

**Impact of pollution controls in Beijing on atmospheric oxygenated  
volatile organic compounds (OVOCs) during the 2008 Olympic  
Games: observation and modeling implications**

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## 1 **Abstract**

2 Oxygenated volatile organic compounds (OVOCs) are important products of the  
3 photo-oxidation of hydrocarbons. They influence the oxidizing capacity and the  
4 ozone forming potential of the atmosphere. In the summer of 2008 two months'  
5 emission restrictions were enforced in Beijing to improve air quality during the  
6 Olympic Games. Observation evidence has been reported in related studies that these  
7 control measures were efficient in reducing the concentrations of primary  
8 anthropogenic pollutants (CO, NO<sub>x</sub> and non-methane hydrocarbons, i.e. NMHCs) by  
9 30-40%. In this study, the influence of the emission restrictions on ambient levels of  
10 OVOCs was explored using a neural network analysis with consideration of  
11 meteorological conditions. Statistically significant reductions in formaldehyde  
12 (HCHO), acetaldehyde (CH<sub>3</sub>CHO), methyl ethyl ketone (MEK) and methanol were  
13 found to be 12.9%, 15.8%, 17.1% and 19.6%, respectively, when the restrictions  
14 were in place. The effect of emission control on acetone was not detected in neural  
15 network simulations, probably due to pollution transport from surrounding areas  
16 outside Beijing. Although the ambient levels of most NMHCs were decreased by  
17 ~35% during the full control period, the emission ratios of reactive alkenes and  
18 aromatics closely related to automobile source didn't present much difference  
19 (<30%). A zero-dimensional box model based on Master Chemical Mechanism  
20 version 3.2 (MCM3.2) was applied to evaluate how OVOCs productions respond to  
21 the reduced precursors during the emission controlled period. On average, secondary  
22 HCHO was produced from the oxidation of anthropogenic alkenes (54%), isoprene

23 (30%) and aromatics (15%). The importance of biogenic source for the total HCHO  
24 formation was almost on a par with that of anthropogenic alkenes during the daytime.  
25 Anthropogenic alkenes and alkanes dominated the photochemical production of  
26 other OVOCs such as acetaldehyde, acetone and MEK. The relative changes of  
27 modelled HCHO, CH<sub>3</sub>CHO, methyl vinyl ketone and methacrolein (MVK+MACR)  
28 before and during the pollution controlled period were comparable to the estimated  
29 reductions in the neural network, reflecting that current mechanisms can largely  
30 explain secondary production of those species under urban conditions. However, it is  
31 worthy to notice that the box model overestimated the measured concentrations of  
32 aldehydes by a factor of 1.4-1.7 without consideration of loss of aldehydes on  
33 aerosols, and simulated MEK was in good agreement with the measurements when  
34 primary sources were taken into consideration. These results suggest that the  
35 understanding of OVOCs budget in the box model remains incomplete, there is still  
36 considerable uncertainty in particular missing sinks (unknown chemical and physical  
37 processes) for aldehydes and absence of direct emissions for ketones.  
38

## 39 1. Introduction

40 Oxygenated Volatile Organic Compounds (OVOCs), such as aldehydes, ketones and  
41 alcohols, are mostly produced in the atmosphere by the oxidation of biogenic,  
42 anthropogenic hydrocarbons and other organic species (Finlayson-Pitts and Pitts,  
43 2000), and also directly emitted by vegetation (Park et al., 2013), biomass burning  
44 (Yokelson et al., 2009; Mason et al., 2001; Andreae and Merlet, 2001), fossil fuel  
45 combustion (Schauer et al., 1999, 2002) and industries (Singh et al., 1994). They are  
46 lost through oxidation by OH, photolysis, and deposition/surface uptake. Aircraft  
47 measurements showed that the vertical distribution (0-12 km) of the total  
48 concentrations of oxygenated organics was 2-5 times as abundant as the sum of  
49 C<sub>2</sub>-C<sub>8</sub> non-methane hydrocarbons (NMHCs) at all altitudes in the remote Pacific  
50 troposphere (Singh et al., 2001). Formaldehyde (HCHO) and other oxygenated  
51 hydrocarbons dominated the total OH loss with VOCs in clean air masses (Goldan et  
52 al., 2004). In polluted atmospheres the interaction of primary and secondary VOCs is  
53 closely coupled with the formation of ozone and secondary organic aerosols (SOA).  
54 And usually OVOCs serve as intermediate products in these oxidation processes,  
55 which helps to estimate the formation potential of ozone (Shao et al., 2011) and other  
56 products. And OVOCs also affect the oxidizing capacity of the atmosphere. Some  
57 previous studies found that carbonyls are one of important radical sources, especially  
58 for the wintertime in polluted urban environments (Emmerson et al., 2005).  
59 Accordingly, it is essential to understand the sources, sinks and chemistry of OVOCs  
60 quantitatively. While the role of OVOCs in heavily polluted regions remains largely

61 unexplored, partly due to the lack of reliable observations of them.

62 Beijing, the capital of China and one of the most populous megacities in the world,  
63 is located in northern China. Accompanied with the rapid population growth and  
64 economic expansion, severe air pollution in Beijing has attracted global attention.  
65 The city has been known for its increasing ozone concentration (Parrish and Zhu,  
66 2009;Shao et al., 2009) and hazy skies (Chan and Yao, 2008). In preparation for the  
67 2008 Summer Olympics and to clean up the city's air, Beijing imposed a number of  
68 pollution control measures during the Games. Thus, coordinated observations on  
69 such restriction occasions create a valuable opportunity for studying how OVOCs  
70 respond to the emission reductions, testing and refining the current knowledge of  
71 formation pathways of secondary OVOCs under polluted conditions.

72 After Beijing was selected as the host of the 2008 Summer Olympics, the Beijing  
73 government started to implement a series of long-term emission control regulations,  
74 such as the closure of heavy polluting industries (chemical factories, cement plants,  
75 steel manufacturing etc.) in the southeast of the city, relocating nearly 200 factories  
76 out of the Beijing area; also tightening vehicle emission and fuel quality standards,  
77 and accelerating retirements of old vehicles. More stringent, short-term measures  
78 were put into effect from 1 July to 20 September 2008, such as temporarily halting  
79 industrial production, suspending construction and evaporative emissions. Nearly 2  
80 million vehicles were banned from the roads step by step (UNEP, 2009): 1) a total of  
81 350,000 yellow-labeled vehicles with high emission were not allowed to enter the  
82 city starting from 1 July; 2) 50% of privately owned vehicles were restricted to run

83 on alternate days (based on their license plate numbers) in the metropolis and 70% of  
84 government-owned vehicles were halted from operating from 21 July to 20  
85 September, which is so called “full control period”. As a result, the traffic emissions  
86 on VOCs, CO, NO<sub>x</sub>, and particulate matter (PM) were estimated to be reduced by 50%  
87 (Wang et al., 2010b).

88 The two months’ emission restrictions had a noticeable impact on major pollutants  
89 directly emitted from fuel combustions, which have been validated by on-road  
90 measurements (Wang et al., 2009a; Wang and Xie, 2009; Wang et al., 2009b),  
91 ground-level monitoring (Wang et al., 2010a; Wang et al., 2010c; Chou et al.,  
92 2011; Zhang et al., 2009) and satellite-based observations (Witte et al., 2009; Worden  
93 et al., 2012; Lyapustin et al., 2011). Satellite measurements over Beijing showed 43%  
94 reduction of tropospheric column NO<sub>2</sub> during the Games (Witte et al., 2009), and 32%  
95 reduction in CO for 2008 with respect to 2007 was estimated from MOPITT satellite  
96 retrievals (Worden et al., 2012). Wang et al. (2009a) found a dramatic decrease of  
97 primary pollutants from on-road measurements, by up to 54% for CO, 41% for NO<sub>x</sub>  
98 and 66% for aromatics (benzene, toluene, ethylbenzene and xylenes, BTEX). And  
99 Wang et al. (2010a) reported the averaged mixing ratios of NMHCs near the  
100 Olympic Stadium during the Games were reduced by 35%, compared with the  
101 concentrations measured in June (before the restrictions). The monthly  
102 concentrations of NO, NO<sub>2</sub> and CO were decreased by 76.8%, 29.7% and 27.8% in  
103 August 2008 compared to previous years for the same month (Chou et al., 2011). In  
104 contrast, the observed mixing ratio of O<sub>3</sub> increased by 16% during the full control,

105 compared to the period prior to 20 July (Wang et al., 2010c). The higher levels of  
106 ozone were influenced by the declined O<sub>3</sub>-NO titration and the shift in different O<sub>3</sub>  
107 formation regimes (Chou et al., 2011), changes in weather conditions, or/and by the  
108 transport of photochemical plumes from the surrounding areas to Beijing (Wang et  
109 al., 2010c). So, the influence of control measures on secondary pollutants still needs  
110 more investigation.

111 The limited OVOCs datasets available in Beijing suggest that the ambient levels of  
112 carbonyls were observed to be 3-5 times higher than the levels in HongKong, about  
113 35% of those in Mexico City (Pang and Mu, 2006), and comparable to those in Rio  
114 de Janeiro, Brazil (Grosjean et al., 2002). In summer, about 60-70% of aldehydes in  
115 Beijing were associated with the photochemical oxidation of anthropogenic and  
116 biogenic VOCs, and 10-15% of them were attributed to the primary emission from  
117 anthropogenic sources (Liu et al., 2009). For ketones and alcohols, anthropogenic  
118 primary emission was shown to be the largest contributor (Liu et al., 2009; Yuan et al.,  
119 2012). The 2008 summer provides the opportunity to estimate the impact of reduced  
120 emissions on ambient OVOCs. In this study, firstly a neural network approach was  
121 used to link VOCs mixing ratios to meteorological conditions, which helps to  
122 ascertain that the observed changes in VOCs are significant due to the emission  
123 restrictions, rather than variations caused by different meteorological conditions.  
124 Secondly, a box model using the Master Chemical Mechanism (MCM) was  
125 employed to investigate secondary formation of OVOCs during the full control  
126 period, in particular, of two most abundant aldehydes (formaldehyde, acetaldehyde),

127 two ketones (acetone and MEK) and unique oxidation products of isoprene  
128 chemistry (MVK+MACR). Moreover, this study also aims to quantify the changes of  
129 secondary OVOCs by the existing mechanisms, responding to the reduced  
130 precursors (NMHCs) and other pollutants (CO, NO, NO<sub>2</sub>, O<sub>3</sub>), and to analyze the  
131 similarity or discrepancy between the measured and modelled changes in OVOCs  
132 before and during the full control.

## 133 **2. Methodologies**

### 134 **2.1. Monitoring sites and experimental methods**

135 As part of the CAREBEIJING-2008 campaign, the measurements of VOCs and  
136 other air pollutants (CO, NO<sub>x</sub>, O<sub>3</sub> et al.) were conducted at an intensive observation  
137 site on the campus of Peking University (PKU) from 3 July to 27 August 2008. The  
138 PKU site (39.99 °N, 116.31 °E) was located in the northwest of downtown Beijing,  
139 which has been considered to be representative of a typical urban environments with  
140 different mixtures of high density traffic, commercial, residential, and electronic  
141 companies (Liu et al., 2009; Cheng et al., 2008; Song et al., 2007). The air inlets for  
142 the instruments were set up on the top of a six-story building (~25m above the  
143 ground level). Three online techniques were used to quantify NMHCs and OVOCs  
144 during the campaign, including a Proton-Transfer-Reaction Mass Spectrometer  
145 (PTR-MS), a gas chromatograph with mass spectrometer and flame ionization  
146 detector (GC-MS/FID) and a Hantzsch fluorimetric monitor.

#### 147 **2.1.1. Online measurements for NMHCs and OVOCs**



148 A high-sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) was used for  
149 ambient measurements of selected NMHCs and OVOCs. This technique ionizes  
150 VOC molecules by transferring proton ( $H^+$ ) from protonated water ions ( $H_3O^+$ ) in a  
151 drift tube, followed by a quadrupole mass spectrometer detection of the product ions  
152 (Lindinger et al., 1998; de Gouw and Warneke, 2007). The air sample was drawn  
153 through an 8m-long perfluoroalkoxy (PFA) tube (0.25in OD  $\times$  0.156in ID) into the  
154 gas handling system by a diaphragm pump at the flow rate of 2-3 slpm. A small flow  
155 of 220-240 sccm was branched from the main flow to the PTR-MS. A 2.0  $\mu$ m  
156 pore-size 47mm PTFE filter at the inlet was used to remove particles from the  
157 sample flow.

158 The operating parameters of PTR-MS used herein are similar to those described  
159 previously in Yuan et al. (2010a). The instrument was operated at 2.3 mbar drift tube  
160 pressure and 600V drift voltage, 35 masses were sampled with the time resolution of  
161 160 s. Instrument background signals were measured every 35 cycles ( $\sim$ 1.5hr) by  
162 switching the sample air to an activated charcoal trap for 5 cycles ( $\sim$ 13min). Target  
163 ions with the dwell time of 5s each cycle included OVOCs such as methanol ( $m/z =$   
164 33), acetaldehyde ( $m/z = 45$ ), acetone ( $m/z = 59$ ), MVK+MACR ( $m/z = 71$ ), methyl  
165 ethyl ketone (MEK,  $m/z = 73$ ); Aromatics such as benzene ( $m/z = 79$ ), toluene ( $m/z$   
166  $= 93$ ), styrene ( $m/z = 105$ ), C8 aromatics ( $m/z = 107$ ) and C9 aromatics ( $m/z = 121$ );  
167 isoprene ( $m/z = 69$ ) and acetonitrile ( $m/z = 42$ ). The PTR-MS was calibrated every  
168 week using a commercial TO15 gas standard (Air Environmental Inc. Denver, U.S.)  
169 at seven concentration levels ranging from 1 ppb to 15 ppb. For most of species, the

170 detection limits were between 23 and 60 pptv, except methanol (141 pptv), acetone  
171 (148 pptv) and MEK (110 pptv). The relative errors of the PTR-MS measurements  
172 decrease with the mixing ratios of target species, as shown in the Supplement Fig.S1,  
173 and the precisions of all detected species were below 5% at the level of 1ppbv.

174 An automated GC-MS/FID system with two-column and two-detector was deployed  
175 by Research Center for Environmental Changes (RCEC) Academia Sinica, Taiwan,  
176 which was used to measure C<sub>2</sub>-C<sub>4</sub> hydrocarbons and C<sub>5</sub>-C<sub>11</sub> hydrocarbons  
177 simultaneously. Technical details for this instrument were presented in Chou et al.  
178 (2011). A total of 65 NMHCs were quantified hourly during the full control period  
179 (24 July through 27 August), the precision for most of the species was within 2% and  
180 the limits of detection were below 30 pptv.

181 The comparison between the PTR-MS and GC-MS data showed a good agreement  
182 for aromatics (benzene, toluene, C<sub>8</sub> aromatics and C<sub>9</sub> aromatics) during the  
183 campaign, as shown in Fig.S2a in the Supplement, with the slopes varying between  
184 0.86 and 1.21 and the correlation coefficients larger than 0.89. The isoprene  
185 concentrations measured by PTR-MS were systematically higher than that measured  
186 by GC-MS, particularly for the mixing ratios lower than 1ppbv, shown in Fig. S2b,  
187 possibly because signals at *m/z* 69 detected by PTR-MS were influenced by some  
188 interferences from pentanal, methyl butanal, pentenol (de Gouw et al., 2003) and  
189 cycloalkanes (Yuan et al., 2014). It should be noticed that the artifact of PTR-MS  
190 measurements on isoprene leads to an additional background in anthropogenic  
191 emission dominated areas. So, the isoprene data from the GC-MS is used in the

192 following model calculations.

193 Formaldehyde (HCHO) was measured by an online Hantzsch fluorimetric monitor at  
194 the time resolution of 10min. The instrument was described in previous publications  
195 (Dasgupta et al., 2005;Li et al., 2010), which was based on sensitive wet chemical  
196 fluorimetric detection of HCHO. A diffusion scrubber was designed to strip and  
197 collect HCHO from the gas phase into the liquid phase. The detection limit for  
198 HCHO was within 100 pptv, and the precision was below 10%.

### 199 **2.1.2. Measurements for other air pollutants and parameters**

200 A comprehensive set of instruments was installed at the PKU site to monitor the air  
201 quality. CO was measured by a nondispersive infrared sensor (NDIR) with an  
202 integration time of 1 min (48CTLE, Thermo Environmental Instruments, TEI, USA).  
203 Zero calibrations were done every two hours and span calibrations were performed  
204 at midnight (0:00-1:00 a.m.) each day during the campaign. Ozone was measured by  
205 a UV absorption detector (Model 49i, TEI). NO was measured using a NO/O<sub>3</sub>  
206 chemiluminescence analyzer (Model 42iTL, TEI), with the instrument sequentially  
207 measuring NO<sub>2</sub> through a photolytic converter.

208 HONO was measured using an online stripping coil sampler/ion chromatography (IC)  
209 system at the time resolution of 15min. The instrument has a detection limit of 8 ppt  
210 with an uncertainty of 7%, other technical details were presented in Cheng et al.  
211 (2013).

212 For aerosol measurements at the site, particle size distributions from 3 to 900 nm

213 (mobility diameter) were measured by a TDMPS (Twin Differential Mobility  
214 Particle Sizer) system with 10 min time resolution, as presented in Wang et al.  
215 (2011). An Aerodyne HR-TOF-AMS (high-resolution time-of-flight aerosol mass  
216 spectrometer) was deployed to measure chemical compositions of PM<sub>1</sub>. A detailed  
217 description of the system was shown in Huang et al. (2010).  
218 A meteorological station was operated simultaneously to monitor meteorological  
219 parameters (temperature, RH, pressure, wind speed and wind direction) on the  
220 campus, which was about 400m away from the air quality intensive site. The  
221 photolysis frequencies of O<sup>1</sup>D and NO<sub>2</sub> were measured at the PKU site by two filter  
222 radiometers (Bohn et al., 2008) with time resolution of 5 s. The uncertainties of *J*  
223 values were within 10%.

## 224 **2.2. Methodology for neural network**

225 The temporal variation of VOCs concentrations at a receptor site reflects a  
226 combination of changes in emission location and strength, meteorological conditions,  
227 chemical loss and secondary formation. Previous studies indicated that  
228 meteorological conditions, especially local wind speed and direction, played an  
229 important role in shaping the air quality of Beijing (Wu et al., 2008). We cannot  
230 quantify the influence of emission restrictions on ambient VOCs by simply  
231 comparing their levels during the control period with those before and after.  
232 Therefore, following the method introduced by Cermak and Knutti (2009), a  
233 feed-forward neural network was used to establish a statistical relationship between

234 VOCs mixing ratios and meteorological parameters from the reference data (i.e.  
235 before the full control), and then to predict the concentrations given the  
236 meteorological conditions during the Games, if there was no restriction measures  
237 taken. Thus, the difference between the observed and predicted VOC concentrations  
238 is helpful to determine the effective changes due to the air quality measures.

239 The Multilayer Perceptron (MLP) Network in SPSS17.0 was used in this work. As  
240 the concentrations of VOCs displayed near log-normal distributions, the natural  
241 logarithm of VOC concentration,  $\ln([\text{VOC}])$ , was selected as the “dependent variable”  
242 of inputs in the MLP network, and the meteorological parameters as “covariates” of  
243 inputs, including wind vector ( $u, v$ , previous day  $u$ , previous day  $v$ ), precipitation,  
244 relative humidity, temperature and pressure. The observed data from 3 July to 20  
245 July (before the full control) were used as the reference data ( $n=1611$ ) to set up a  
246 relationship between  $\ln([\text{VOC}])$  and meteorological parameters. 70% of the  
247 reference data was chosen randomly as training sample to train the neural network,  
248 20% of the data as testing sample used to track errors during training in order to  
249 prevent overtraining, and the rest of data (10%) as holdout sample used to assess the  
250 final neural network for validation. The network contained one hidden layer, *Sigmoid*  
251 functions were chosen as the activation functions for hidden layer and output layer.

252 Given that there was no statistically difference between the prediction and the  
253 corresponding observation for validation data, the same approach was used for  
254 predicting the concentrations of VOCs during 21 July through 27 August.

### 255 **2.3. Model description for OVOC simulation**

256 A zero-dimensional box model, which is similar to the one used by Lu et al. (2012)  
257 and Li et al. (2014), was employed in this work to examine the change of OVOC  
258 production under the influence of emission restrictions. The box model uses a subset  
259 of the MCM3.2 (available online at <http://mcm.leeds.ac.uk/MCM>) which contains  
260 fully explicit chemical mechanisms for 57 kinds of VOCs (including 7 oxygenated  
261 hydrocarbons) plus CH<sub>4</sub> and CO. The model calculations were constrained by  
262 measured C<sub>2</sub>-C<sub>11</sub> NMHCs, CO, CH<sub>4</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>, HONO, and physical parameters  
263 (i.e., photolysis frequencies, water vapor concentration, temperature, and pressure).  
264 The time step of the model calculation was set to 30 minutes. Here, 57 VOCs were  
265 measured by online GC-MS/FID and PTR-MS including 20 C<sub>2</sub>-C<sub>11</sub> alkanes, 11  
266 C<sub>2</sub>-C<sub>5</sub> alkenes, 15 aromatics, acetylene, isoprene, pinenes, formaldehyde,  
267 acetaldehyde, methanol, acetone, MEK and MVK+MACR. The CH<sub>4</sub> concentration  
268 was assumed to 2.5 ppm taken from previous observations in Beijing (Su, 2003).  
269 The photolysis rates for O<sup>1</sup>D and NO<sub>2</sub> were constrained with the measured values at  
270 the site. The photolysis rates for HONO, aldehydes and ketones were calculated by  
271 the model for clear sky conditions (Saunders et al., 2003) and then scaled by the  
272 measured  $J(\text{NO}_2)$ . Dry deposition rate for all modelled species was set to 1.2 cm s<sup>-1</sup>  
273 by assuming a well-mixed boundary layer with a height of 1000 m, corresponding to  
274 a lifetime ( $\tau_D$ ) of 24h. Several additional model scenarios (listed in Table 3) were  
275 constructed to test the sensitivity of simulated OVOCs concentrations with assumed  
276 deposition rates and boundary layer evolution. The model was operated for the full  
277 control period (26 July- 27 August) with 2 days spin-up time to reach steady state.

278 The relative changes of the model results responding to the controlled emissions  
279 were compared with the observed changes of OVOCs before and during the full  
280 control (Section 4).

281 The model uncertainty is mainly caused by the uncertainty of all input parameters  
282 (VOCs, trace gas, meteorological parameters, etc.) and reaction rates used in the  
283 model. Here, the total uncertainty was estimated by the error propagation from the  
284 errors of all considered parameters, as described in Li et al. (2014). The modelled  
285 concentrations of OVOCs in the base model had an uncertainty of 40-50%.

### 286 **3. Results and discussion based on observations**

#### 287 **3.1. Diurnal variations of VOCs before and during the control**

288 Table 1 summarizes the averaged meteorological parameters before (3-20 July) and  
289 during the full control period (21 July-27 August). Meteorological conditions in the  
290 two time periods were similar, except that the average ambient  $T$  and UVA before the  
291 control were slightly higher than respective values during the full control, which  
292 would affect the emission of biogenic VOCs (dominated by isoprene). As an  
293 overview of the changes in VOC concentrations between the two periods, the  
294 10min-average diurnal variations of the mixing ratios of 12 VOC species were  
295 compared in Fig. 1. Aromatics, as a group of primary anthropogenic NMHCs,  
296 mainly come from vehicle exhaust and solvent usage in Beijing (Liu et al.,  
297 2005; Yuan et al., 2010b). They dropped to the minima at 2:00 – 3:00 p.m. for both of  
298 the two time periods (Fig. 1 a – f). Compared to the period prior to 20 July, an

299 obvious decrease (50-60%) in aromatics occurred after 21 July, especially at rush  
300 hours, which may be caused by the traffic restrictions. Oxygenated species at PKU  
301 site, from both secondary photochemical production and primary emissions, reached  
302 high concentrations at noon and in the late evening (Fig. 1 h – l). Some differences  
303 of ketones and aldehydes between the two time periods were found, but not as  
304 prominent as aromatics. It is difficult to assess the effect of control measures on  
305 OVOC species, merely based on the changes in their absolute concentrations before  
306 and during the control. In the following section a neural network analysis is used to  
307 subtract meteorological effects and quantify the influence of emission reductions on  
308 ambient levels of NMHCs and OVOCs.

### 309 **3.2. Effect of emission control measures on mixing ratios of VOCs**

310 Assuming that no emission restrictions had been in place from 21 July to 27 August,  
311 the “uncontrolled” VOCs corresponding to the meteorological conditions  
312 encountered at that time were predicted by MLP network using the relationship  
313 between VOCs and meteorological parameters from the reference data (before 21  
314 July). Figures 2 and 3 present the probability distributions of the observed (red) and  
315 predicted (blue)  $\ln([\text{VOC}])$  before and during the control period for NMHCs and  
316 OVOCs, respectively. For most of aromatics, the observation and prediction values  
317 from the uncontrolled period matched well with each other, but the observed data  
318 from the controlled period clearly shifted towards lower values compared to the  
319 prediction. This suggests that the influence of the traffic restriction on aromatics was  
320 effective. Acetonitrile ( $\text{CH}_3\text{CN}$ ), unlike other NMHCs, didn't show any difference



321 between the observed and predicted values for both the controlled and uncontrolled  
322 periods. As acetonitrile is usually considered as a tracer for biomass burning and is  
323 seldom detected in automobile emissions (Wang et al., 2007), its concentration  
324 should be hardly affected by the traffic control. The measured median value of  
325 acetonitrile before 21 July was slightly higher than that after 21 July. This  
326 discrepancy (15%) in the absolute concentrations between the two time periods  
327 could be explained by the changes in meteorological conditions or pollution  
328 transport. The reductions of most OVOCs were also observed relative to what was to  
329 be expected without emission controls, although the deviations in OVOCs were not  
330 as notable as aromatics (Fig. 3).

331 The predicted and observed results of NMHCs and OVOCs in the controlled period  
332 are compared in Table 2, and the results for the uncontrolled period are listed in  
333 Table S1. The median concentrations of aromatics dropped by 32-47% compared to  
334 the levels expected under the same meteorological conditions without traffic controls.  
335 The median values of formaldehyde, acetaldehyde, MEK and methanol were  
336 decreased by 12.9%, 15.8%, 17.1% and 19.6%, respectively. Isoprene, unlike  
337 aromatics, exhibited a broad peak from the early morning to the afternoon (Fig.1g),  
338 which followed the solar radiation and temperature cycles and showed the  
339 characteristics of local biogenic emissions in the daytime. In addition, their low  
340 concentrations at night likely indicate small local emissions from vehicles near the  
341 site. Compared to the values before the control isoprene and MVK+MACR were  
342 estimated to be decreased by 26% and 11% from 21 July to 27 August, respectively,

343 which was caused by a combined effect of the lower temperature, solar radiation and  
344 the control measures.

345 The relative difference between predicted and measured acetone was as small as 1%,  
346 implying that the emission controls had little or no effect on acetone. The unchanged  
347 acetone levels were probably influenced by its high regional background, which was  
348 around 1.7-2 ppb at PKU site accounting for 43-47% of acetone concentration (Liu  
349 et al., 2009; Yuan et al., 2012). Acetone background was closely related to transport  
350 of photochemical plumes from the surrounding areas (such as Hebei Province and  
351 Tianjin) to Beijing. As the emission reductions were implemented within the Beijing  
352 area, i.e. in a range of about 150 km radius, regional background of acetone should  
353 be hardly affected by the emission controls. So, it seems to be difficult to reduce the  
354 level of acetone in Beijing if relying solely on the control of local emissions.

355 Except acetonitrile and acetone, the deviation for all other species between the full  
356 control period and the uncontrolled days is statistically significant from Student's  
357 *T*-test at the 95% level ( $P(t) < 0.05$ ). By contrast, the reference data from the  
358 uncontrolled period were well predicted by the MLP simulations (as shown in  
359 Fig.S3), with correlation coefficients ranging from 0.79 to 0.94 and successful  
360 *T*-tests for all the species (presented in Table S1). Thus, the emission restrictions  
361 implemented in Beijing had significant effects on the NMHCs dominated by  
362 vehicular emissions, which is consistent with those results in Wang et al. (2010a).  
363 The reductions in OVOCs species are moderate in comparison to their precursors  
364 (e.g. NMHCs), which are subject to the combined influence of controlled direct

365 emissions, local production from reduced precursors and regional formation  
366 processes (transport). In subsequent model analysis (Section 4), the changes of  
367 OVOCs produced from local NMHCs oxidation will be discussed.

### 368 **3.3. Emission ratios for anthropogenic NMHCs**

369 As NMHCs play significant roles on the formation of secondary OVOCs, emission  
370 ratios (ERs) of NMHCs before and during the full control were compared in this  
371 section to determine whether the emission restrictions also altered the relative  
372 emission of OVOC precursors (i.e. source pattern of NMCHs), in addition to  
373 reducing their total emission amounts. From previous studies on NMHCs source  
374 apportionment in Beijing (Liu et al., 2005; Song et al., 2007; Lu et al., 2007; Wang et  
375 al., 2010a), vehicle exhaust is the largest contributor to ambient NMHCs with a  
376 percentage of 40-58%, followed by solvent usage and painting processes (18-30%),  
377 gasoline evaporation (7-13%) and chemical plants (3-15%).

378 The emission ratio for VOCs is defined as the ratio of VOC species relative to a  
379 reference compound in fresh emissions without undergoing photochemical processes.  
380 It can be determined using a photochemical-age based method presented in de Gouw  
381 et al. (2005), Warneke et al. (2007) and Borbon et al. (2013). The degradation of  
382 NMHCs by their reactions with OH is described as Eq. (1), where  $ER_{\text{NMHC}}$   
383 represents emission ratio of NMHC species relative to CO,  $k_{\text{NMHC}}$  and  $k_{\text{CO}}$  are the  
384 OH rate coefficients for NMHC and CO, respectively. The ERs reflect the  
385 comprehensive effect of all emission sources on ambient NMHCs at the site. Here,  
386 the photochemical age of the sampled air masses was calculated by the measured

387 ratio of toluene/benzene (T/B) using Eq. (2), and the initial T/B was set to  $2.8 \pm 0.7$ .  
 388 The 24 h averaged concentration of OH was taken as  $2.5 \times 10^6$  molecules  $\text{cm}^{-3}$  that  
 389 was from OH measurements at a suburban site near Beijing during CAREBEIJING  
 390 2006 campaign (Lu et al., 2013). The ratio of NMHCs (e.g., toluene, m,p-xylene) to  
 391 CO decreases with the photochemical age (Fig. 4). The yellow line in Fig. 4a is the  
 392 linear fit between  $\ln([\text{toluene}]/[\text{CO}])$  and the photochemical age. The emission ratio  
 393 of toluene relative to CO ( $ER_{\text{toluene}}$ ) is determined by the intercept of the linear fit. It  
 394 is noted that CO data used for the fitting was subtracted by a constant background of  
 395 120 ppbv, which was determined from the minimum concentrations when prevailing  
 396 wind were from northeast and relatively clean air were measured.

$$397 \quad \frac{[\text{NMHC}]}{[\text{CO}]} = \frac{[\text{NMHC}]}{\Delta\text{CO}} = ER_{\text{NMHC}} \times \exp[-(k_{\text{NMHC}} - k_{\text{CO}})[\text{OH}]\Delta t] \quad (1)$$

$$398 \quad \Delta t = \frac{1}{[\text{OH}](k_{\text{toluene}} - k_{\text{benzene}})} \times \left[ \ln\left(\frac{[\text{toluene}]}{[\text{benzene}]}\bigg|_{t=0}\right) - \ln\left(\frac{[\text{toluene}]}{[\text{benzene}]}\bigg|_{t=t}\right) \right] \quad (2)$$

399 As discussed in Warneke et al. (2007), the error of emission ratio arises from the  
 400 uncertainty of measured benzene and toluene, and the estimation of initial T/B in  
 401 equation (2) as well. The total ER error was then calculated conservatively by linear  
 402 addition of the above two errors. The measurement uncertainty of benzene and  
 403 toluene by PTR-MS or GC-MS is about 10-15%. As initial T/B from the same source  
 404 category varies with different operating conditions, the error from selecting initial  
 405 ratios can be regarded as the uncertainty of source profiles, which is usually in the  
 406 range of 15-20%. So, the total uncertainty of ER estimation is around 30-35%.

407 Since the GC-MS/FID data was only available for the full control period of 2008,

408 VOCs data measured at PKU site in August 2005 (Liu et al., 2009) were used as a  
409 reference for uncontrolled situations. The emission ratios for all measured  
410 hydrocarbons versus CO in Beijing for Aug 2008 and Aug 2005 are compared in Fig.  
411 5, and the values are tabulated in Table S2 together with some ER results from two  
412 U.S. cities in previous work (Warneke et al., 2007; Borbon et al., 2013). In general,  
413 the ERs for all groups of NMHCs in the two years agree with each other within a  
414 factor of 1.5 (indicated by the shaded area in Fig. 5). For traffic-related NMHCs  
415 including most of alkenes, acetylene, benzene, toluene and ethylbenzene, the  
416 difference of the ERs between 2005 and 2008 ranged from  $\pm 6.5\%$  to  $\pm 29\%$ , within  
417 the range of combined error (30%) for ER calculations. This suggests that the  
418 pollution control measures didn't significantly change the emission composition of  
419 the species closely related to vehicular emissions, although the absolute  
420 concentrations of those species did drop by half (e.g., toluene/CO in Fig.4a). A  
421 recent work by Wang et al. (2014) also reported a good agreement of emission ratios  
422 for most NMHCs at PKU site in the summertime of 2008, 2010 and 2011. These  
423 results reflect the similarity of NMHCs composition for typical urban emissions of  
424 Beijing.

425 Some alkanes (ethane, *n*-butane, *i*-butane, *n*-pentane) and aromatics (m,p-xylene and  
426 o-xylene, labeled in Fig. 5) showed a larger variability (35-50%) in the two ER  
427 datasets for 2005 and 2008. For example, the emission ratio for m,p-xylene in Aug  
428 2008 was observed to be 38% lower than the value in Aug 2005, shown in Fig.4b.  
429 Besides an additional error (5-10%) by subtracting a constant CO background in ER

430 estimation, one possible reason for this larger difference is that abovementioned  
431 species also come from “other” emission sources in addition to vehicles.  
432 C<sub>8</sub>-aromatics were observed as the main components from solvent usage in Beijing  
433 (Yuan et al., 2010b). The 2008 control measures included temporary closures of  
434 chemical plants, painting process and constructions involving evaporation emissions.  
435 If the influence of the control measures on emissions of solvent usage and of  
436 automobile source occurred to different degrees, the averaged emission profiles of  
437 the city would be changed for the characteristic species (i.e., xylenes) of solvent  
438 usage.

439 The ERs of hydrocarbons related to vehicle emissions (acetylene, ethylene, propene,  
440 benzene and toluene) in Beijing generally agree with those in two US cities (in Table  
441 S2), indicating that emission patterns of automobile source in different cities showed  
442 a similarity. Greater deviations of lighter alkanes, some C<sub>4</sub>-C<sub>5</sub> alkenes and higher  
443 aromatics were found, probably because of unique characteristics of emission  
444 sources (e.g. fuel types, vehicle fleet ages, solvent and paint types, industrial  
445 procedures and etc.) for each city.

#### 446 **4. Modeling analysis for the changes of OVOCs**

447 To better understand the relationship between reduced precursors (NMHCs) and  
448 OVOCs concentrations during CAREBEIJING-2008 experiment, a box model using  
449 the recent version of MCM was applied in this study. According to the source  
450 apportionments of OVOCs in Beijing (Liu et al., 2009; Yuan et al., 2012), 60-70% of  
451 aldehydes are attributed to hydrocarbon oxidation (secondary formation), the

452 contributions from primary sources are more important for ketones (38-80%) and  
453 alcohols (48-74%), and the contribution of secondary formation was not detected in  
454 methanol. Therefore, the following sections will focus on the formation of aldehydes  
455 and ketones. The primary emissions for aldehydes and ketones are not included in  
456 the base model, but added to subsequent model scenarios for comparison.

#### 457 **4.1. Description of model scenarios and OH simulation results**

458 Six model scenarios for OVOCs simulation are summarized in Table 3. M0 is the  
459 base case model with the settings described in section 2.3. In M1, the variation of the  
460 boundary layer height (BLH) at a suburban site near Beijing taken from Liu et al.  
461 (2011) was included in model run. The dry deposition rate in M1 was set to 1.2 cm  
462  $s^{-1}$ , as used in the model scenario M0. In M2, different dry deposition rates were  
463 applied to the simulated species. The values were taken from Emmerson et al. (2007)  
464 for  $HNO_3$  (2  $cm s^{-1}$ ), organic peroxides (0.5  $cm s^{-1}$ ),  $H_2O_2$  and organic nitrates (1.1  
465  $cm s^{-1}$ ), from Li et al. (2014) for HCHO and other aldehydes (1  $cm s^{-1}$ ). Also the  
466 vertical dilution rates that represent entrainment of a growing boundary layer were  
467 introduced to all modelled species in M2. It is estimated from the growth rate of  
468 boundary layer heights (Riemer et al., 2009), described by the equation given in  
469 Table 3. In M3, the loss of two aldehydes on particle surface was estimated by using  
470 uptake coefficient of  $10^{-3}$  from literature (Jayne et al., 1996; Li et al., 2011), the  
471 equation (Jayne et al., 1996) for calculating uptake rate shown in Table 3. In M4, the  
472 primary sources for formaldehyde, acetaldehyde, acetone and MEK were included  
473 by employing the emission ratios of OVOCs relative to CO and measured CO

474 concentration.

475 OH concentrations were not directly measured in Aug 2008. As strong relations  
476 between observed OH and ozone photolysis frequency ( $J(O^1D)$ ) were found in field  
477 studies (Rohrer et al., 2014; Rohrer and Berresheim, 2006), it makes sense to  
478 estimate OH radicals using the empirical OH- $J(O^1D)$  relations when lacking of direct  
479 measurements of OH. Here, the modelled OH by the box model were compared with  
480 calculated OH by an observed dependence of OH on  $J(O^1D)$  that was obtained from  
481 OH measurements in CAREBEIJING-2006 (Lu et al., 2013). Fig.6a shows the  
482 average diurnal profiles of modelled and calculated OH, indicating that the modelled  
483 OH in the daytime shows a broader peak and it was overestimated by ~22%  
484 compared to the calculations from the empirical relation. Relatively higher nighttime  
485 OH were determined from the calculation, due to the intercept of the empirical  
486 OH- $J(O^1D)$  function. This intercept includes all processes that are light-independent  
487 (Rohrer and Berresheim, 2006), implying that unknown OH production probably  
488 occurred at night (Lu et al., 2014). As the uncertainty of OH measurement and  
489  $J(O^1D)$  measurement is 20% and 10%, respectively, from Lu et al. (2013), in  
490 addition to a fitting error between OH and  $J(O^1D)$ , the difference between the  
491 modelled and calculated OH is acceptable. This give a hint that box model employed  
492 here provides a reasonable explanation of radical chemistry in the urban  
493 environments.

## 494 **4.2. OVOCs simulation**

### 495 **4.2.1. HCHO and CH<sub>3</sub>CHO**



496 Unlike OH, a large difference of a factor of 2-4 was found between the measured and  
497 modelled concentrations of aldehydes by the base model (M0), as summarized in  
498 Table S3. After modifying deposition rates or/and vertical dilution, the averaged  
499 concentrations of HCHO and acetaldehyde in M1 and M2 were decreased by 30-37%  
500 compared to the base case. But the modelled concentrations of the two aldehydes are  
501 still higher (>1.5 times) than the measured values. The considerations of BLH  
502 variation, different deposition and vertical dilution can help to explain 40-50% of the  
503 large discrepancy between M0 and observation. Those results are consistent with a  
504 recent study on modelling of formaldehyde and glyoxal in PRD (Li et al., 2014).  
505 Li et al. (2014) estimated that the uptake of formaldehyde and glyoxal by aerosols  
506 had the largest contribution (~50%) to aldehydes sinks in the presence of acidic  
507 aerosols. The  $H_{\text{aer}}^+$  presented in the particle phase was calculated from inorganic  
508 ions ( $NH_4^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $Cl^-$ ) by HR-TOF-AMS using the method in Zhang  
509 et al. (2007). For most days of campaign the average acidity of aerosols was close to  
510 neutral due to high ammonia in Beijing. However, for several days (such as 31 July,  
511 1 August, 4 August, 11 August and 14 August) the averaged  $H_{\text{aer}}^+$  in the daytime  
512 was up to 0.01448 mol/L, corresponding to a pH value of 1.84, which indicates high  
513 aerosol acidity occasionally occurred during the campaign. Jayne et al. (1996)  
514 reported a large uptake of formaldehyde by aqueous surface at low temperature and  
515 high aerosol acidity. Some lab experiments (Li et al., 2011) and field studies also  
516 showed loss of HCHO on aerosols are possible and driven by the liquid water  
517 content of the aerosol phase (Toda et al., 2014). In this study, the loss of aldehydes

518 on aerosols through heterogeneous uptake processes was included in M3 and M4 by  
519 using the uptake coefficient of  $10^{-3}$  for two aldehydes. On average, the modelled  
520 HCHO and CH<sub>3</sub>CHO by M3 were decreased by 64% and 58%, respectively,  
521 compared to M2. Therefore, the loss of aldehydes on aerosol particles might be  
522 important in the polluted areas with high production rates of aerosols. Further  
523 research on sinks of aldehydes, particularly for heterogeneous uptake processes, is  
524 still needed in future studies.

525 The model scenarios M0-M3 only estimated photochemical production of OVOCs  
526 (secondary OVOCs) and didn't include their primary emissions from sources. As  
527 OVOCs source apportionment showed that Beijing is characterized by high  
528 anthropogenic emissions of OVOCs (primary OVOCs) (Yuan et al., 2012;Chen et al.,  
529 2014), primary aldehydes were added to model simulation M4 by using the ERs of  
530 OVOCs relative to CO (HCHO/CO=2.74, CH<sub>3</sub>CHO/CO=2.82) and measured CO.

531 The ERs of OVOCs were calculated from the multivariate regression results for  
532 OVOCs data at PKU site in Yuan et al. (2012). Compared with M0-M3, the average  
533 of modelled HCHO and CH<sub>3</sub>CHO by M4 show a better agreement with the  
534 observations. As shown in Fig. 6b and 6c, the maximum of modelled HCHO in M4  
535 occurred at 3:00 – 4:00 p.m., which was about 3 hours delayed from the observations.

536 The diurnal pattern of simulated acetaldehyde was well matched with the observed  
537 variation for most of the time. The calculated primary HCHO and CH<sub>3</sub>CHO by M4  
538 contributed 41% and 58% of the total modelled concentrations, respectively, higher  
539 than those corresponding results (33% for HCHO and 42% for CH<sub>3</sub>CHO) from PMF

540 model (Chen et al., 2014).

#### 541 **4.2.2. MACR**

542 The model overpredicted the overall concentrations of MVK+MACR by 25% (Table  
543 S3). The diurnal cycle of modelled MVK+MACR is similar in shape and magnitude  
544 to the measurements for early morning and nighttime, while the model overestimated  
545 the midday peak by a factor of 1.5 in the afternoon (Fig. 6d). It suggests that the box  
546 model is able to represent nocturnal sinks of MVK+MACR, but cannot fully explain  
547 their productions or/and sinks in the daytime. Karl et al. (2010) found that the  
548 observed deposition velocities for MVK+MACR in tropical ecosystems were up to  
549 2.4 cm/s, 3-4 times higher than as used in our model runs (0.6-0.8 cm/s). And they  
550 reported that the uptake of MVK+MACR by vegetation followed an exponential  
551 increase with leaf temperature, and a light dependency presented as well. So, more  
552 MVK+MACR possibly deposit on leaves in the afternoon, which gives evidence of  
553 the gap between modelled and observed MVK+MACR during that period.

#### 554 **4.2.3. Acetone and MEK**

555 The modelled concentrations of MEK in M0 underestimated the measurements by  
556 56% (given in Table S3), which is probably caused by the absence of direct  
557 anthropogenic emissions of MEK in the model. Sommariva et al. (2011) also found  
558 the underprediction of ketones using box model in the ICARTT campaign. Similar to  
559 HCHO and CH<sub>3</sub>CHO, the primary ketones were added in M4 by using measured CO  
560 and emission ratios of ketones (acetone/CO=2.23, MEK/CO=1.22). The modelled

561 ketones in M4 were comparable to the measurements, as listed in Table S3. For  
562 diurnal variations, the agreement between modelled and measured MEK  
563 concentrations is generally good (shown in Fig. 6f). Fig. 7 indicates the simulated  
564 contributions of primary and secondary sources to MEK at PKU site. Primary  
565 sources dominated the ambient MEK concentration (~80%) on a 24-h basis, and the  
566 contribution of secondary MEK increased to 25% at noon and early afternoon.

567 The model cannot reproduce the observed variations of acetone. The acetone peak at  
568 noon was probably attributed to some temperature-related emissions (e.g. solvent  
569 evaporation). As direct emissions of acetone have not always kept pace with CO, the  
570 primary acetone derived from the ER expressed by acetone/CO cannot explain it.

571 Besides combustion sources, in urban areas acetone also directly comes from solvent  
572 usage and evaporation, particularly in chemical processing procedures. So, it needs  
573 to find a slightly reactive or inert species to work as an indicator of non-combustion  
574 sources of acetone. CO and acetylene are frequently used as reference compounds in  
575 ERs, while they come most from automobile exhaust and fuel combustion, seldom  
576 observed in solvent usage. Other relatively inert VOCs such as ethane and propane  
577 show more variable emission ratios for different sources, so they are also not suitable  
578 to be a unique tracer for non-combustion sources. Thus, more detailed measurements  
579 on emission characteristics of acetone sources need to be investigated in further  
580 studies.

581 In summary, the box model overestimated the concentrations of aldehydes by a

582 factor of 1.4-1.7 without considering the uptake by aerosols. This discrepancy is  
583 mainly attributed to missing sinks, such as vertical dilution, transport and  
584 heterogeneous uptake on aerosols. In the presence of fresh emissions, the box model  
585 predicted the concentrations and variations of MEK well, but it cannot explain  
586 observed acetone, likely to be affected by unidentified primary emissions or high  
587 backgrounds. Despite the existence of drawbacks on estimation of sinks, the box  
588 model still can give an overview of the relative importance of different precursors on  
589 the production of secondary OVOCs. It also can be used as a tool to quantify the  
590 relative changes in OVOCs production due to the reduced precursors and other  
591 pollutants during the emission control period.

### 592 **4.3. Secondary production of OVOCs**

593 Fig.8a-c illustrates averaged diurnal variations of the production of formaldehyde,  
594 acetaldehyde and acetone from different groups of NMHCs in M2 during the full  
595 control period. As a average, the photooxidation of alkenes contributed most to  
596 secondary HCHO production with a percentage of 54%, followed by the oxidation of  
597 isoprene (30%) and aromatics (15%), the contributions of pinenes and alkanes were  
598 negligible (<1%). The contributions of C<sub>2</sub>-C<sub>4</sub> alkenes and isoprene were  
599 well-matched, accounting for 39.7% and 37.5% of the total of averaged HCHO  
600 production, respectively (listed in Table S4).

601 For acetaldehyde production, it was found to be dominantly through alkenes  
602 oxidation (91%), and the contributions of alkanes and aromatics were minor (7% and  
603 1%, respectively). Usually the dominant secondary CH<sub>3</sub>CHO source is from alkane

604 oxidation (ethane, n-butane, i-butane) via the reaction of  $C_2H_5O_2$  peroxy radical  
605 (Carter, 1990;Sommariva et al., 2008). But Sommariva et al. (2011) found that in  
606 urban plumes in northeastern US propene and other alkenes significantly contributed  
607 to the formation of acetaldehyde via the reaction of *HYPROPO* alkoxy radical,  
608 especially in more fresh air masses for the first two days, their contribution to  
609 acetaldehyde production is more important (up to 25%). Then the role of C3-C5  
610 alkenes decreases very quickly because of their high reactivity. Compared to urban  
611 plumes in U.S., air masses in Beijing are much more fresh and close to the emission  
612 sources. From Fig.4, we can see that the majority of photochemical ages of air  
613 masses during the campaign are smaller than 40 hr, i.e. within two days. In this case,  
614 alkene oxidations become the most important processes for  $CH_3CHO$  formation.  
615 For acetone, 60% of its production was from alkenes, 29% from alkanes, 10% from  
616 pinenes, and the resting 1% was attributed to aromatics and isoprene. Secondary  
617 MEK was predominantly produced from the oxidation of alkanes (>95%). The  
618 averaged results show that the oxidation of anthropogenic precursors is the dominant  
619 production pathway for secondary OVOCs in Beijing.

620 The NMHCs oxidation for all OVOC compounds displays an obvious diurnal pattern  
621 with a peak at noon. Table 4 summarizes the averaged production rates and  
622 corresponding percentages of HCHO from different NMHCs groups. For the full  
623 control period (M4), the pathway of isoprene oxidation accounted for up to 40% of  
624 the total production in the daytime, comparable to that of anthropogenic alkenes  
625 (46%). And the rests (13%) of HCHO production was attributed to aromatics. The

626 contribution of biogenic source decreased to 23% during the night, accordingly  
627 anthropogenic source became the dominant contributor to HCHO production with a  
628 combined percentage of 76% (alkenes + aromatics). The differences in contributions  
629 between day and night are closely related to different diurnal patterns of  
630 anthropogenic and biogenic NMHCs.

#### 631 **4.4. Changes in OVOCs responding to the control measures**

632 As indicated above, ambient concentrations of NMHCs were decreased by 30-45%  
633 due to cutting the city's emissions from 21 July to 27 August. Here, the effect of the  
634 reduced precursors together with other gas pollutants (CO, NO, NO<sub>2</sub> and O<sub>3</sub>) on  
635 secondary OVOCs has been estimated using the box model.

636 Since the whole group of NMHCs were not measured by online GC-MS before the  
637 full control (3-20 July), the model scenario M5 ran with increased concentrations of  
638 alkanes, alkenes, aromatics and isoprene by 30%, 35%, 40% and 15%, respectively,  
639 according to the results from this work and a previous study on NMHCs by Wang et  
640 al. (2010a), in order to simulate the situation of the uncontrolled period. The  
641 concentrations of NO, NO<sub>2</sub> and CO in M5 were increased by 35%, 25% and 17%,  
642 while O<sub>3</sub> was decreased by 16%, taken from the observed changes in Wang et al.  
643 (2010c) and Chou et al. (2011). Then, the relative changes of secondary OVOCs  
644 responding to the control measures were determined by the difference between the  
645 model scenario of M5 (the uncontrolled period) and M4 (the full control period).  
646 The modelled reductions in HCHO, CH<sub>3</sub>CHO and MVK+MACR from M5 to M4

647 agree quite well with the corresponding results from the MLP network (given in  
648 Table 5), suggesting the measurable changes of those three species can be reasonably  
649 represented by the photochemical production from the oxidation of reduced  
650 precursors in the box model. For MEK, the relative change from box model is 3.7%  
651 lower than the MLP results, likely related to the uncertainty of primary emissions.  
652 However, it is found a large discrepancy of acetone changes in the two methods. The  
653 modelled changes (12.8%) of acetone were much larger than MLP result (1%). As  
654 discussed in section 3.2, there is no significant change in measured acetone during  
655 the full control period probably due to high backgrounds in the region. The change  
656 (12%) of secondary production of acetone estimated by the model is relatively less  
657 important compared to transport in Beijing, it was covered by the high levels of  
658 acetone from neighboring region. It seems to be difficult for the box model to  
659 evaluate such effect of background or transport.

660 The HCHO production rates from most of the precursors have been lowered during  
661 the full control period, but the ranks of different precursors didn't change much,  
662 details listed in Table S4. Due to the emission restrictions the total production rate of  
663 HCHO decreased from 7.50 to 6.75 ppbh<sup>-1</sup>, and the daytime production of HCHO  
664 from the oxidation of alkenes, aromatics and isoprene were reduced by 13%, 12%  
665 and 6%, respectively (from Table 5). The relative contribution of alkene oxidations  
666 in the daytime was decreased by 1.5% from the uncontrolled days (M5) to the full  
667 control period (M4), and accordingly the contribution of isoprene was increased by  
668 1.7%. Here, it should be aware that the relative importance of isoprene chemistry has



669 been enhanced when the NMHCs precursors from anthropogenic sources were  
670 reduced by 30-40%. This would affect the relative potentials of reactive NMHCs for  
671 the formation of secondary pollutants (such as OVOCs and ozone).

## 672 **5. Conclusion**

673 In the summer of 2008 the pollution control measures implemented in Beijing  
674 provides a unique opportunity for studying how the primary and secondary air  
675 pollutants react to the reductions of anthropogenic emissions. Using a neural  
676 network analysis, we concluded that the emission controls taken in Beijing had a  
677 notable effect on reducing the ambient concentrations of formaldehyde, acetaldehyde,  
678 MEK and methanol. The influence of emission restrictions on OVOCs (except  
679 acetone) was found to be statistically significant when the variations due to  
680 meteorological conditions have been excluded by the MLP network analysis.  
681 However, the effect of local emission controls on acetone seems to have been  
682 submerged in high background levels, and no obvious changes were detected in  
683 acetone during the full control period. This highlights the complexity of secondary  
684 air pollutants (like OVOCs and O<sub>3</sub>), which needs to be treated as a regional issue.  
685 The chemical production and degradation of OVOCs in Beijing under the emission  
686 controlled conditions have been determined quantitatively using a box model  
687 constrained with measurements of OVOCs precursors, gas pollutants and other  
688 physical parameters. The most important precursor of HCHO is isoprene, accounting  
689 for 30% of the total HCHO production. While, as a whole, anthropogenic source is  
690 still the main contributor to secondary HCHO formation, with alkene oxidation

691 accounting for 54% and aromatics for 15%. Unlike HCHO, anthropogenic NMHCs  
692 were found to play predominant roles on the chemical production of acetaldehyde,  
693 acetone and MEK. Approximately 90% of acetaldehyde production can be attributed  
694 to the oxidation of alkenes. Anthropogenic alkenes and alkanes contributed 60% and  
695 29% of acetone formation, respectively; and biogenic precursors (pinenes)  
696 contributed the rest 10%. The relative changes in the modelled aldehydes and  
697 MVK+MACR due to the emission restrictions are shown to be consistent with the  
698 estimated results from the neural network, reflecting that the current chemical  
699 mechanisms can largely represent the realistic formation processes of aldehydes and  
700 MVK+MACR in the high NO<sub>x</sub> urban conditions.

701 Compared to measurements of OVOCs, the box model overestimated the measured  
702 aldehydes by a factor of 1.4-1.7 without taking consideration of their loss on  
703 aerosols, while it was able to roughly explain diurnal variations of acetaldehyde for  
704 most of time. The model-measurement discrepancy for aldehydes is mostly caused  
705 by missing sinks in the model, including physical dilution, transport and  
706 heterogeneous processes on the surface of aerosols. After adding the primary  
707 concentrations of ketones to the box model, the concentrations and diurnal cycles of  
708 MEK can be well represented by the model simulations. But the modelled changes  
709 of acetone become unimportant, due to high background and transport of acetone in  
710 Beijing and its surrounding areas

711 The analysis of the summer 2008 situation in Beijing improves our understanding of  
712 the complicated relationship between anthropogenic emissions and pollution levels

713 of primary and secondary VOCs. The concentrations of NMHCs were reduced by  
714 30-40% due to the emission controls. As vehicular emissions is the most important  
715 emitter of VOCs in the city, the emission ratios of the traffic-related species ( $C_2$ - $C_3$   
716 alkenes and light aromatics) in the controlled days are found to be fairly similar to  
717 the values before the controls and other urban areas. The relatively similar emission  
718 ratios for above hydrocarbons in cities will help to provide a general idea of the  
719 photochemical evolution of gas-phase organic carbons in urban plumes based on  
720 model simulations. As China is currently in the midst of a sustained effort to improve  
721 air quality in megacities, the results presented in this study can be served as a case  
722 for further understanding of the atmospheric chemistry not only for Beijing but also  
723 for large regions, and it is also important for aiding policymakers in considering  
724 ways to reduce pollution more efficiently in the long term.

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## Table captions

Table 1. Summary of meteorological parameters at PKU site before and during the full control (average  $\pm 1\sigma$  s.d.)

Table 2. Comparison of the observed and predicted values of median  $\ln(\text{VOC})$  and their corresponding concentrations during the full control period, and the deviations between observed and predicted concentrations, together with the outputs from Student's T-test for the two datasets, where  $P(t) < 0.05$  implies that the difference in the two datasets is statistically significant at the confidence level of 95%.

Table 3. Model scenarios performed in OVOC simulations during the CAREBEIJING 2008

Table 4. The average of production rates and corresponding percentages of formaldehyde from different precursors in the model simulations for the full control period (M4) and the scenario without the control measures (M5). All the values are presented in "average $\pm$ s.d."

Table 5. The average of relative changes in OVOCs concentrations from the scenario without pollution control measures (M5) to the control period (M4), compared to the corresponding values from MLP network. Modelled change  $\% = (M2 - M3) / M3 * 100.0$

## Figure captions

Fig. 1. 10min-average diurnal variations of several NMHCs and OVOCs measured by PTR-MS at PKU site before (1-20 July, blue) and during the full control (21 July-27 August, red), respectively. (a) benzene; (b) toluene; (c) styrene; (d) C8-aromatics; (e) C9-aromatics; (f) C10-aromatics; (g) isoprene; (h) MVK+MACR; (i) formaldehyde; (j) acetaldehyde; (k) acetone; (l) MEK. The error bars represent standard deviations for those compounds before (blue) and during the full control (red)

Fig. 2. Probability density distribution of the observed  $\ln(\text{VOC})$  (red) and the predicted values (blue) before the full control (left column) and after the full control (right column) for NMHCs species: a-b) Benzene, c-d) Toluene, e-f) C8-aromatics, g-h) Acetonitrile.

Fig. 3. Probability density distribution of the observed  $\ln(\text{VOC})$  (red) and the predicted values (blue) before the full control (left column) and after the full control (right column) for OVOCs species: a-b) Methanol, c-d) HCHO, e-f) Acetaldehyde, g-h) MEK.

Fig. 4. The ratios of toluene/ $\Delta\text{CO}$  (a) and m,p-xylene/ $\Delta\text{CO}$  (b) versus the photochemical age of the sampled air mass in Beijing for Aug 2008 (pink) and Aug 2005 (blue).

Fig. 5. Comparison of the emission ratios (ERs) of NMHCs relative to CO in the 2008 and 2005 summer at PKU site, where each point represents one compounds and different colors indicate the classes of NMHCs. The black line represents 1:1 line and

the shaded area shows the agreements within a factor of 1.5.

Fig. 6. 30min-average modelled and measured (or calculated) concentrations of (a) OH radical, (b) HCHO, (c) Acetaldehyde, (d) MVK+MACR, (e) Acetone and (f) MEK plotted as diurnal patterns from 26 July to 27 Aug. The dashed black lines with solid dots indicates measured (or calculated) data, grey areas show one standard deviation from the averaged values. The dash-dotted yellow lines, dashed green lines, dash-dotted blue lines and solid magenta lines represent the modelled concentrations by simulation M1, M2, M3 and M4, respectively

Fig. 7. Partitioning of MEK to primary emissions (yellow area) and secondary chemical formation (green area) at PKU site, and the dashed black lines with solid dots represents measured concentrations

Fig. 8. Averaged production of (a) formaldehyde, (b) acetaldehyde and (c) acetone during the full control period in the simulation of M4

Table 1. Summary of meteorological parameters at PKU site before and during the full control (average  $\pm 1\sigma$  s.d.)

Time period		T (°C)	RH (%)	Precipitation (mm)	WS (m/s)	UVA (w/m <sup>2</sup> )
Before the full control	Jul.3-Jul 20	28.9 $\pm$ 4.5	66.9 $\pm$ 20.0	0.04 $\pm$ 0.37	1.1 $\pm$ 0.9	6.6 $\pm$ 8.7
During the full control	Jul 21-Aug 27	28.0 $\pm$ 4.1	67.9 $\pm$ 17.5	0.05 $\pm$ 0.51	0.9 $\pm$ 0.8	5.3 $\pm$ 7.1

Table 2. Comparison of the observed and predicted values of median  $\ln([\text{VOC}])$  and their corresponding concentrations during the full control period, and the deviations between observed and predicted concentrations, together with the outputs  $P(t)$  from Student's T-test for the two datasets, where  $P(t) < 0.05$  implies that the difference in the two datasets is statistically significant at the confidence level of 95%.

	Median_ $\ln([\text{VOC}])$			Concentration (ppbv)		Deviation of concentrations	
	observation	prediction	$P(t)$	observation	prediction	(%)	R
Benzene	-0.23	0.25	0.00	0.79	1.28	-38.2	0.48
Toluene	0.24	0.63	0.00	1.27	1.88	-32.5	0.41
C8-aromatics	0.12	0.73	0.00	1.12	2.08	-46.0	0.44
C9-aromatics	-0.63	-0.17	0.00	0.53	0.84	-37.0	0.26
C10-aromatics	-1.70	-1.05	0.00	0.18	0.35	-47.5	0.32
Styrene	-2.11	-1.66	0.00	0.12	0.19	-36.5	0.22
Acetonitrile	-1.45	-1.46	0.72	0.23	0.23	0.4	0.36
HCHO	1.72	1.85	0.00	5.56	6.38	-12.9	0.45
Acetaldehyde	0.78	0.95	0.00	2.18	2.59	-15.8	0.52
Acetone	1.39	1.40	0.36	4.02	4.06	-1.0	0.36
MEK	-0.11	0.08	0.00	0.90	1.08	-17.0	0.64
Methanol	1.95	2.17	0.00	7.06	8.78	-19.6	0.31
Isoprene	-0.07	0.24	0.00	0.94	1.27	-26.6	0.55
MVK+MACR	-0.27	-0.15	0.00	0.76	0.86	-11.3	0.72

Table 3. Model scenarios performed in OVOC simulations during the CAREBEIJING 2008

Simulation	Description
M0	MCM3.2 mechanism, $\tau_D = 24\text{h}$ , the boundary layer height (BLH) was assumed to 1000m, i.e. $v_{\text{depo}} = 1.2 \text{ cms}^{-1}$ ;
M1	as M0, the variation of BLH was taken into consideration, $\tau_D = v_{\text{depo}}/\text{BLH}$ , and $v_{\text{depo}}$ was set to $1.2 \text{ cms}^{-1}$ as what was in M0;
M2	as M1, $\tau_D = v_{\text{depo}}/\text{BLH}$ , but $v_{\text{depo}}$ were different for calculated species, vertical dilution rates ( $\lambda_{\text{dil,vert}}$ ) were added, $\lambda_{\text{dil,vert}} = \max\left(0, \frac{1}{H(t)} \frac{dH(t)}{dt}\right)^{[1]}$ ;
M3	as M2, uptake of formaldehyde and acetaldehyde by aerosol were included, i.e. $\frac{dC}{dt} = -\frac{\gamma \times S_{RH} \times v \times C}{4}$ , $\gamma$ , $S_{RH}^{[2]}$ , $v$ represent uptake coefficient, RH corrected aerosol surface concentration, and molecular velocity, respectively; here assumed $\gamma = 10^{-3}$ for HCHO and CH <sub>3</sub> CHO;
M4	as M3, using emission ratios of OVOCs relative to CO ( $ER_{\text{OVOC}}$ ) and measured CO, the primary aldehydes and ketones were added to the model run;
M5	as M4, the concentrations of NMHCs, CO, NO <sub>x</sub> , O <sub>3</sub> were increased in order to simulate the scenario without traffic restrictions.

<sup>[1]</sup> Vertical dilution rates were determined by the method used in Riemer et al. (2009)

<sup>[2]</sup>  $S_{RH}$  is the RH corrected aerosol surface concentration, it was estimated by an empirical function: i.e.  $S_{RH} = f(RH) \times S_{\text{dry}} = (1 + a \times RH^b) \times S_{\text{dry}}$ . Here a and b were set to 4.34 and 6.72, respectively, taken from Liu et al. (2013);  $S_{\text{dry}}$  was from SMPS measurement during the campaign.



Table 4. The average of production rates and corresponding percentages of formaldehyde from different precursors in the model simulations for the full control period (M4) and the scenario without the control measures (M5). All the values are presented in “average±s.d.”.

	<u>9:00 -17:00 LT</u>		<u>18:00 - 8:00 LT</u>	
	M4	M5	M4	M5
P <sub>alkanes</sub> (ppbh <sup>-1</sup> )	0.01 ±0.00	0.01 ±0.00	0.00 ±0.00	0.00 ±0.00
P <sub>alkenes</sub> (ppbh <sup>-1</sup> )	3.08 ±1.65	3.53 ±1.93	0.75 ±0.72	0.87 ±0.82
P <sub>aromatics</sub> (ppbh <sup>-1</sup> )	0.88 ±0.50	1.00 ±0.58	0.20 ±0.18	0.23 ±0.20
P <sub>isoprene</sub> (ppbh <sup>-1</sup> )	2.77 ±1.76	2.95 ±1.97	0.35 ±0.45	0.37 ±0.48
P <sub>pinenes</sub> (ppbh <sup>-1</sup> )	0.01 ±0.01	0.01 ±0.01	0.01 ±0.01	0.01 ±0.01
P <sub>total</sub> (ppbh <sup>-1</sup> )	6.75 ±3.68	7.50 ±4.22	1.31 ±1.32	1.47 ±1.46
P <sub>alkanes</sub> (%)	0.1 ±0.1	0.1 ±0.1	0.2 ±0.2	0.2 ±0.2
P <sub>alkenes</sub> (%)	46.5 ±8.1	48.0 ±8.3	59.2 ±5.5	60.3 ±5.5
P <sub>aromatics</sub> (%)	13.2 ±1.9	13.3 ±2.0	16.8 ±2.6	16.7 ±2.7
P <sub>isoprene</sub> (%)	40.0 ±8.5	38.4 ±8.6	23.1 ±6.2	22.1 ±6.0
P <sub>pinenes</sub> (%)	0.2 ±0.1	0.1 ±0.1	0.8 ±0.6	0.6 ±0.5

Table 5. The average of relative changes in OVOCs concentrations from the scenario without pollution control measures (M5) to the control period (M4), compared to the corresponding values from MLP network. Modelled change  $\% = (M2 - M3) / M3 * 100.0$

Compounds	Reduction from MLP %	Modelled changes (%) average $\pm$ s.d.
Formaldehyde	-12.9	-11.1 $\pm$ 2.4
Acetaldehyde	-15.8	-15.1 $\pm$ 1.9
MVK+MACR	-11.3	-12.0 $\pm$ 3.6
Acetone	-1.0	-12.8 $\pm$ 1.4
MEK	-17.0	-13.3 $\pm$ 0.1
OH		11.2 $\pm$ 5.5
HO <sub>2</sub>		22.3 $\pm$ 8.1

Fig. 1. 10min-average diurnal variations of several NMHCs and OVOCs measured by PTR-MS at PKU site before (1-20 July, blue) and during the full control (21 July-27 August, red), respectively. (a) benzene; (b) toluene; (c) styrene; (d) C8-aromatics; (e) C9-aromatics; (f) C10-aromatics; (g) isoprene; (h) MVK+MACR; (i) formaldehyde; (j) acetaldehyde; (k) acetone; (l) MEK. The error bars represent standard deviations for those compounds before (blue) and during the full control (red).

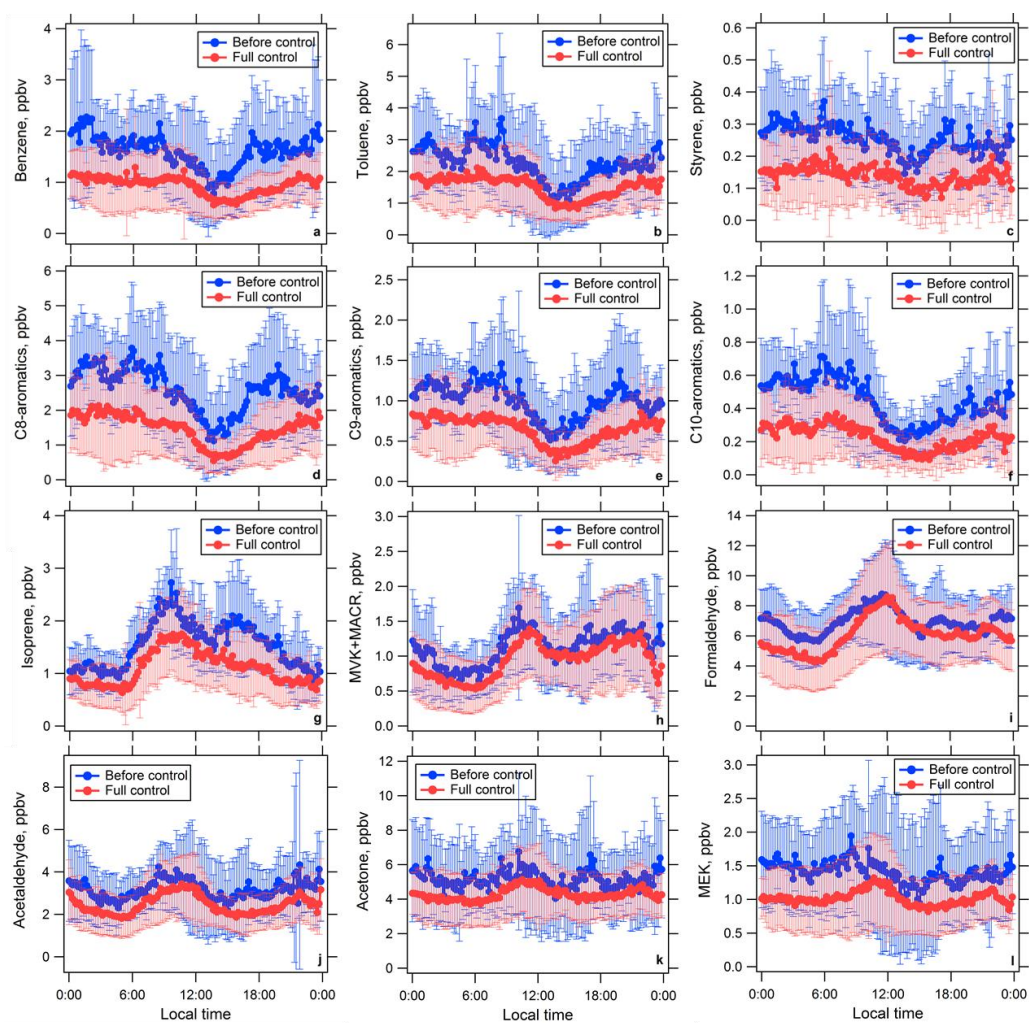


Fig. 2. Probability density distribution of the observed  $\ln(\text{VOC})$  (red) and the predicted values (blue) before the full control (left column) and after the full control (right column) for NMHCs species: a-b) Benzene, c-d) Toluene, e-f) C8-aromatics, g-h) Acetonitrile.

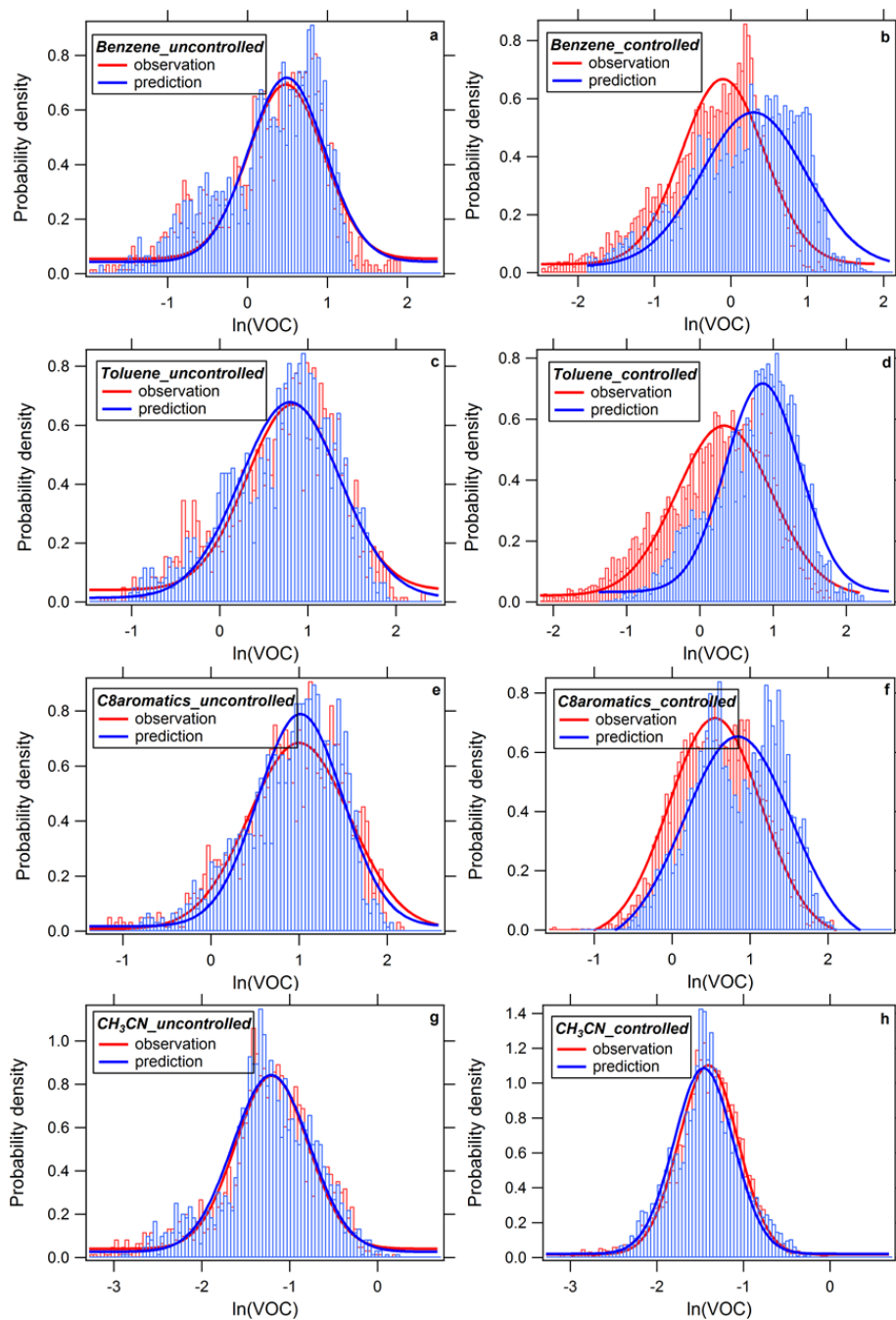


Fig. 3. Probability density distribution of the observed  $\ln(\text{VOC})$  (red) and the predicted values (blue) before the full control (left column) and after the full control (right column) for OVOCs species: a-b) Methanol, c-d) HCHO, e-f) Acetaldehyde, g-h) MEK.

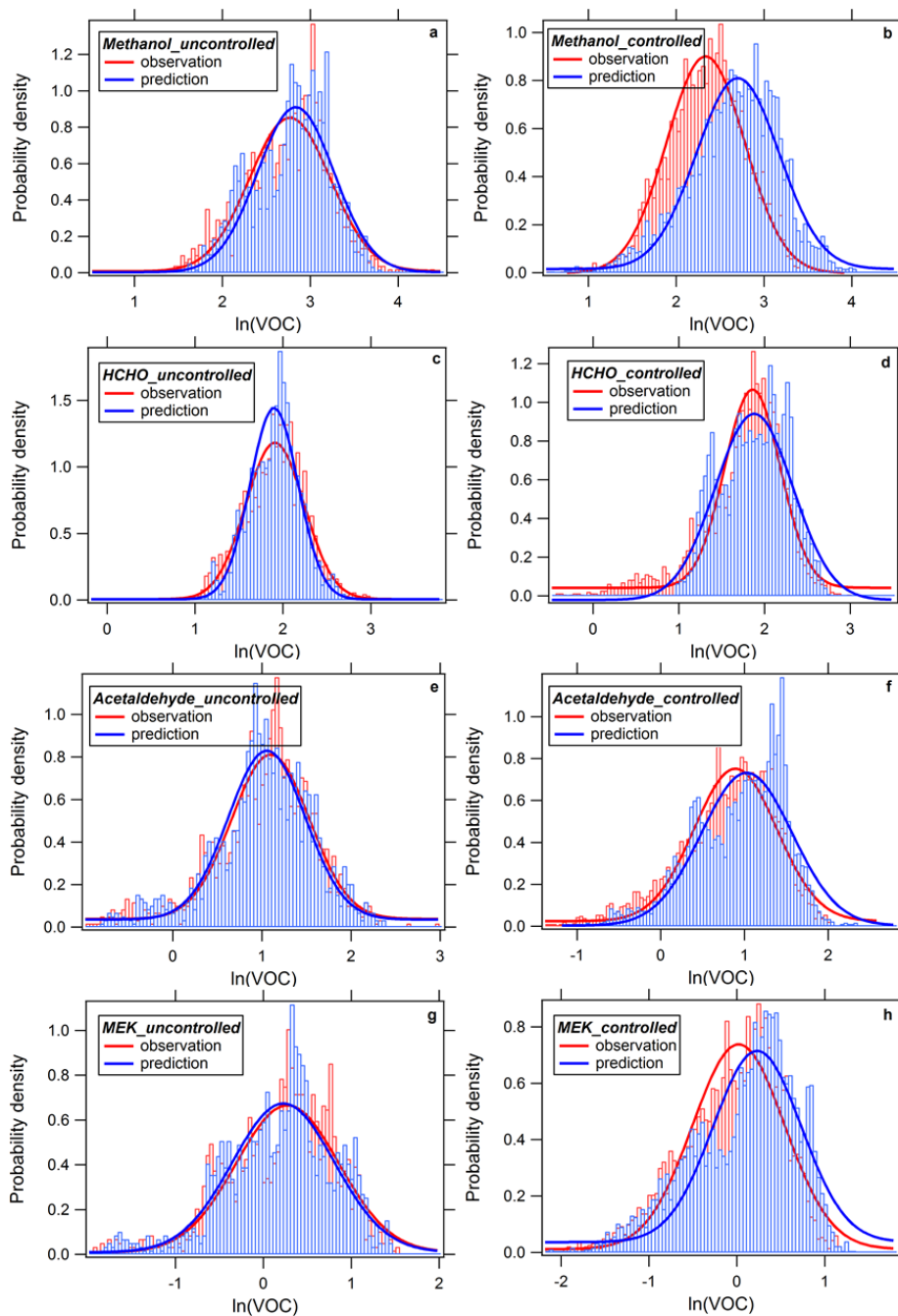


Fig. 4. The ratios of toluene/ $\Delta$ CO (a) and m,p-xylene/ $\Delta$ CO (b) versus the photochemical age of the sampled air mass in Beijing for Aug 2008 (pink) and Aug 2005 (blue).

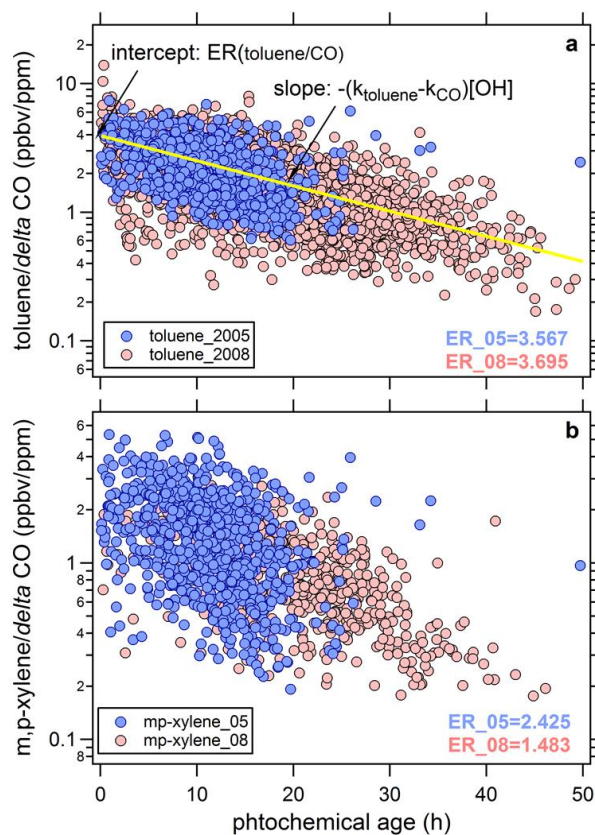


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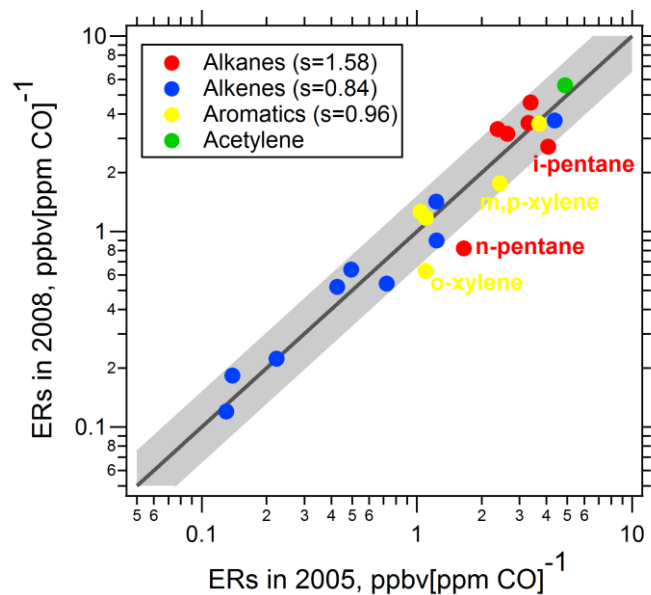


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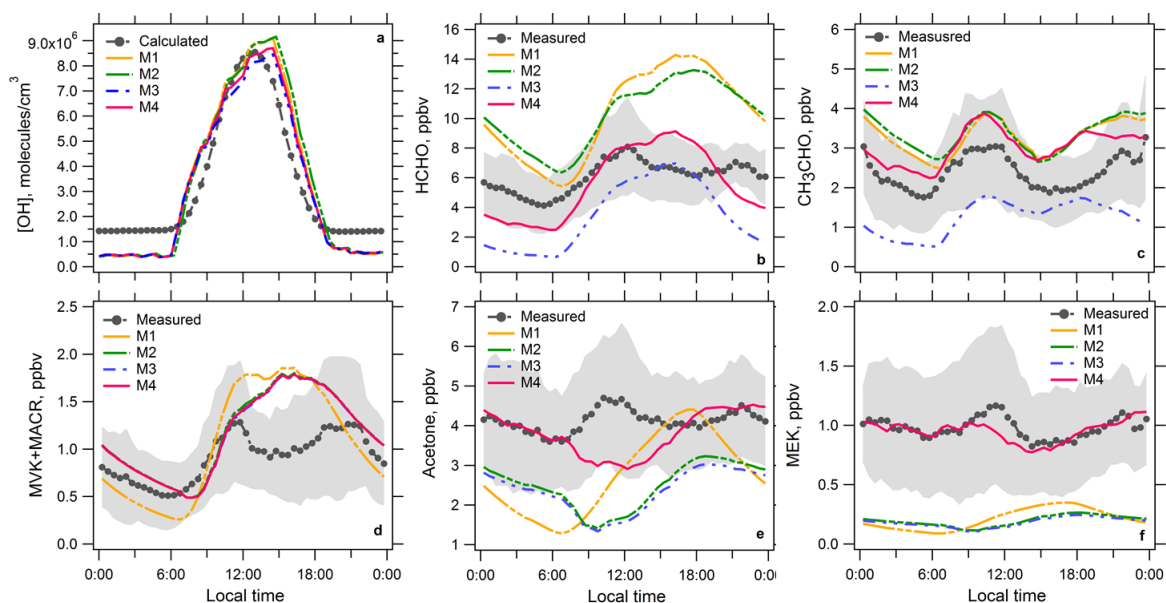




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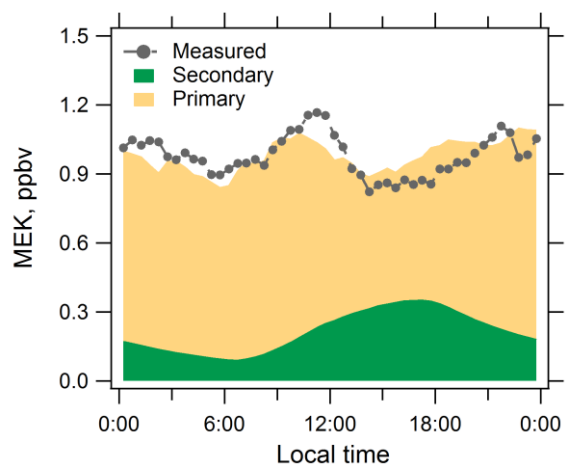


Fig. 8. Averaged secondary production of (a) formaldehyde, (b) acetaldehyde and (c) acetone during the full control period in the simulation of M4

