Table S1 Performance of major photochemical instruments used in summer 2013 in Beijing

Parameter	Technique	Accuracy (1δ)	LOD [a] (1δ)	sampling period
NO, NOx	chemiluminescence	10%	25 pptV	Aug 10th-27th
O3	UV photometry	5%	0.3 ppbV	Aug 10th-27th
CO	IR photometry	5%	10 ppbV	Aug 10th-27th
SO2	pulsed fluorescence	5%	50 pptV	Aug 10th-27th
C2-C10 NMHCs, C2-C6 OVOCs	GC-MS/FID	10%	10-50 pptV	Aug 10th-27th
HCHO	Hantszch	10%	10 pptV	Aug 10th-27th
j-value	SR [b]	10%		Aug 10th-27th

a. limit of detection;

b. spectral radiometer This type of SR measures $J(O1D)$, $J(NO_2)$, $J(HONO)$, $J(H_2O_2)$, $J(HCHO\_M)$, $J(HCHO\_R)$, $J(NO_3\_M)$, $J(NO_3\_R)$

Table S2 Performance of major photochemical instruments used in autumn 2014 in Heshan

Parameter	Technique	Accuracy (1δ)	LOD (1δ)	sampling period
NO, NOx	chemiluminescence	10%	25 pptV	Oct 20th-Nov 22nd
O3	UV photometry	5%	0.3 ppbV	Oct 20th-Nov 22nd
CO	IR photometry	5%	10 ppbV	Oct 20th-Nov 22nd
SO2	pulsed fluorescence	5%	50 pptV	Oct 20th-Nov 22nd
C2-C10 NMHCs, C2-C6 OVOCs	GC-MS/FID	10%	10-50 pptV	Oct 20th-Nov 22nd
HCHO	Hantszch	10%	10 pptV	Oct 20th-Nov 22nd
HONO	LOPAP [a]	10%	10 pptV	Oct 20th-Nov 22nd
j-value	SR [b]	10%		Oct 20th-Nov 22nd

a. Long-Path Absorption Photometry

b. This set of SR measures $J(O1D)$, $J(NO_2)$, $J(NO_3\_R)$

Table S3 Mean values of mixing ratios and reactivity of measured VOCs in Beijing 2013

Species	mean mixing ratios (ppbV)	k_{OH} (s^{-1})	Species	mean mixing ratios (ppbV)	k_{OH} (s^{-1})
Alkanes			**_Aromatics_**		
ethane	4.55	0.028	benzene	1.01	0.030
propane	4.31	0.116	toluene	3.74	0.518
i-butane	1.90	0.098	ethylbenzene	1.09	0.188
n-butane	1.85	0.104	styrene	0.63	0.900
acetylene	3.42	0.084	m/p-xylene	1.62	0.754
cyclonepentane	0.09	0.011	o-xylene	0.58	0.194
i-pentane	1.90	0.168	n-propylbenzene	0.03	0.004
n-pentane	1.45	0.136	i-propylbenzene	0.02	0.004
2,2-dimethylbutane	0.06	0.003	3-ethyltoluene	0.09	0.026
2,3-dimethylbutane	0.09	0.013	4-ethyltoluene	0.06	0.027
2-methylpentane	0.58	0.077	1,3,5-trimethylbenzene	0.03	0.042
3-methylpentane	0.37	0.047	2-ethyltoluene	0.04	0.018
n-hexane	0.43	0.055	1,2,4-trimethylbenzene	0.10	0.080
2,4-dimethylpentane	0.59	0.069	1,2,3-trimethylbenzene	0.03	0.028
methylcyclopentane	0.19	0.024	1,3-diethylbenzen	0.01	
2-methyhexane	0.25	0.035	1,4-diethylbenzene	0.02	
cyclohexane	0.12	0.015	**_OVOCs_**		
2,3-dimethylpentane	0.18	0.007	HCHO	5.51	1.153
3-methylhexane	0.28	0.039	acetaldehyde	2.43	0.905
2,3,4-trimethylpentane	0.22	0.036	acrolein	0.02	0.009
n-heptane	0.20	0.033	propanal	0.28	0.139
methylcyclohexane	0.12	0.015	acetone	2.47	0.010
1,2-dimethylpropane	0.27	0.034	MTBE	0.10	-
2,3,4-trimethylpropane	0.10	0.031	MACR	0.10	0.072
2-methylheptane	0.04	0.007	butanal	0.10	0.059
3-methylheptane	0.04	0.007	MVK	0.08	0.039
n-octane	0.07	0.014	MEK	0.67	0.020
n-nonane	0.04	0.010	2-pentanone	0.02	0.001
n-decane	0.03	0.008	pentanal	0.04	0.028
n-undecane	0.02	0.006	3-pentanone	0.02	0.002
n-dodecane	0.01	0.003	MIBK	0.02	0.001

	mixing ratios	koH	Species		
Alkenes			hexanal	0.07	0.055
ethane	2.94	0.617	**Others**		
propene	0.49	0.464	acetonitrile	0.31	0.001
t-2-butene	0.04	0.063			
1-butene	0.10	0.077			
c-2-butene	0.06	0.084			
1-pentene	1.47	1.136			
c-2-pentene	0.05	0.080			
t-2-pentene	0.04	0.066			
1-hexene	0.02	0.018			
isoprene	0.35	0.8617			

Table S4 Mean values of mixing ratios and reactivity of measured VOCs in Heshan 2014

Species	mean mixing ratios (ppbV)	k_{OH} (s^{-1})	Species	mean mixing ratios (ppbV)	k_{OH} (s^{-1})
Alkanes			**Aromatics**		
ethane	4.55	0.028	benzene	1.01	0.030
propane	4.31	0.116	toluene	3.74	0.518
i-butane	1.90	0.098	ethylbenzene	1.09	0.188
n-butane	1.85	0.104	styrene	0.63	0.900
acetylene	3.42	0.084	m/p-xylene	1.62	0.754
cyclonepentane	0.09	0.011	o-xylene	0.58	0.194
i-pentane	1.90	0.168	n-propylbenzene	0.03	0.004
n-pentane	1.45	0.136	i-propylbenzene	0.02	0.004
2,2-dimethylbutane	0.06	0.003	3-ethyltoluene	0.09	0.026
2,3-dimethylbutane	0.09	0.013	4-ethyltoluene	0.06	0.027
2-methylpentane	0.58	0.077	1,3,5-trimethylbenzene	0.03	0.042
3-methylpentane	0.37	0.047	2-ethyltoluene	0.04	0.018
n-hexane	0.43	0.055	1,2,4-trimethylbenzene	0.10	0.080
2,4-dimethylpentane	0.59	0.069	1,2,3-trimethylbenzene	0.03	0.028
methylcyclopentane	0.19	0.024	1,3-diethylbenzen	0.01	
2-methyhexane	0.25	0.035	1,4-diethylbenzene	0.02	
cyclohexane	0.12	0.015	**OVOCs**		

2,3-dimethylpentane	0.18	0.007	HCHO	5.51	1.153
3-methylhexane	0.28	0.039	acetaldehyde	2.43	0.905
2,3,4-trimethylpentane	0.22	0.036	acrolein	0.02	0.009
n-heptane	0.20	0.033	propanal	0.28	0.139
methylcyclohexane	0.12	0.015	acetone	2.47	0.010
1,2-dimethylpropane	0.27	0.034	MTBE	0.10	-
2,3,4-trimethylpropane	0.10	0.031	MACR	0.10	0.072
2-methylheptane	0.04	0.007	butanal	0.10	0.059
3-methylheptane	0.04	0.007	MVK	0.08	0.039
n-octane	0.07	0.014	MEK	0.67	0.020
n-nonane	0.04	0.010	2-pentanone	0.02	0.001
n-decane	0.03	0.008	pentanal	0.04	0.028
n-undecane	0.02	0.006	3-pentanone	0.02	0.002
n-dodecane	0.01	0.003	MIBK	0.02	0.001
Alkenes			hexanal	0.07	0.055
ethane	2.94	0.617	**Others**		
propene	0.49	0.464	acetonitrile	0.31	0.001
t-2-butene	0.04	0.063			
1-butene	0.10	0.077			
c-2-butene	0.06	0.084			
1-pentene	1.47	1.136			
c-2-pentene	0.05	0.080			
t-2-pentene	0.04	0.066			
1-hexene	0.02	0.018			
isoprene	0.35	0.8617			

Table S5 Major contributors to modeled reactivity compared with calculated reactivity contributions in PKU, 2013.

Species	k_{cal} (s^{-1})	k_{mod} (s^{-1})
ALD	1.37	2.3
HCHO	--	1.31
GLY+MGLY	--	0.38
ISOP	--	0.31
DCB	--	0.21

Table S6 Major contributors to modeled reactivity compared with calculated reactivity contributions in Heshan, 2014.

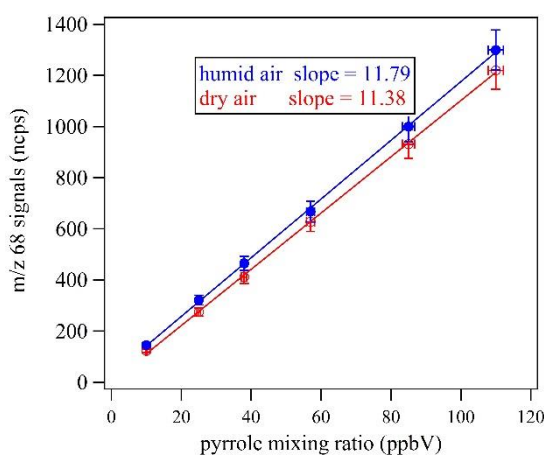| Species	k_{cal} (s^{-1})	k_{mod} (s^{-1})
ALD	1.37	2.3
HCHO	--	1.31
GLY+MGLY	--	0.38
ISOP	--	0.31
DCB	--	0.21

Fig S1 Calibration curve of pyrrole in PTR-MS
(blue lines and points: pyrrole diluted by humidified synthetic air; red lines and points: pyrrole diluted by dry synthetic air)
Error bars: estimated uncertainties from measured and calculated uncertainties of pyrrole

Humidity corrections for CRM
For the interference tests, the systems are set in the C2 mode. First, the needle valve in the synthetic air pathway is turned off to obtain a signal for the lower relative humidity (RH) situation. Then the valve is switched on and on to provide different RH situations. The pyrrole signals vary with the changes of RH, which is quantified by the ratios of m/z 39 to m/z 21. Then the curve is fit by the spots observed as in Fig S2. In the ambient measurements, the fitting curve is used to correct the difference in RH between C2 mode and C3 mode.
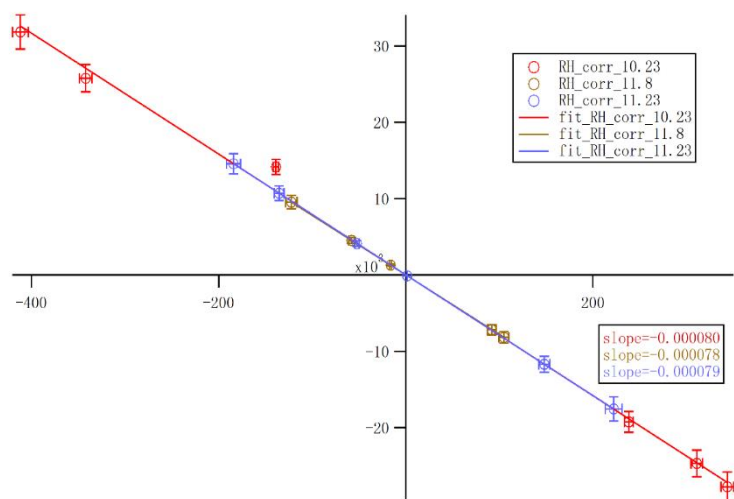
Fig S2. Variation in the pyrrole signal (m/z 68) with variations of relative humidity.