



Supplement of

Impacts of an unknown daytime HONO source on the mixing ratio and budget of HONO, and hydroxyl, hydroperoxyl, and organic peroxy radicals, in the coastal regions of China

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b) Beijing, (c, d) Shanghai, and (e, f) Guangzhou in August 2007. $(HONO+hv)_{net}$ means the net OH production rate from HONO photolysis (subtracting OH + NO = HONO).



Fig. S1. Correlations of the unknown daytime HONO source $(P_{unknown})$ (ppb h⁻¹) with NO₂ mixing ratios (ppb) and [NO₂] $J(NO_2)$ (ppb s⁻¹) in (a), (b) the coastal regions of China, (c), (d) the other countries, and (e), (f) the globe, respectively, based on the field experiment data shown in Fig. 1 in the revised version.



Fig. S3. Production [P(HONO)] and loss [L(HONO)] rates of HONO for cases R (dashed lines), R_p (solid lines) and sensitivity ranges (based on R_{inc} and R_{dec}) in (a), (b) Beijing, (c), (d) Shanghai, and (e), (f) Guangzhou in August 2007. Case R_{inc} includes case R_p with an increase of 25% (the maximum uncertainty range according to the previous studies above) in the slope factor (19.60); Case R_{dec} is the same as case R_p with a decrease of 25% in the slope factor (19.60).

1	Table S1. The calculated unknown daytime HONO source (Punknown), NO2 mixing ratios and photolysis frequency of NO2 [J(NO2)] from field experiments in Figure
2	1.

Site	Date	Time	P _{unknown} (ppb h ⁻¹)	[NO ₂] (ppb)	$ \overline{J(NO_2)} \\ (\times 10^{-3} \text{ s}^{-1}) $	Measurement techniques /Uncertainties	Reference
		09:30	2.36	29.65	2.31	HONO: WD/IC;	
		10:30	3.57	36.46	4.09	NO ₂ : estimated from NO and NO _v	
Xinken	2004.10.23-	11:30	4.39	39.51	5.46	(measured by the NO-O ₃	0 (1(0000)
(22.6 N,	2004.10.30	12:30	4.90	33.33	5.83	chemiluminescence detector (Kondo et	Su et al. (2008)
113.6 E)		13:30	3.96	33.54	5.93	al., 1997))/22%;	Su et al. (2011)
		14:30	2.93	32.43	4.92	J(NO ₂): TUV/18%;	
		15:30	2.46	26.94	3.85	P _{unknown} : 10~30%.	
		8:00	2.59	22.66	6.29		
	2007.00.17	10:00	1.66	22.67	8.16		
	2007.08.17	12:00	1.00	24.09	8.35		
		14:00	3.12	19.39	6.82		
		8:00	1.39	27.96	6.29		
D	2007.00.10	10:00	3.52	21.37	8.16	HONO: Annular denuders;	
Beijing	2007.08.18	12:00	4.12	16.66	8.35	NO ₂ : means of commercial ECOTECH	0 (2012)
(39.99 N,		14:00	2.06	12.90	6.82	Ltd. (Australia analyzer)/ 1%;	Spataro et al. (2013)
116.30 E)		8:00	4.38	29.50	6.29	$J(NO_2)$: calculated by $J(HONO)$;	
		10:00	5.91	37.53	8.16		
	2007.08.19	12:00	2.26	18.67	8.35		
		14:00	0.73	12.54	6.82		
		8:00	5.51	36.69	6.29		
	2007.08.20	10:00	6.57	40.94	8.16		

		12:00	2.59	18.78	8.35		
		14:00	4.18	18.79	6.82		
		10:00	2.87	27.62	5.45		
T CI		11:00	3.82	32.62	6.59	HONO: LOPAP;	
Tung Chung	2011.08.25-	12:00	5.34	31.31	7.41	NO ₂ : TEI;	$W_{1} = (2012)$
(22.30 N, 112.02 F)	2011.08.31	13:00	4.90	27.86	7.92	J(NO ₂): Optical actinometer.	wu et al. (2015)
113.93 E)		14:00	4.80	24.40	7.17		
		15:00	4.12	23.33	6.02		
		10:30	0.03	-	4.73		
		11:00	0.03	-	6.03	HONO: LOPAP;	
	2009.03.13- 2009.04.14	11:30	0.06	4.23	8.16	NO ₂ : estimated from NO and NO _y	
Alaska		12:00	0.09	-	8.81	(measured by the $NO-O_3$	
(71.32 N,		12:30	0.05	-	9.46	chemiluminescence detector;	Villena et al. (2011)
156.65 W)		13:00	0.08	-	8.69	J(NO ₂): estimated as a function of solar	
		13:30	0.07	17.31	7.63	zenith angle using the TUV radiative	
		14:00	0.05	12.24	6.33	transfer model.	
		14:30	0.03	8.85	4.79		
						HONO: LOPAP;	
Michigan						NO ₂ : Custom-built analyzer using the	
Michigan	2008.07.17-	n 00 n	0.35	1.00	Q 1Q	chemiluminescence technique;	Then $a t a (2012)$
(43.30 N, 84.70 W)	2008.08.07	HOOH	0.55	1.00	0.40	J(NO ₂): estimated as a function of UV	Zhang et al. (2012)
84.70 W)						measured by the TUV radiative transfer	
						model/10%.	
Michigan						HONO: Two-channel measurement	
(45.50 N,	2000.07.27	noon	1.60	0.13	8.48	system (Zhou et al., 1999);	Zhou et al. (2002a)
84.70 W)						NO ₂ : TEI Model.	

		10:00	0.11	2.15	5.39		
C	2008 07 17	11:00	0.10	1.38	6.26	HONO: LOPAP/12%;	
Spain	2008.07.17-	12:00	0.08	0.95	6.76	NO ₂ : Droplet Measurement Technologies	C ∺
(37.10 N, 674.00)	2008.08.07	13:00	0.09	0.84	6.68	(Hosaynan-Beygi et al., 2011)/8%;	S orgen et al. (2011)
6.74 W)	(cloud-free)	14:00	0.08	0.79	6.03	J(NO ₂): Filter radiometers/5%;	
		15:00	0.05	0.66	4.62	P _{unknown} : 18%.	
New York (42.09 N, 77.21 W)	1998.06.26- 1998.07.14	noon	0.22	1.00	8.48	HONO: Two-channel measurement system (Zhou et al., 1999); NO ₂ : TEI Model.	Zhou et al. (2002b)
Santiago (33.45 S, 70.67 W)	2005.03.08- 2005.03.20	noon	1.70	10.00	8.00	HONO: LOPAP; NO ₂ : DOAS-OPSIS optical system; J(NO ₂): Filter radiometers.	Elshorbany et al. (2009)
		10:00	0.40	7.50	7.29		
TT (11:00	0.59	6.02	7.77	HONO: LP-DOAS/5%;	
Houston	2000 04 21	12:00	0.74	5.45	8.03	NO_2 : LP-DOAS/3%;	We may at al. (2012)
(29.70 N, 05.27 gW)	2009.04.21	13:00	0.66	4.89	8.03	$J(NO_2): SAFS;$	wong et al. (2012)
95.57 W)		14:00	0.51	5.45	7.76	$\Gamma_{unknown}$. 10~20%.	
		15:00	0.57	5.91	7.18		
		10:00	0.05	6.04	5.84		
Calarada		11:00	0.08	5.49	6.39	HONO: NI-PT-CIMS;	
	2011.02.19-	12:00	0.46	2.39	6.64	NO2: a cavity ring-down spectrometer	VandenBoer et al.
(40.03 N, 105.00 W)	2011.02.25	13:00	0.37	1.55	6.39	(Wagner et al., 2011)/5%;	(2013)
103.00 W)		14:00	0.28	1.27	6.02	J(NO ₂): Filter radiometers.	
		15:00	0.22	1.47	5.22		
Jülich	2003.07.29	noon	0.50	0.35	6.63	HONO: LOPAP;	Kleffmann et al. (2005)

(50.92 N,						NO ₂ : Chemiluminescence analyzer	
6.36 E)						equipped with a photolytic converter for	
						NO ₂ to NO conversion;	
						J(NO ₂): derived from actinic flux spectra	
						measured by a scanning	
						spectroradiometer.	
		10:00	0.42	3.91	6.31		
		11:00	0.38	3.42	7.76		
	2009.07.09-	12:00	0.52	3.14	8.08		
	2009.07.27	13:00	0.67	3.00	8.24	HONO: Wet chemical derivatization	
Dorio		14;00	0.38	3.00	7.29	(SA/NED), HPLC detection	
Paris		15:00	0.35	3.11	7.88	(NitroMAC)/12%;	Michoud et al. (2014)
(40.72 N, 2.21 GC)		10:00	0.08	10.49	1.16	NO ₂ : Luminol chemiluminescence/5%;	Michoud et al. (2014)
2.21 L)		11:00	0.11	10.49	1.80	J(NO ₂): filter radiometer/ 20–25%.	
	2010.01.15-	12:00	0.18	9.44	2.60		
	2010.02.15	13:00	0.21	8.76	2.20		
		14;00	0.20	9.12	2.34		
		15:00	0.22	9.07	1.99		

3 WD/IC: Wet Denuder sampling/Ion Chromatograph analysis system; TUV: Ultraviolet-Visible Model; TEI: Thermo Environmental Instruments; LOPAP: Long path

4 absorption photometer; LP-DOAS: Long path Differential Optical Absorption Spectroscopy instrument; SAFS: scanning actinic flux spectroradiometer;

5 NI-PT-CIMS: Negative-Ion Proton-Transfer Mass Spectrometer; SA/NED: an aqueous sulphanilamide/ N-(1-naphthyl)-ethylenediamine solution; NitroMAC: an

6 instrument developed at the laboratory (Afif et al., 2014); HPLC: High Performance Liquid Chromatography.

7 Note that: Since J(NO₂) data of Wu et al. (2013), Zhang et al. (2012), Zhou et al. (2002b), VandenBoer et al. (2013), Kleffmann et al. (2005) were not measured,

8	they were calculated from the J(HONO) measurement data ($J(NO_2) = 5.3J(HONO)$) (Kraus and Hofzumahaus, 1998); J(NO ₂) data of Zhou et al. (2002ab) were
9	derived from the campaign of Zhang et al. (2012) (The experiments were conducted in summer and the studied sites were close to each other). J(NO2) data of
10	Spataro et al. (2013) were also calculated from the J(HONO) at noon ($J(NO_2) = 5.3J(HONO)$), then we computed the hourly J(NO ₂) (8:00~14:00 LST) through
11	multiplying by the cosine of solar zenith angle. The NO ₂ mixing ratios of Zhang et al. (2012) and Zhou et al. (2002b) were not shown and derived from NO _x mixing
12	ratios. Similarly, NO ₂ mixing ratios of Kleffmann et al. (2005) were inferred from NO mixing ratios.
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	Ca	se R	Case	R _{wop}	Case	e R _p
Reaction	Rate	Contribution	Rate	Contribution	Rate	Contribution
	$(ppb h^{-1})$	(%)	$(ppb h^{-1})$	(%)	$(ppb h^{-1})$	(%)
			HO ₂ production			
OH+CO	0.785/0.203/0.576	33.42/28.27/38.26	0.932/0.227/0.637	34.63/29.12/38.73	2.573/0.506/1.001	41.34/32.93/40.82
CH ₃ O ₂ +NO	0.543/0.161/0.328	23.12/22.53/21.75	0.580/0.170/0.346	21.56/21.79/21.04	1.165/0.258/0.522	18.72/16.80/21.29
HCHO+hv	0.243/0.086/0.112	10.34/11.97/7.42	0.262/0.090/0.116	9.74//11.47/7.06	0.400/0.102/0.125	6.43/6.65/5.11
OH+HCHO	0.150/0.050/0.146	6.40/7.00/9.71	0.166/0.053/0.156	6.17/6.75/9.46	0.544/0.096/0.242	8.73/6.26/9.86
OH+OLET/OLEI	0.192/0.054/0.059	8.17/7.47/3.92	0.264/0.065/0.077	9.83/8.31/4.67	0.537/0.206/0.095	8.63/13.44/3.88
OH+H ₂	0.038/0.021/0.050	1.62/2.91/3.29	0.040/0.022/0.052	1.49/2.76/3.17	0.095/0.027/0.075	1.53/1.74/3.06
$OH+SO_2$	0.054/0.030/0.035	2.30/4.20/2.33	0.064/0.034/0.041	2.37/4.34/2.48	0.172/0.116/0.072	2.77/7.53/2.95
OH+O ₃	0.028/0.006/0.035	1.18/0.88/2.31	0.029/0.006/0.036	1.08/0.82/2.20	0.072/0.005/0.046	1.15/0.30/1.88
OH+XYL	0.052/0.022/0.023	2.21/3.10/1.50	0.066/0.026/0.029	2.46/3.34/1.75	0.141/0.078/0.045	2.27/5.11/1.84
$OH+H_2O_2$	0.015/0.008/0.027	0.63/1.14/1.77	0.016/0.008/0.029	0.59/1.08/1.78	0.040/0.010/0.043	0.65/0.66/1.74
OH+TOL	0.027/0.007/0.011	1.16/0.94/0.76	0.034/0.008/0.014	1.27/1.02/0.86	0.086/0.025/0.024	1.38/1.60/0.97
ALD2/MGLY	0.046/0.012/0.012	1.05/1.60/0.90	0.051/0.012/0.012	1 01/1 66/0 92	0 074//0 014/0 012	1 10/0 02/0 51
/ANOE+hv	0.046/0.012/0.012	1.95/1.69/0.80	0.051/0.013/0.013	1.91/1.00/0.82	0.074//0.014/0.013	1.19/0.93/0.51
OH+ETH/OPEN	0.007/0.002/0.004	0.28/0.31/0.29	0.008/0.002/0.005	0.30/0.32/0.30	0.036/0.009/0.011	0.30/0.56/0.44
O ₃ +OLET/OLEI	0.036/0.009/0.009	1.55/1.21/0.59	0.035/0.009/0.009	1.28/1.11/0.52	0.030/0.008/0.009	0.48/0.50/0.38
RO ₂ +NO	0.017/0.004/0.007	0.69/0.62/0.44	0.017/0.005/0.007	0.64/0.62/0.42	0.024/0.005/0.009	0.38/0.34/0.37
others+hv	0.020/0.007/0.007	0.86/0.94/0.47	0.025/0.008/0.008	0.92/0.96/0.50	0.046/0.010/0.008	0.74/0.63/0.33
NO+ETHP	0.013/0.003/0.005	0.54/0.44/0.31	0.013/0.003/0.005	0.47/0.42/0.30	0.019/0.004/0.007	0.30/0.26/0.28
NO+ISOPP	0.030/0.005/0.003	1.26/0.70/0.20	0.031/0.005/0.004	1.15/0.66/0.24	0.038/0.007/0.004	0.61/0.43/0.17
OH+CH ₃ OH	0.002/0.001/0.002	0.09/0.09/0.11	0.002/0.001/0.002	0.09/0.09/0.11	0.007/0.002/0.003	0.11/0.11/0.12

Table S2. Daytime (06:00–18:00 LST) average HO₂ budgets in Beijing/Shanghai/Guangzhou in August 2007.

/ANOL/CRES						
HNO ₄ +hv	0.004/0.001/0.002	0.19/0.09/0.14	0.004/0.001/0.002	0.17/0.09/0.13	0.007/0.001/0.003	0.11/0.06/0.11
CH3OOH/ET HOOH+hv	0.002/0.012/0.002	0.09/0.39/0.13	0.002/0.003/0.002	0.08/0.37/0.12	0.002/0.003/0.002	0.12/0.18/0.06
O ₃ +ETH	0.003/<0.001/0.001	0.12/0.06/0.03	0.003/<0.001/0.001	0.10/0.05/0.03	0.003/<0.001/0.001	0.04/0.02/0.02
O ₃ +ISOP	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
O ₃ +others	0.001/<0.001/<0.001	0.03/0.02/0.02	0.001 / < 0.001 / < 0.001	0.03/0.02/0.02	0.001 / < 0.001 / < 0.001	0.02/0.01/0.01
NO ₃ +HCHO	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
NO ₃ +others	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/0.001/<0.001	<0.01/<0.01/<0.01
HNO ₄ dec	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
Total	2.349/0.716/1.506	100/100/100	2.691/0.780/1.644	100/100/100	6.223/1.536/2.451	100/100/100
			$HO_2 loss$			
HO ₂ +NO	2.778/0.732/1.748	99.34/99.61/98.29	2.829/0.793/1.608	99.38/99.63/98.37	7.101/1.402/2.552	99.15/99.55/98.04
HO₂+NO HO ₂ +O ₃	2.778/0.732/1.748 0.009/0.001/0.014	99.34/99.61/98.29 0.30/0.08/0.70	2.829/0.793/1.608 0.008/0.001/0.011	99.38/99.63/98.37 0.28/0.08/0.67	7.101/1.402/2.552 0.026/0.001/0.019	99.15/99.55/98.04 0.36/0.08/0.74
HO₂+NO HO ₂ +O ₃ HO ₂ +NO ₂	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72
HO ₂ +NO HO ₂ +O ₃ HO ₂ +NO ₂ HO ₂ +OH	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37
HO_2+NO HO_2+O_3 HO_2+NO_2 HO_2+OH HO_2+HO_2	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03
HO_2+NO HO_2+O_3 HO_2+NO_2 HO_2+OH HO_2+HO_2 $HO_2+CH_3O_2$	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02 0.01/<0.01/0.03	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001/<0.001 <0.001/<0.001/0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01 <0.01/<0.01/0.03	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001 0.001/<0.001/0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03 0.01/<0.01/0.04
HO_2+NO HO_2+O_3 HO_2+NO_2 HO_2+OH HO_2+HO_2 $HO_2+CH_3O_2$ $HO_2+C_2O_3$	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02 0.01/<0.01/0.03 <0.01/<0.01/0.01	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001/<0.001 <0.001/<0.001/0.001 <0.001/<0.001/<0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01 <0.01/<0.01/0.03 <0.01/<0.01/0.01	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001 0.001/<0.001/0.001 <0.001/<0.001/<0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03 0.01/<0.01/0.04 <0.01/<0.01/0.01
$HO_{2}+NO \\HO_{2}+O_{3} \\HO_{2}+NO_{2} \\HO_{2}+OH \\HO_{2}+HO_{2} \\HO_{2}+CH_{3}O_{2} \\HO_{2}+C_{2}O_{3} \\HO_{2}+RO_{2}$	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02 0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01 <0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001 0.001/<0.001/0.001 <0.001/<0.001/<0.001 <0.001<0.001/<0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03 0.01/<0.01/0.04 <0.01/<0.01/0.01 <0.01/<0.01/<0.01
$\begin{array}{c} \textbf{HO}_{2} + \textbf{NO} \\ HO_{2} + O_{3} \\ HO_{2} + NO_{2} \\ HO_{2} + OH \\ HO_{2} + HO_{2} \\ HO_{2} + CH_{3}O_{2} \\ HO_{2} + C_{2}O_{3} \\ HO_{2} + RO_{2} \\ HO_{2} + XO_{2} \end{array}$	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02 0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 0.02/<0.01/0.04	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001/<0.001 <0.001/<0.001/0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01 <0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001 0.001/<0.001/0.001 <0.001/<0.001/<0.001 <0.001<0.001/<0.001 0.002/<0.001/0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03 0.01/<0.01/0.04 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 0.03/<0.01/0.05
HO_2+NO HO_2+O_3 HO_2+NO_2 HO_2+OH HO_2+HO_2 $HO_2+CH_3O_2$ $HO_2+C_2O_3$ HO_2+RO_2 HO_2+XO_2 HO_2+AO_2 HO_2+AO_2	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02 0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 0.02/<0.01/0.04 <0.01/<0.01/0.01	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001/<0.001 <0.001/<0.001/0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01 <0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 0.01/<0.01/0.04 <0.01/<0.01/0.01	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001 0.001/<0.001/0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03 0.01/<0.01/0.04 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 0.03/<0.01/0.05 <0.01/<0.01/0.01
HO_2+NO HO_2+O_3 HO_2+NO_2 HO_2+OH HO_2+HO_2 $HO_2+CH_3O_2$ $HO_2+C_2O_3$ HO_2+RO_2 HO_2+XO_2 HO_2+AO_2 HO_2+AO_2 HO_2+AO_2 HO_2+AO_2 HO_2+AO_2 HO_2+AO_2	2.778/0.732/1.748 0.009/0.001/0.014 0.007/0.002/0.009 0.001/<0.001/0.004 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.34/99.61/98.29 0.30/0.08/0.70 0.28/0.29/0.60 0.06/0.02/0.30 <0.01/<0.01/0.02 0.01/<0.01/0.03 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 <0.01/<0.01/0.01 <0.01/<0.01/<0.01	2.829/0.793/1.608 0.008/0.001/0.011 0.007/0.002/0.010 0.002/<0.001/0.005 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.38/99.63/98.37 0.28/0.08/0.67 0.25/0.27/0.58 0.06/0.02/0.28 <0.01/<0.01/0.01 <0.01/<0.01/0.03 <0.01/<0.01/0.01 0.01/<0.01/<0.01 <0.01/<0.01/0.01 <0.01/<0.01/0.01	7.101/1.402/2.552 0.026/0.001/0.019 0.023/0.005/0.019 0.008/<0.001/0.010 <0.001/<0.001/0.001 0.001/<0.001/0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001 <0.001/<0.001/<0.001	99.15/99.55/98.04 0.36/0.08/0.74 0.32/0.33/0.72 0.11/0.03/0.37 <0.01/<0.01/0.03 0.01/<0.01/0.04 <0.01/<0.01/0.01 <0.01/<0.01/<0.01 0.03/<0.01/0.05 <0.01/<0.01/<0.01 <0.01/<0.01/<0.01

27 ETHP: ethylperoxy; ISOPP: lumped peroxyradical of isoprene.

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	Case	e R	Case	R _{wop}	Case	e R _p
Reaction	Rate	Contribution	Rate	Contribution	Rate	Contribution
	$(ppb h^{-1})$	(%)	$(ppb h^{-1})$	(%)	$(ppb h^{-1})$	(%)
			RO ₂ production			
OH+OLET/OLEI	0.192/0.054/0.060	22.45/21.07/14.88	0.264/0.065/0.077	25.81/22.92/17.10	0.537/0.110/0.114	25.62/22.20/16.73
OH+ETH	0.157/0.030/0.041	18.36/11.91/10.24	0.197/0.036/0.049	19.26/12.61/11.00	0.484/0.068/0.080	21.98/13.73/11.78
OH+CH ₄	0.103/0.057/0.135	12.09/22.44/33.97	0.109/0.059/0.142	10.65/20.81/31.55	0.260/0.115/0.223	11.46/23.33/32.73
OH+AONE	0.092/0.018/0.045	10.76/7.09/11.24	0.109/0.020/0.049	10.65/6.99/10.87	0.323/0.047/0.081	13.65/9.55/11.95
OH+XYL	0.052/0.022/0.023	6.06/8.74/5.69	0.066/0.026/0.029	6.45/9.21/6.42	0.141/0.046/0.044	6.63/9.32/6.52
AONE/ETH+hv(C ₂ O ₃)	0.037/0.011/0.011	4.37/4.24/2.71	0.042/0.012/0.012	4.07/4.10/2.67	0.062/0.013/0.012	2.83/2.68/1.74
O ₃ +OLET/OLEI(C ₂ O ₃)	0.031/0.007/0.008	3.63/2.90/1.89	0.029/0.007/0.007	2.87/2.61/1.62	0.025/0.007/0.008	1.33/1.32/1.15
others+ $hv(C_2O_3)$	0.020/0.007/0.007	2.29/2.58/1.67	0.024/0.007/0.008	2.35/2.59/1.75	0.045/0.010/0.008	1.98/1.92/1.11
O ₃ +OLET/OLEI(otherR O ₂)	0.018/0.004/0.004	2.05/1.66/1.07	0.017/0.004/0.004	1.63/1.49/0.91	0.014/0.004/0.004	0.75/0.76/0.65
OH+TOL	0.027/0.007/0.011	3.20/2.66/2.89	0.034/0.008/0.014	3.32/2.80/3.13	0.086/0.015/0.023	3.88/3.13/3.45
OH+ISOP	0.019/0.004/0.002	2.21/1.64//0.49	0.020/0.004/0.003	1.96/1.54/0.60	0.017/0.007/0.003	0.91/1.35/0.46
O ₃ +OLET/OLEI(XO ₂)	0.015/0.003/0.004	1.70/1.36/0.89	0.014/0.003/0.003	1.35/1.22/0.76	0.012/0.003/0.004	0.62/0.62/0.54
AONE/ETH+hv(CH ₃ O ₂)	0.014/0.003/0.004	1.68/1.10/0.92	0.016/0.003/0.004	1.54/1.00/0.83	0.019/0.002/0.003	0.87/0.49/0.49
O ₃ +OLET/OLEI(CH ₃ O ₂)	0.016/0.004/0.004	1.91/1.52/0.99	0.015/0.004/0.004	1.51/1.37/0.86	0.013/0.003/0.004	0.70/0.70/0.61
OH+PEROXID	0.010/0.011/0.014	1.18/4.37/3.40	0.011/0.004/0.014	1.08/4.13/3.23	0.022/0.020/0.022	1.02/4.04/3.28
OH+C ₂ H ₆	0.005/0.002/0.004	0.57/0.87/1.03	0.007/0.003/0.005	0.68/0.93/1.03	0.015/0.005/0.007	0.70/1.03/0.97
NO ₃ +OLET/OLEI (otherRO ₂)	0.005/0.001/0.002	0.53/0.41/0.56	0.005/0.001/0.002	0.45/0.39/0.51	0.005/0.001/0.003	0.24/0.19/0.41
O ₃ +OLET/OLEI (ETHP)	0.008/0.002/0.002	0.97/0.77/0.51	0.008/0.002/0.002	0.77/0.70/0.43	0.007/0.002/0.002	0.35/0.35/0.31

Table S3. Daytime (06:00–18:00 LST) average RO₂ budgets in Beijing/Shanghai/Guangzhou in August 2007.

$OH+C_2H_6$	0.002/0.001/0.002	0.29/0.27/0.48	0.003/0.001/0.002	0.29/0.27/0.48	0.008/0.002/0.004	0.35/0.33/0.54
OH+CH ₃ OH/AN OL/CRES	0.002/0.001/0.001	0.20/0.20/0.23	0.002/0.001/0.001	0.20/0.20/0.23	0.007/0.001/0.002	0.31/0.30/0.30
O_3 +others(C_2O_3)	0.001/<0.001/<0.001	0.07/0.05/0.05	0.001/<0.001/<0.001	0.06/0.04/0.04	0.001/<0.001/<0.001	0.04/0.03/0.04
others+hv(XO ₂)	<0.001/<0.001/<0.001	0.05/0.04/0.05	<0.001/<0.001/<0.001	0.04/0.03/0.04	<0.001/<0.001/<0.001	0.02/0.01/0.03
$H_2O_2+hv(XO_2)$	<0.001/<0.001/<0.001	0.02/0.01/0.01	<0.001/<0.001/<0.001	0.02/0.01/0.01	<0.001/<0.001/<0.001	<0.01/<0.01/0.01
O_3 +ISOP(C_2O_3)	<0.001/<0.001/<0.001	0.02/0.01/<0.01	<0.001/<0.001/<0.001	0.01/0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
others+hv(CH ₃ O ₂)	<0.001/<0.001/<0.001	0.03/0.01/<0.01	<0.001/<0.001/<0.001	0.02 / < 0.01 / < 0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
O ₃ +others(CH ₃ O ₂)	<0.001/<0.001/<0.001	0.01 / < 0.01 / < 0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
H ₂ O ₂ +hv (ETHP)	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
others+hv (ETHP)	<0.001/<0.001/<0.001	0.01/<0.01/0.01	<0.001/<0.001/<0.001	<0.01/<0.01/0.01	<0.001/<0.001/<0.001	<0.01/<0.01/0.01
$NO_3 + AONE/ETH(C_2O_3)$	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
NO ₃ +others(C ₂ O ₃)	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	$<\!0.01/\!<\!0.01/\!<\!0.01$	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
O_3 +others(XO ₂)	<0.001/<0.001/<0.001	0.01 / < 0.01 / < 0.01	<0.001/<0.001/<0.001	0.01 / < 0.01 / < 0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
O ₃ +ISOP(XO ₂)	<0.001/<0.001/<0.001	0.02/0.01/<0.01	<0.001/<0.001/<0.001	0.01/0.01/<0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
OH+others	0.028/0.005/0.016	3.22/2.06/4.13	0.030/0.006/0.018	2.93/1.98/3.91	0.077/0.014/0.029	3.34/2.61/4.20
Total	0.854/0.254/0.397	100/100/100	0.852/0.283/0.449	100/100/100	2.183/0.494/0.680	100/100/100
			RO ₂ loss			
CH ₃ O ₂ +NO	0.543/0.161/0.328	94.56/95.28/96.07	0.580/0.170/0.346	94.68/95.24/96.06	1.165/0.258/0.522	95.76/96.27/96.30
RO ₂ +NO	0.016/0.004/0.007	2.81/2.64/1.93	0.017/0.005/0.007	2.80/2.69/1.93	0.024/0.005/0.009	1.96/1.94/1.68
NO+ETHP	0.013/0.003/0.005	2.19/1.86/1.36	0.013/0.003/0.005	2.07/1.84/1.36	0.019/0.004/0.007	1.54/1.48/1.25
otherRO2 term	0.002/<0.001/0.001	0.32/0.22/0.27	0.002/<0.001/0.001	0.32/0.22/0.28	0.005/0.001/0.002	0.43/0.29/0.28
CH ₃ O ₂ term	<0.001/<0.001/0.001	0.04/<0.01/0.15	<0.001/<0.001/0.001	0.04/<0.01/0.15	0.001/<0.001/0.001	0.08/<0.01/0.20
HO_2+RO_2	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01	<0.001/<0.001/<0.001	$<\!0.01/\!<\!0.01/\!<\!0.01$	<0.001/<0.001/<0.001	0.01 / < 0.01 / 0.01
XO ₂ term	<0.001/<0.001/<0.001	0.07 / < 0.01 / 0.02	<0.001/<0.001/0.001	0.07/<0.01/0.19	0.002/<0.001/0.001	0.18/0.02/0.26
C_2O_3 term	<0.001/<0.001/<0.001	0.01/<0.01/0.01	<0.001/<0.001/<0.001	<0.01/<0.01/0.02	0.001/<0.001/<0.001	0.05/0.01/0.03

ETHP term	<0.001/<0.001/0.001	<0.01/<0.01/0.19	<0.001/<0.001/<0.001	<0.01/<0.01/0.01	<0.001/<0.001/<0.001	<0.01/<0.01/<0.01
Total	0.574/0.169/0.341	100/100/100	0.613/0.1/9/0.360	100/100/100	1.216/0.268/0.542	100/100/100
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