Supplement information for:

Significant concentrations of nitryl chloride sustained in the morning: Investigations of the causes and impacts on ozone production in a polluted region of northern China

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Table S1. Validation of meteorological simulations by WRF.

	T (ºC)	RH (%)	WD (º)	WS (m/s)
Observation Average	24.00	74.31	161.03	1.75
Simulation Average	23.03	78.03	162.76	2.15
mean bias	-0.96	3.72	1.72	0.39
root mean square error	2.70	10.67	122.26	1.54

Table S2. Mean concentrations and standard deviations (σ) of each species and meteorological conditions used as input in the box-model simulations. Concentrations are in ppbv unless stated.

Species	Average		Megacity case	
	Mean	± σ	Mean	± σ
$ClNO_2$	0.19	0.16	0.52	0.65
NO	1.32	1.30	0.65	0.76
NO_2	13.11	5.96	10.37	5.28
O_3	54.3	30.2	54.6	29.1
SO_2	6.75	3.51	4.373	4.18
CO	549	63	541	207
HONO	0.75	0.37	0.51	0.29
HCl	1.15	0.40	1.26	0.93
methane	2361	362	2090	233
methanol	24.707	5.673	15.698	4.805
acetaldehyde	1.887	0.357	1.349	0.383
acetic acid	5.013	0.897	2.437	0.610
acetone	4.796	0.583	3.345	0.353
formaldehyde	7.247	1.394	3.475	0.545
ethane	2.950	0.454	2.465	0.717
ethene	1.813	0.860	1.034	0.721
propane	1.171	0.304	1.186	0.456
propene	0.310	0.170	0.221	0.161
i-butane	0.413	0.130	0.359	0.159
n-butane	0.701	0.249	0.591	0.292
ethyne	1.490	0.282	0.835	0.267
1-butene	0.031	0.017	0.038	0.036
2-methylpropene	0.063	0.034	0.032	0.035
trans-2-butene	0.177	0.027	0.062	0.023
cis-2-butene	0.015	0.006	0.011	0.011
i-pentane	0.411	0.141	0.310	0.181
n-pentane	0.322	0.124	0.204	0.129
1,3-butadiene	0.022	0.016	0.014	0.012
1-pentene	0.017	0.008	0.016	0.009
isoprene	0.664	0.473	0.249	0.237
2,3-dimethylbutane	0.090	0.029	0.062	0.022
2-methylpentane	0.154	0.055	0.144	0.086

MTBE	0.121	0.045	0.073	0.048
3-methylpentane	0.119	0.047	0.086	0.054
1-hexene	0.056	0.021	0.044	0.017
n-hexane	0.148	0.064	0.120	0.085
methylethylketone	2.004	0.106	3.401	0.562
2-methylhexane	0.033	0.012	0.028	0.017
cyclohexane	0.051	0.022	0.042	0.027
3-methylhexane	0.056	0.019	0.044	0.022
benzene	1.007	0.265	0.592	0.229
n-heptane	0.080	0.025	0.061	0.037
toluene	0.786	0.273	0.566	0.291
n-octane	0.054	0.014	0.029	0.020
ethylbenzene	0.198	0.066	0.160	0.089
n-nonane	0.028	0.010	0.019	0.012
o-xylene	0.097	0.036	0.069	0.034
styrene	0.047	0.030	0.033	0.026
m-ethyltoluene	0.021	0.008	0.019	0.010
1,3,5-trimethylbenzene	0.019	0.006	0.019	0.008
1,2,4-trimethylbenzene	0.095	0.027	0.058	0.025
1,2,3-trimethylbenzene	0.017	0.005	0.016	0.006
Aerosol surface area (μm^2 m^{-3})	1.60×10^{-3}	3.72×10^{-4}	1.24×10^{-3}	4.92×10^{-4}
Temperature (K)	300.00	3.12	296.49	3.56
Relative Humidity (%)	64	12	67	17
j_{NO2} (s^{-1})[a]	3.16×10^{-3}	2.01×10^{-3}	3.33×10^{-3}	2.52×10^{-3}
$j_{O3}(O^1D)$ (s^{-1})[a]	7.25×10^{-6}	6.36×10^{-6}	7.33×10^{-6}	6.99×10^{-6}
j_{HONO} (s^{-1})[a]	5.38×10^{-4}	3.45×10^{-4}	5.68×10^{-4}	4.29×10^{-4}
j_{ClNO2} (s^{-1})[a]	1.27×10^{-4}	8.06×10^{-5}	1.53×10^{-4}	1.26×10^{-4}

[a] from sunrise to sunset

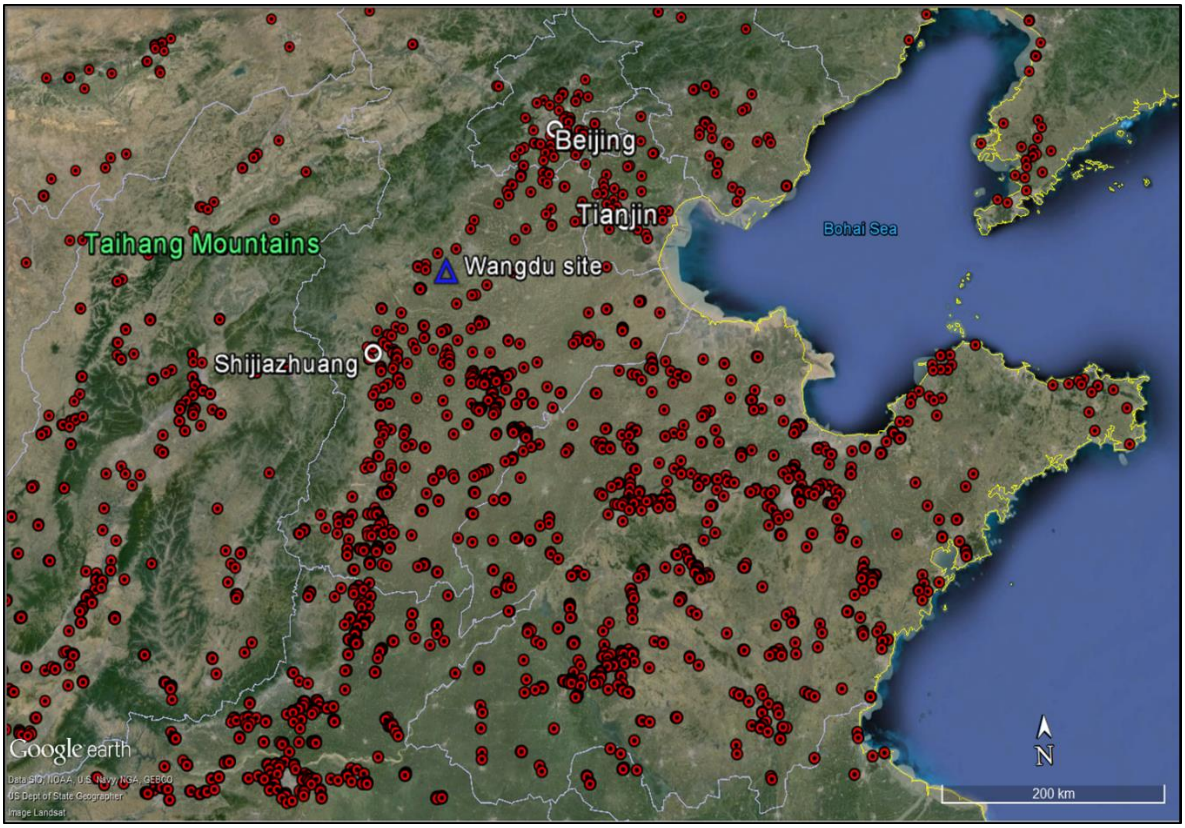


Figure S1. Active fire hotspots (red dots) in NCP from FIRMS covering the study period of 20 June – 9 July 2014 (Data available at https://earthdata.nasa.gov/firms).

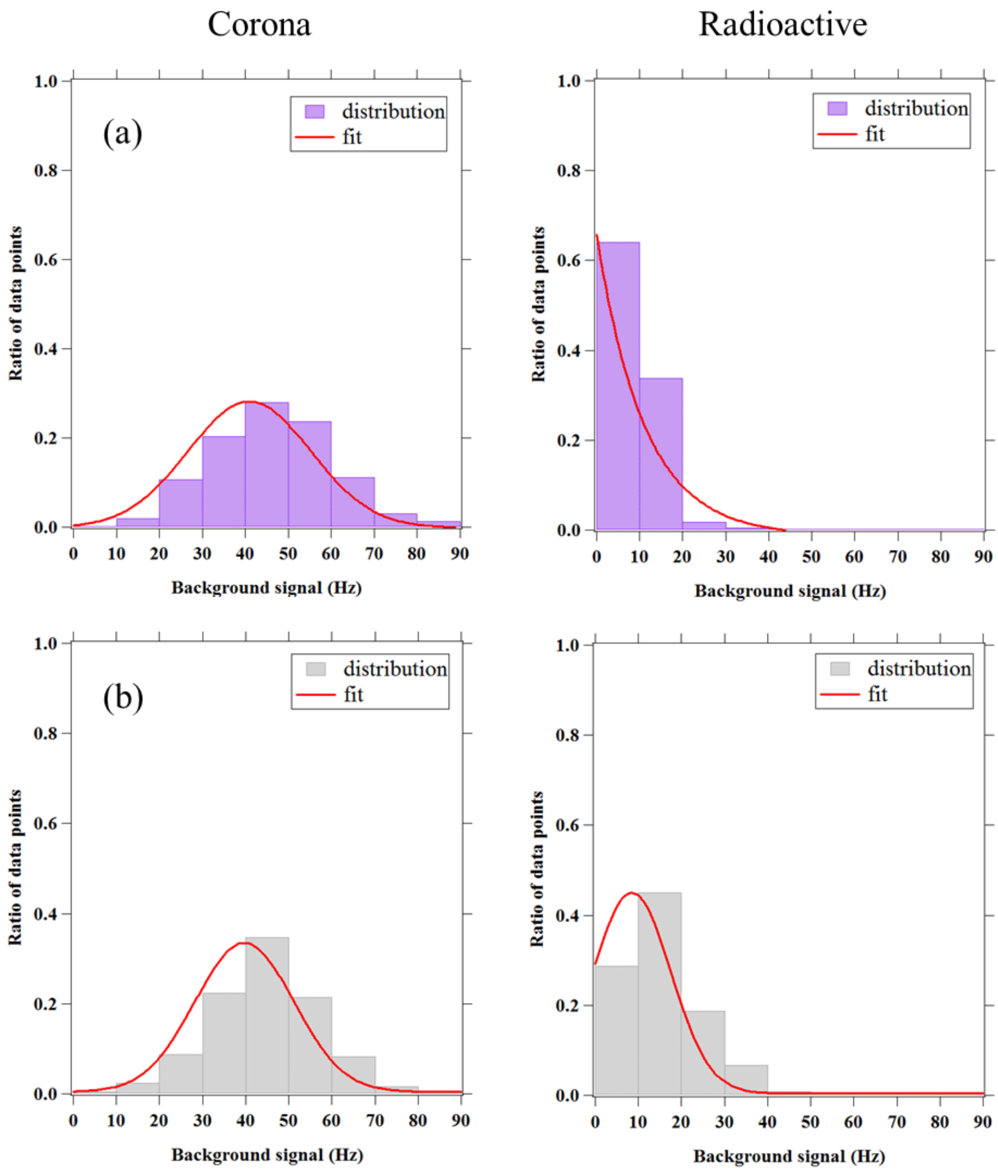


Figure S2. Distributions of ambient background signals of $ClNO_2$ (in purple) and N_2O_5 (in grey) from CIMS operated with corona discharge source and ^{210}Po radioactive source (*N* = 902).

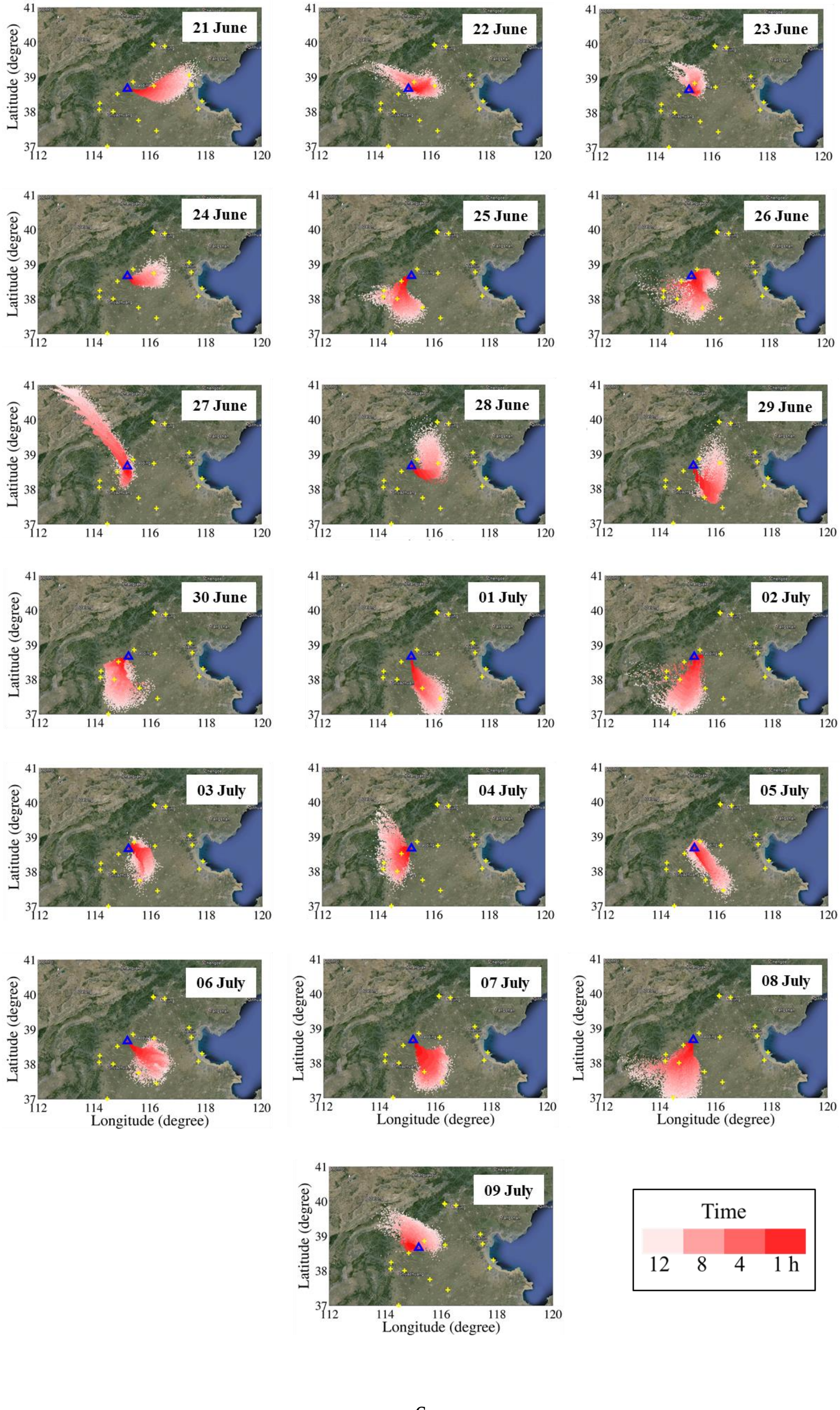

21 June
22 June
23 June
24 June
25 June
26 June
27 June
28 June
29 June
30 June
01 July
02 July
03 July
04 July
05 July
06 July
07 July
08 July
09 July
Latitude (degree)
Longitude (degree)
Time
12
8
4
1 h

Figure S3. History of air masses that arrived Wangdu sampling site at 00:00.

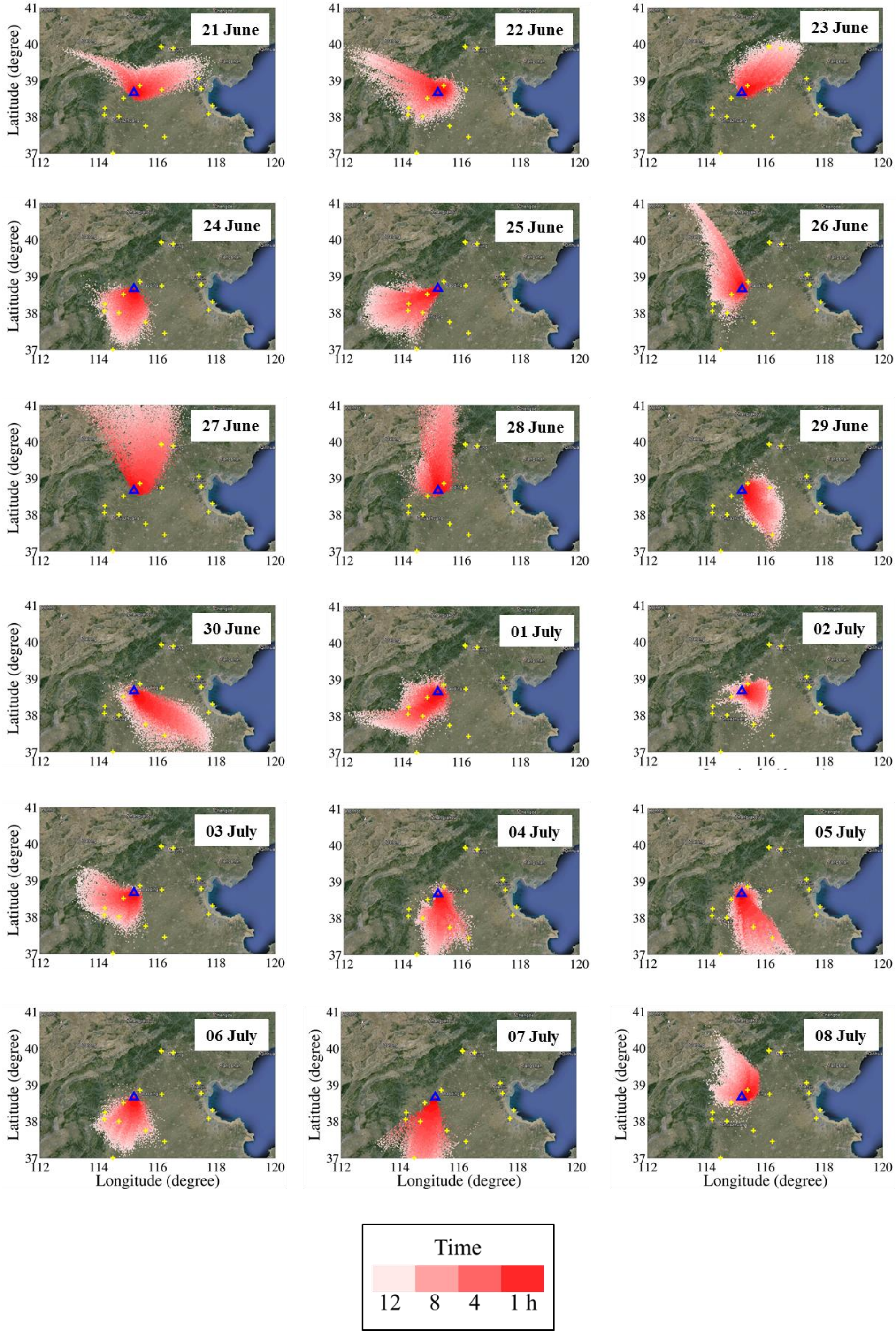


Figure S4. History of air masses that arrived Wangdu sampling site at 14:00.

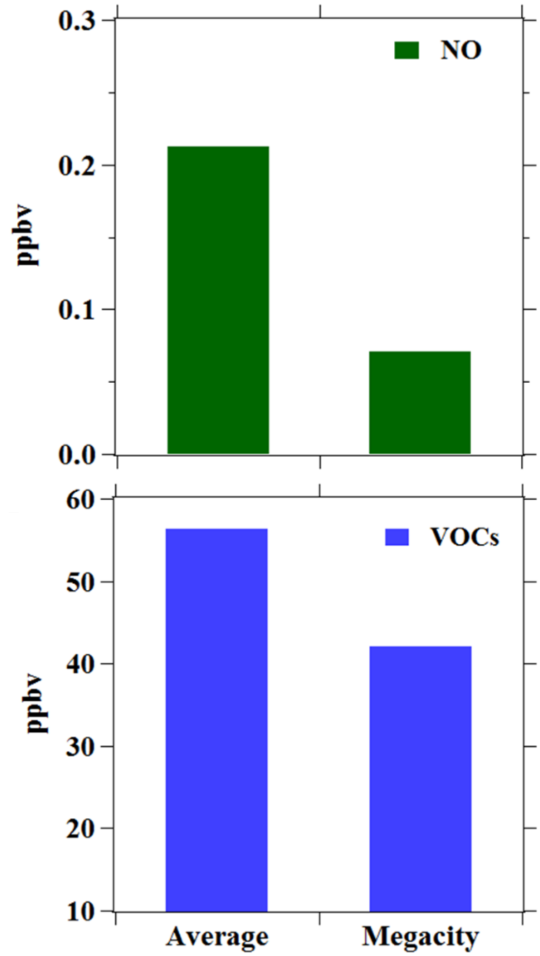


Figure S5. Different level of NO (upper) and total VOCs (lower) between campaign average and the megacity case (averaged between 20:30 to 23:30 of the night).

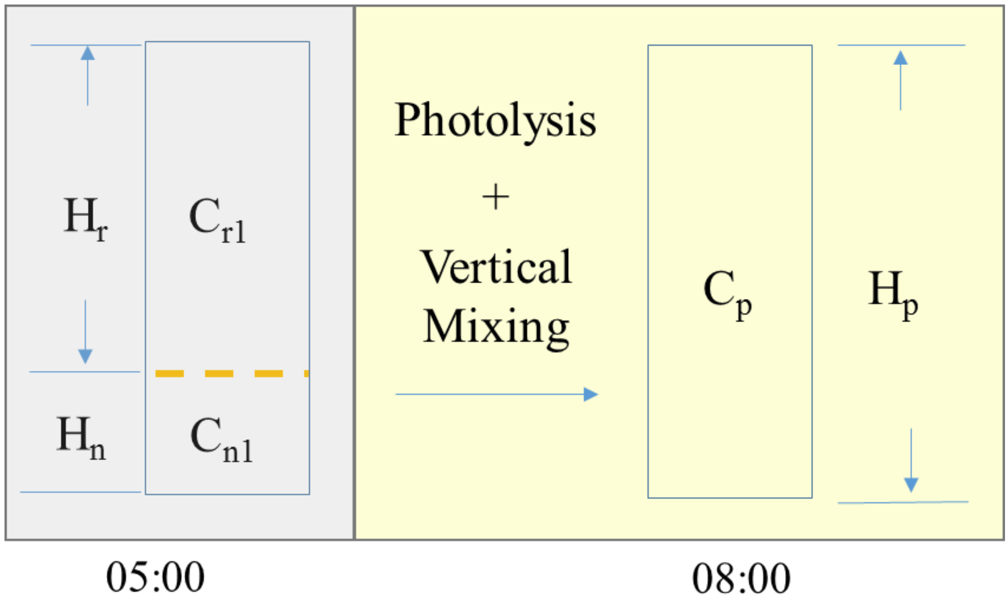


Figure S6. Conceptual diagram of 1-D model used for the estimation of $ClNO_2$ mixing ratios in the RL before sunrise.

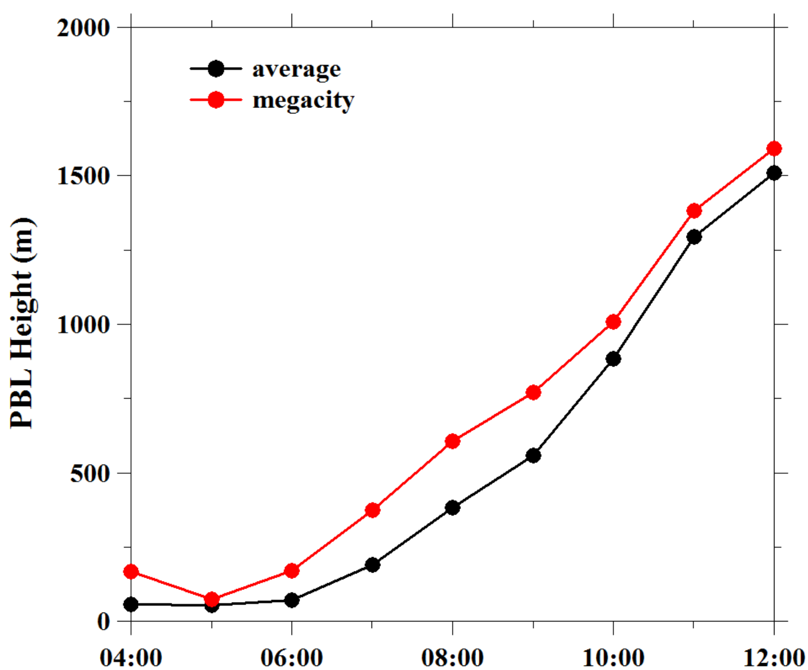


Figure S7. WRF simulated PBL heights (a.g.l.) for the campaign average and the megacity case.

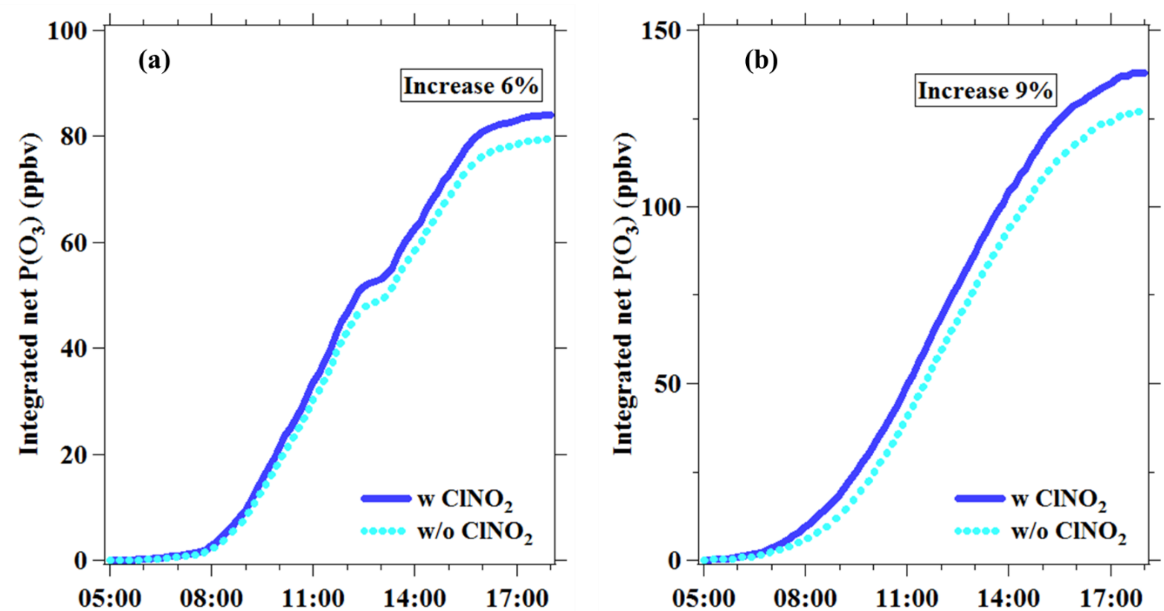


Figure S8. Daily integrated net O_3 production simulated with and without $ClNO_2$ input; (a) the $ClNO_2$ concentration in megacity case was decreased similar to that of average condition, and b) the $ClNO_2$ concentration in average condition was increased to that of megacity case.

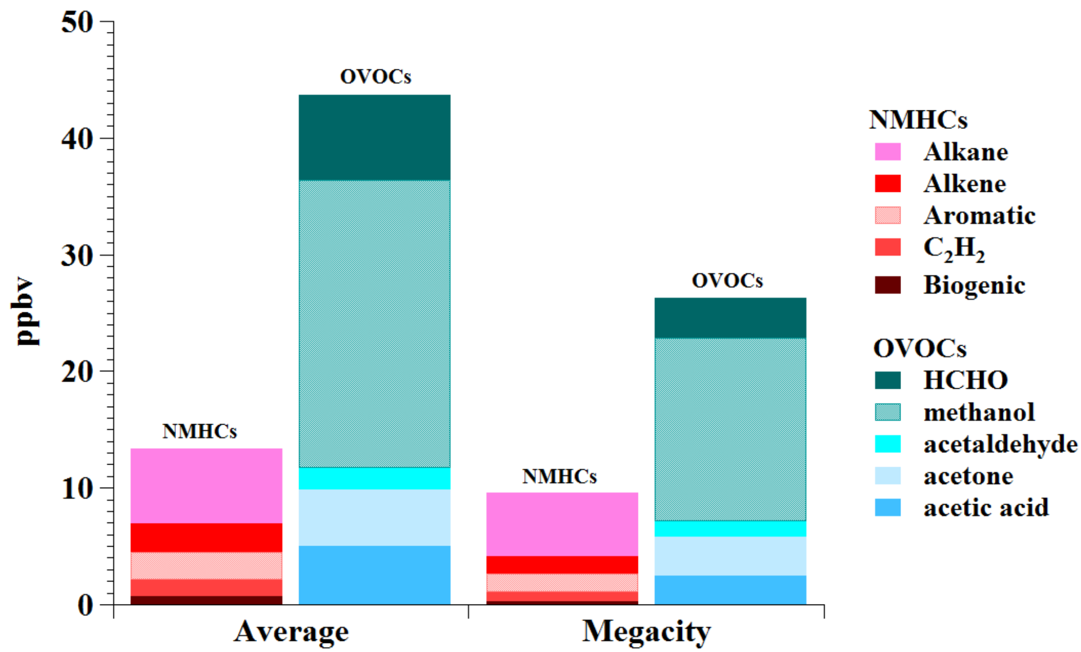


Figure S9. 24-hour average concentrations of different NMHCs and OVOCs groups/species for campaign average and the megacity case.

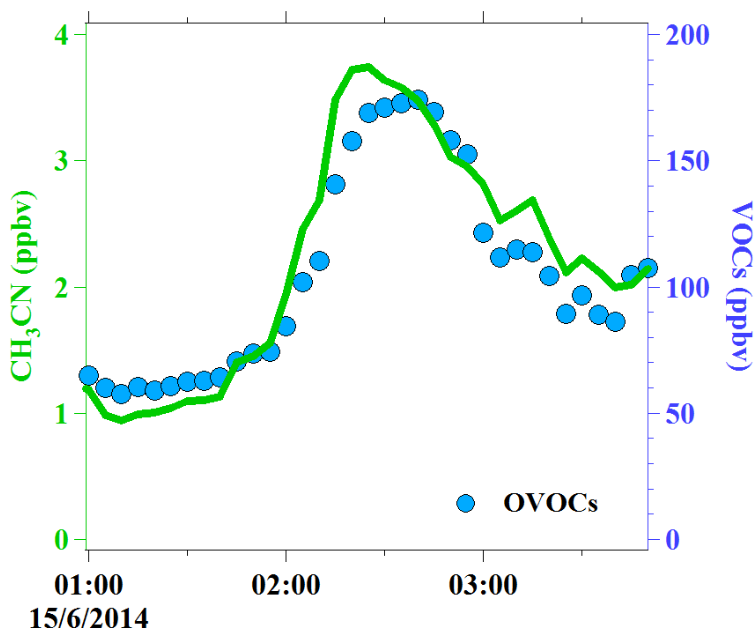
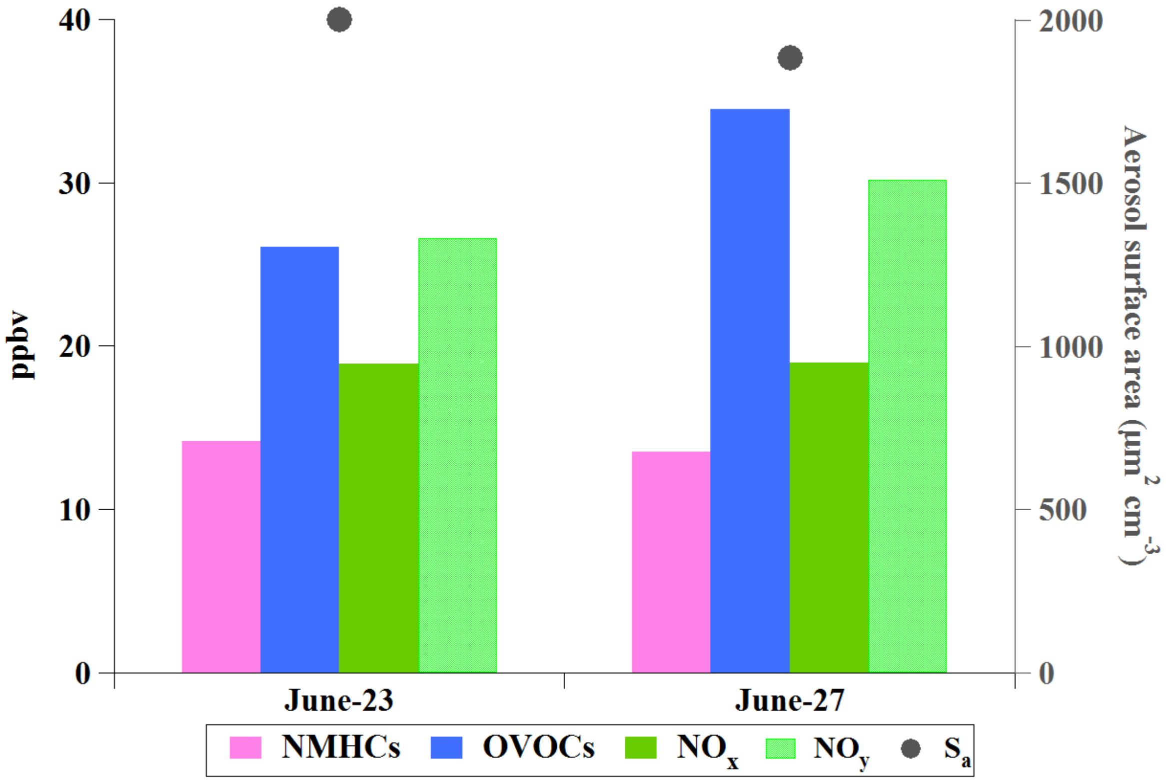


Figure S10. Huge amount of OVOC observed in a fresh biomass burning plume in early morning of 15 June 2014 (as indicated by high CH_3CN).



5 **Figure S11. Examples of smaller OVOC to NMHC ratios and similar mean mixing ratio of NO_x, NO_y, and S_a in other cases of megacity outflow from Beijing/Tianjin on 23 and 27 June 2014.**