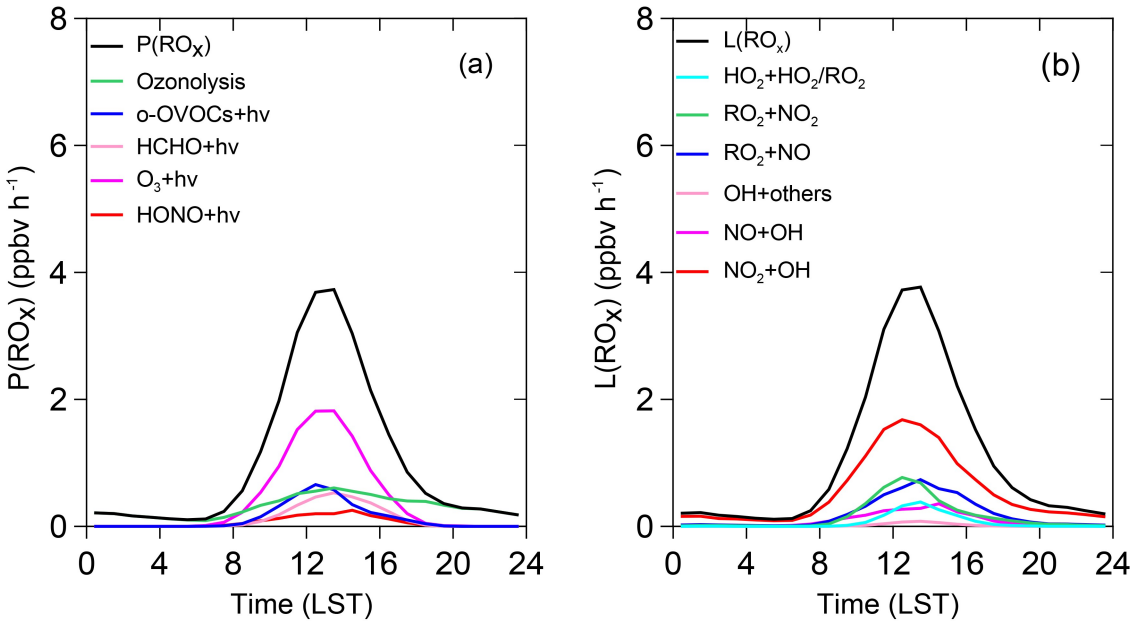

Fig. S3. Same as Fig. 5, but without the HONO constraint.

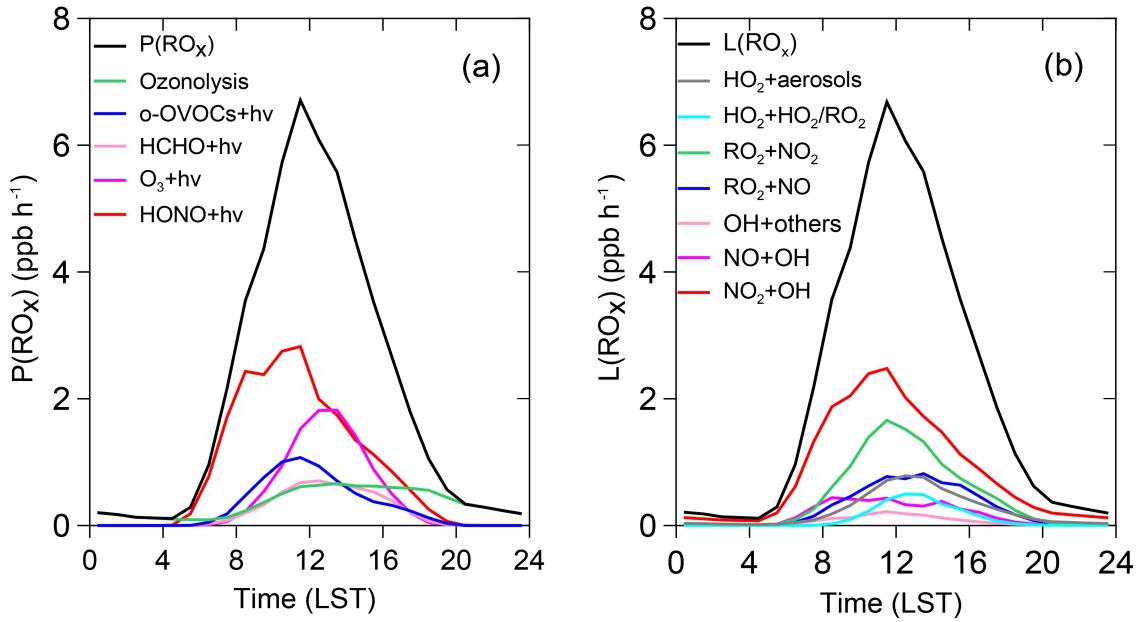

Fig. S4. Same as Fig. 5, but considering heterogeneous reactions of gases and radicals on aerosols.

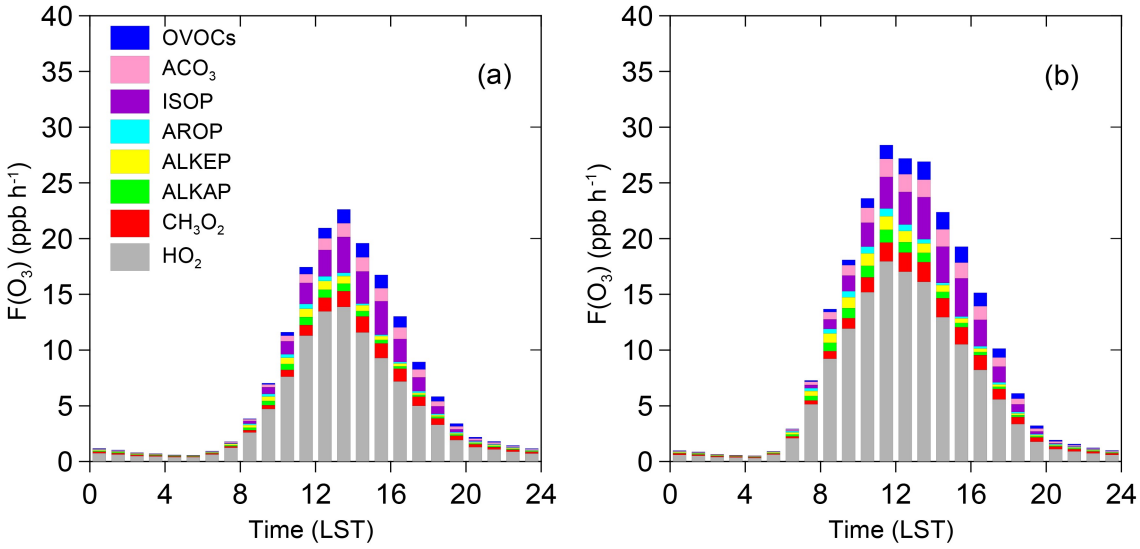

Fig. S5. Same as Fig. 7a, but without the HONO constraint (a); considering heterogeneous reactions of gases and radicals on aerosols (b).

liquid flow rate is 0.3 mL min^{-1} with a sampling gas flow rate of 1.0 L min^{-1}. During the field campaigns under the optimized conditions, the detection limit was 10 pptv at a time resolution of 1 min. In addition, the LOPAP instrument was calibrated weekly using a known concentration of HNO_2 standard solution. By sampling zero air (high-purity nitrogen), zero measurements were carried out every 7 h and each time lasting 1 h. A side by side inter-comparison between the custom-made HONO analyzer and a commercial LOPAP instrument was carried out by Hou et al. (2016), which certified the accuracy and reliability of HONO analyzer.

Table S2. Statistic of daytime (0600–1800 LST) meteorological parameters and trace gas concentrations (mean value ± standard deviation, and maximum value) observed at the Xianghe site.

Parameter	Day average	SD	Max (1 hourly)
Temperature (°C)	31.1	4.4	40.1
RH (%)	78.9	16.6	100.0
O_3	55.4	33.4	136.6
O_x	65.5	30.9	144.9
NO	2.3	2.2	21.1
NO_2	10.1	4.4	37.7
NO_x	12.5	5.9	50.1
CO	786.5	552.0	3032.0
Hono	0.9	0.5	2.7
Ethane	3.14	1.49	8.65
propane	3.37	2.08	12.66
iso-butane	1.10	0.82	5.25
n-butane	1.88	1.59	12.04
cyclopentane	0.01	0.01	0.17
isopentane	1.11	0.73	7.15
n-pentane	0.69	0.50	2.98
2,2-dimethylbutane	0.04	0.06	0.34
2,3-dimethylbutane	0.11	0.11	1.21
2-methylpentane	0.11	0.11	0.74
3-methylpentane	0.13	0.11	1.06
n-hexane	0.16	0.16	0.87
2,4-dimethylpentane	0.01	0.01	0.04
methylcyclopentane	0.14	0.21	1.07
2-methylhexane	0.02	0.02	0.17
2,3-dimethylpentane	0.02	0.07	1.04
cyclohexane	0.29	0.36	2.22
3-methylhexane	0.03	0.02	0.18
2,2,4-trimethylpentane	0.02	0.02	0.15
n-heptane	0.04	0.03	0.20
methylcyclohexane	0.02	0.02	0.12
2,3,4-trimethylpentane	0.01	0.00	0.05
2-methylheptane	0.01	0.01	0.08
n-octane	0.02	0.06	2.71
n-nonane	0.02	0.04	0.87
n-decane	0.01	0.01	0.31
n-undecane	0.01	0.00	0.03
n-dodecane	0.01	0.00	0.02
ethylene	1.46	1.11	5.80
propylene	0.31	0.25	3.51
t-2-butene	0.05	0.02	0.23
1-butene	0.14	0.09	1.27
c-2-butene	0.09	0.06	0.31
1,3-butadiene	0.02	0.03	0.44
1-pentene	0.02	0.06	0.70
c-2-pentene	0.01	0.01	0.07
acetylene	1.61	0.82	7.26
benzene	0.61	0.42	2.13
toluene	0.56	0.36	3.73
ethylbenzene	0.37	0.54	4.65
m,p-xylene	1.15	1.46	12.27
o-xylene	0.41	0.58	5.61
styrene	0.14	0.57	8.33

Table S2. (Continued.)

Parameter	Day average	SD	Max (1 hourly)
isopropybenzene	0.01	0.01	0.10
n-propybenzene	0.01	0.01	0.08
m-ethyltoluene	0.04	0.03	0.39
p-ethyltoluene	0.02	0.02	0.22
1,3,5-trimethylbenzene	0.01	0.01	0.16
o-ethyltoluene	0.01	0.01	0.12
1,2,4-trimethylbenzene	0.02	0.02	0.19
1,2,3-trimethylbenzene	0.01	0.00	0.04
p-diethylbenzene	0.01	0.00	0.04
Alkanes	12.5	7.6	39.6
Alkenes	3.7	2.0	10.3
Aromatics	3.4	3.1	25.8
Isoprene	1.1	1.1	7.0

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