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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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Abstract

Oxygenated volatile organic compounds (OVOCs) are important products of the photo-oxidation of hydrocarbons. They influence the oxidizing capacity and the ozone forming potential of the atmosphere. In the summer of 2008 two months' emission restrictions were enforced in Beijing to improve air quality during the Olympic Games. Observation evidence has been reported in related studies that these control measures were efficient in reducing the concentrations of primary anthropogenic pollutants (CO, NO_x and non-methane hydrocarbons, i.e. NMHCs) by 30–40 %. In this study, the influence of the emission restrictions on ambient levels of OVOCs was explored using a neural network analysis with consideration of meteorological conditions. Statistically significant reductions in formaldehyde (HCHO), acetaldehyde (CH_3CHO), methyl ethyl ketone (MEK) and methanol were found to be 12.9, 15.8, 17.1 and 19.6 %, respectively, when the restrictions were in place. The effect of emission control on acetone was not detected in neural network simulations, probably due to pollution transport from surrounding areas outside Beijing. Although the ambient levels of most NMHCs were decreased by ~ 35 % during the full control period, the emission ratios of reactive hydrocarbons attributed to vehicular emissions did not present obvious difference. A zero-dimensional box model based on Master Chemical Mechanism version 3.2 (MCM3.2) was applied to evaluate how OVOCs productions respond to the reduced precursors during the emission controlled period. On average, secondary HCHO was produced from the oxidation of anthropogenic alkenes (54 %), isoprene (30 %) and aromatics (15 %). The importance of biogenic source for the total HCHO formation was almost on a par with that of anthropogenic alkenes during the daytime. Anthropogenic alkenes and alkanes dominated the photochemical production of other OVOCs such as acetaldehyde, acetone and MEK. The relative changes of modelled aldehydes, methyl vinyl ketone and methacrolein (MVK + MACR) before and during the pollution controlled period were comparable to the estimated reductions in the neural network, reflecting that current mechanisms can largely explain secondary production of those species under urban

conditions. However, it is worthy to notice that the box model overestimated the measured concentrations of aldehydes by a factor of 1.4–1.7, and simulated MEK was in good agreement with the measurements when primary sources were taken into consideration. These results suggest that the understanding of OVOCs budget in the box model remains incomplete, there is still considerable uncertainty in particular missing sinks (unknown chemical reactions and physical dilution processes) for aldehydes and absence of direct emissions for ketones.

1 Introduction

Oxygenated Volatile Organic Compounds (OVOCs), such as aldehydes, ketones and alcohols, are mostly produced in the atmosphere by the oxidation of biogenic, anthropogenic hydrocarbons and other organic species (Finlayson-Pitts and Pitts, 2000), and also directly emitted by vegetation (Park et al., 2013), biomass burning (Yokelson et al., 2009; Mason et al., 2001; Andreae and Merlet, 2001), fossil fuel combustion (Schauer et al., 1999, 2002) and industries (Singh et al., 1994). They are lost through oxidation by OH, photolysis, and deposition/surface uptake. Aircraft measurements showed that the vertical distribution (0–12 km) of the total concentrations of oxygenated organics was 2–5 times as abundant as the sum of C_2–C_8 non-methane hydrocarbons (NMHCs) at all altitudes in the remote Pacific troposphere (Singh et al., 2001). Formaldehyde (HCHO) and other oxygenated hydrocarbons dominated the total OH loss with VOCs in clean air masses (Goldan et al., 2004). In polluted atmospheres the interaction of primary and secondary VOCs is closely coupled with the formation of ozone and secondary organic aerosols (SOA), OVOCs serve as intermediate products in these oxidation processes, which helps to estimate the formation potential of ozone (Shao et al., 2011) and other products. And OVOCs also affect the oxidizing capacity of the atmosphere. Some previous studies found that carbonyls are one of important radical sources, especially for the wintertime in polluted urban environments (Emmerson et al., 2005). Accordingly, it is essential to understand the sources, sinks and chemistry of OVOCs quantitatively. While the role of OVOCs in heavily polluted regions remains largely unexplored, partly due to the lack of reliable observations of them.

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

After Beijing was selected as the host of the 2008 Summer Olympics, the Beijing government started to implement a series of long-term control regulations on pollution emissions, such as the closure of heavy polluting industries (chemical factories, cement plants, steel manufacturing etc.) in the southeast of the city, relocating nearly 200 factories out of the Beijing area; also tightening vehicle emission and fuel quality standards, and accelerating retirements of old vehicles. More stringent, short-term measures were put into effect from 1 July to 20 September 2008, such as temporarily halting industrial production, suspending construction and evaporative emissions. Great efforts of transport sector were stepped up to get nearly 2 million vehicles off the roads (UNEP, 2009), which included that (1) a total of 350 000 yellow-labeled vehicles with high emission were not allowed to enter the city starting from 1 July, (2) 50 % of privately owned vehicles were restricted to run on alternate days (based on their license plate numbers) in the metropolis and 70 % of government-owned vehicles were halted from operating from 21 July to 20 September, which is so called "full control period". As a result, the traffic emissions on VOCs, CO, NO_x, and particulate matter (PM) were estimated to be reduced by 50 % (S. X. Wang et al., 2010).

The two months' emission restrictions had a noticeable impact on ambient concentrations of pollutants directly emitted from fuel combustions, which have been validated by on-road measurements (M. Wang et al., 2009; Wang and Xie, 2009; X. Wang et al., 2009) and ground-based observations (B. Wang et al., 2010, T. Wang et al., 2010; Chou et al., 2011). The results from on-road mobile measurements showed a dramatically decrease of primary pollutants, by up to 54 % for CO, 41 % for NO_x and 66 % for aromatics (benzene, toluene, ethylbenzene and xylenes, BTEX) (M. Wang et al., 2009). Compared with the concentrations measured in June (before the restrictions), the averaged mixing ratios of NMHCs were reduced by 35 % during the Games (B. Wang et al., 2010). The monthly concentrations of NO, NO_2 and CO were decreased by 76.8, 29.7 and 27.8 % in August 2008 compared to the measurements in the same month of 2006 (Chou et al., 2011). In contrast, the observed mixing ratio of O_3 near the Olympic Stadium increased by 16 % during the full control, compared to the period prior to 20 July (T. Wang et al., 2010). The higher levels of ozone were influenced by the declined O_3–NO titration and the shift in different O_3 formation regimes (Chou et al., 2011), changes in weather conditions, or/and by the transport of photochemical plumes from the surrounding areas to Beijing (T. Wang et al., 2010). So, the influence of the control measures on secondary pollutants still needs more investigation.

The limited OVOCs datasets available in Beijing suggest that the ambient levels of carbonyls were observed to be 3–5 times higher than the levels in Hong Kong, about 35 % of those in Mexico City (Pang and Mu, 2006), and comparable to those in Rio de Janeiro, Brazil (Grosjean et al., 2002). In summer, about 60–70 % of aldehydes in Beijing were associated to the photochemical oxidation of anthropogenic and biogenic VOCs, and 10–15 % of them were attributed to the primary emission from anthropogenic sources (Liu et al., 2009). For ketones and alcohols, anthropogenic primary emission was shown to be the largest contributor (Liu et al., 2009; Yuan et al., 2012). The 2008 summer provides the opportunity to estimate the impact of reduced emissions on ambient levels of OVOCs. In this study, firstly a neural network approach was used to link VOCs mixing ratios to meteorological conditions, which helps to ascertain that the observed changes in VOCs are significant due to the emission restrictions, rather than random variations caused by different meteorological conditions. Secondly, a box model using the Master Chemical Mechanism (MCM) was employed to investigate secondary formation of OVOCs during the full control period, in particular, of two most abundant aldehydes (formaldehyde, acetaldehyde), two ketones (acetone and MEK) and unique oxidation products of isoprene chemistry (MVK + MACR). Moreover, this study also aims to quantify the changes of secondary OVOCs by the existing mechanisms, responding to the reduced precursors (NMHCs) and other pollutants (CO, NO, NO_2, O_3), and to analyze the similarity or discrepancy between the measured and modelled changes in OVOCs before and during the full control.

2 Methodologies

2.1 Monitoring sites and experimental methods

As part of the CAREBEIJING-2008 campaign, the measurements of VOCs and other air pollutants (CO, NO_X, O_3 et al.) were conducted at an intensive observation site on the campus of Peking University (PKU) from 3 July to 27 August 2008. The PKU site (39.99° N, 116.31° E) was located in the northwestern of downtown Beijing, which has been considered to be representative of a typical urban environments with different mixtures of high density traffic, commercial, residential, and electronic companies (Liu et al., 2009; Cheng et al., 2008; Song et al., 2007). The air inlets for the instruments were set up on the top of a six-story building (~ 25 m above the ground level).Three online techniques were used to quantify NMHC and OVOC species during the campaign, including a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS), a gas chromatograph with mass spectrometer and flame ionization detector (GC-MS/FID) and a Hantzsch fluorimetric monitor.

2.1.1 Online measurements for NMHCs and OVOCs

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

The operating parameters of PTR-MS used herein are similar to those described previously in Yuan et al. (2010a). The instrument was operated at 2.3 mbar drift tube pressure and 600 V drift voltage, 35 masses were sampled with the time resolution of 160 s. Instrument background signals were measured every 35 cycles (~ 1.5 h) by switching the sample air to an activated charcoal trap for 5 cycles (~ 13 min). Target ions with the dwell time of 5 s each cycle included OVOCs such as methanol ($m/z = 33$), acetaldehyde ($m/z = 45$), acetone ($m/z = 59$), MVK + MACR ($m/z = 71$), methyl ethyl ketone (MEK, $m/z = 73$); Aromatics such as benzene ($m/z = 79$), toluene ($m/z = 93$), styrene ($m/z = 105$), C8 aromatics ($m/z = 107$) and C9 aromatics ($m/z = 121$); isoprene ($m/z = 69$) and acetonitrile ($m/z = 42$). The PTR-MS was calibrated every week using a commercial TO15 VOCs standard (Air Environmental Inc. Denver, US) at seven concentration levels ranging from 1 to 15 ppb. For most of species, the detection limits were between 23 and 60 pptv, except methanol (141 pptv), acetone (148 pptv) and MEK (110 pptv). The relative errors of the PTR-MS measurements decrease with the mixing ratios of target species, as shown in the Supplement Fig. S1, and the precisions of all detected species were below 5 % at the level of 1 ppbv.

An automated GC-MS/FID system with two-column and two-detector was deployed by Research Center for Environmental Changes (RCEC) Academia Sinica, Taiwan, which was used to measure C_2–C_4 hydrocarbons and C_5–C_{11} hydrocarbons simultaneously. Technical details for this instrument were presented in Chou et al. (2011). A total of 65 NMHCs were quantified hourly during the full control period (24 July through 27 August), the precision for most of the species was within 2 % and the limits of detection were below 30 pptv.

The comparison between the PTR-MS and GC-MS data showed a good agreement for aromatics (benzene, toluene, C_8 aromatics and C_9 aromatics) during the campaign, as shown in Fig. S2a in the Supplement, with the slopes varying between 0.86 and 1.21 and the correlation coefficients larger than 0.89. The isoprene data measured by the PTR-MS were systematically higher than that measured by GC-MS, in particular the mixing ratios lower than 1 ppbv, shown in Fig. S2b, possibly because the signals at m/z 69 were influenced by some interferences from pentanal, methyl butanal and pentenol (de Gouw et al., 2003), and alkyo cyclohexanes (Yuan et al., 2014). The isoprene data from the GC-MS is used in the following model calculations.

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

2.1.2 Measurements for other air pollutants and parameters

A comprehensive set of instruments was installed at the PKU site to monitor the air quality. CO was measured by a nondispersive infrared sensor (NDIR) with an integration time of 1 min (48CTLE, Thermo Environmental Instruments, TEI, USA). Zero calibrations were done every two hours and span calibrations were performed at midnight (0:00–1:00 a.m.) each day during the campaign. Ozone was measured by a UV absorption detector (Model 49i, TEI). NO was measured using a NO/O_3 chemiluminescence analyzer (Model 42iTL, TEI), with the instrument sequentially measuring NO_2 through a photolytic converter.

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

A meteorological station was operated simultaneously to monitor meteorological parameters (temperature, RH, pressure, wind speed and wind direction) on the campus, which was about 400 m away from the air quality intensive site. The photolysis frequencies of O^1D and NO_2 were measured at the PKU site by two filter radiometers (Bohn et al., 2008) with time resolution of 5 s, and the uncertainty of J values were within 10 %.

2.2 Methodology for neural network

The temporal variation of VOCs concentrations at a receptor site reflects a combination of changes in emission location and strength, meteorological conditions, chemical loss and secondary formation. Previous studies indicated that meteorological conditions, especially local wind speed and direction, played an important role in shaping the air quality of Beijing (Wu et al., 2008). We cannot quantify the influence of emission restrictions on ambient VOCs by simply comparing their levels during the control period with those before and after. Therefore, following the method introduced by Cermak and Knutti (2009), a feed-forward neural network was used to establish a statistical relationship between VOCs mixing ratios and meteorological parameters from the reference data (i.e. before the control period), and then to predict the concentrations given the meteorological conditions during the Games, if there was no restriction measures taken. Thus, the difference between the observed and predicted concentrations for VOCs is helpful to determine the effective changes due to the air quality measures.

The Multilayer Perceptron (MLP) Network in SPSS17.0 was used in this work. As the concentrations of VOCs displayed near log-normal distributions, the natural logarithm of VOC concentration, In([VOC]), was selected as the "dependent variable" of inputs in the MLP network, and the meteorological parameters as "covariates" of inputs, including wind vector (u, v, previous day u, previous v), precipitation, relative humidity, temperature and pressure. The observed data from 3 July to 20 July (before the full control) were used as the reference data ($n = 1611$) to set up a relationship between ln([VOC]) and meteorological parameters. 70 % of the reference data was chosen randomly as training sample to train the neural network, 20 % of the data as testing sample used to track errors during training in order to prevent overtraining, and the rest of data (10 %) as holdout sample used to assess the final neural network for validation. The network contained one hidden layer, *Sigmoid* functions were chosen as the activation functions for hidden layer and output layer. Given that there was no statistically difference between the prediction and the corresponding observation for validation data, the same approach was used for predicting the concentrations of VOCs during 21 July through 27 August.

2.3 Model description for OVOC simulation

A zero-dimensional box model, which is similar to the one used by Lu et al. (2012) and Li et al. (2013), was employed in this work to examine the production of OVOCs under the influence of emission restrictions. The box model uses a subset of the MCM3.2 (available online at http://mcm.leeds.ac.uk/MCM) which contains fully explicit chemical mechanisms for 57 kinds of VOCs (including 7 oxygenated) plus CH_4 and CO. The model calculations were constrained by measured C_2–C_{11} NMHCs, CO, CH_4, O_3, NO, NO_2, HONO, and physical parameters (i.e., photolysis frequencies, water vapor, temperature, and pressure). The time step of the model calculation was set to 30 min. Here, 57 VOCs were measured by GC-MS/FID and PTR-MS included 20 C_2–C_{11} alkanes, 11 C_2–C_5 alkenes, 15 aromatics, acetylene, isoprene, pinenes, formaldehyde, acetaldehyde, methanol, acetone, MEK and MVK + MACR. The CH_4 concentration was assumed to 2.5 ppm taken from previous observations in Beijing (Su, 2003). The photolysis rates for O^1D and NO_2 were constrained with the measured values at the site. The photolysis rates for HONO, aldehydes and ketones were calculated by the model for clear sky conditions and then scaled by the measured $J(\mathrm{NO_2})$ (Saunders et al., 2003). Dry deposition rate for all modelled species was set to 1.2 cm s^{-1} by assuming a well-mixed boundary layer with a height of 1000 m, corresponding to a lifetime (τ_D) of 24 h. Several model scenarios with different deposition rates were built to reproduce the OVOCs measurements. The model was operated for the full control period (26 July-27 August) with 2 days spin-up time to reach steady state. The relative changes of the model results responding to the controlled emissions were compared with the observed changes of OVOCs before and during the full control (Sect. 4).

The model uncertainty is mainly caused by the uncertainty of all input parameters (VOCs, trace gas, meteorological parameters, etc.) and reaction rates used in the model. Here, the total uncertainty was estimated by the error propagation from the errors of all considered parameters, which has been described in Li et al. (2013). The modelled concentrations of OVOCs in the base model had an uncertainty of 40–50 %.

3 Results and discussion based on observations

3.1 Diurnal variations of VOCs before and during the control

Table 1 summarizes the averaged meteorological parameters before (3–20 July) and during the full control period (21 July–27 August). Meteorological conditions in the two time periods were similar, except that the average ambient T and UVA before the control were slightly higher than respective values during the full control period, which would affect the emission of biogenic VOCs (dominated by isoprene). As an overview of the changes in VOC concentrations between the two periods, the 10 min-average diurnal variations of the mixing ratios of 12 VOC species were compared in Fig. 1. Aromatics, as a group of primary anthropogenic NMHCs, mainly come from vehicle exhaust and solvent usage in Beijing (Liu et al., 2005; Yuan et al., 2010b). They dropped to the minima at 2.00–3.00 p.m. for both of the two time periods (Fig. 1a–f). Compared to the period prior to 20 July, an obvious decrease (50–60 %) in aromatics occurred after 21 July, especially at rush hours, which may be caused by the traffic restrictions. Oxygenated species at PKU site, from both secondary photochemical production and primary emissions, reached high concentrations at noon and in the late evening (Fig. 1h–l). Some differences of ketones and aldehydes between the two time periods were found, but not as prominent as aromatics. It is difficult to assess the effect of control measures on OVOC species, merely based on the changes in their absolute concentrations before and during the control. In the following section a neural network analysis is used to subtract meteorological effects and to quantify the influence of the traffic restrictions on aromatics and OVOCs.

3.2 Effect of the emission control measures

The neural network is used here as a tool to quantify the controlling effect of the emission reductions on ambient levels of NMHCs and OVOCs. Assuming that no emission restrictions had been in place from 21 July to 27 August, the "uncontrolled" VOCs corresponding to the meteorological conditions encountered at that time were predicted by MLP network using the relationship between VOCs and meteorological parameters from the reference data (before 21 July). Figures 2 and 3 present the probability distributions of the observed (red) and predicted (blue) ln([VOC]) before and during the control period for NMHCs and OVOCs, respectively. For aromatics (such as benzene, toluene and C8-armoatics), the observation and prediction values from the uncontrolled period match well with each other, but the observed data from the controlled period clearly shift towards lower values compared to the prediction. This suggests that the influence of the traffic restriction on aromatics is effective. Acetonitrile (CH_3CN), unlike other NMHCs, did not show any difference between the observed and predicted values for both the controlled and uncontrolled periods. As acetonitrile is usually considered as a tracer for biomass burning and is seldom detected in automobile emissions (Wang et al., 2007), its concentration should be hardly affected by the traffic control. The measured median value of acetonitrile before 21 July was slightly higher than that after 21 July. This discrepancy (15 %) in the absolute concentrations between the two time periods could be explained by the changes in meteorological conditions or pollution transport. The reductions of most OVOCs were also observed relative to what was to be expected without emission controls, although the deviations in OVOCs were not as notable as aromatics (Fig. 3).

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

The relative difference between predicted and measured acetone was as small as 1 %, implying that the emission controls had little or no influence on ambient level of acetone. Regional background (1.7–2 ppbv) was estimated to be a main contributor to measured acetone at PKU with the percentage of 43–47 % (Liu et al., 2009; Yuan et al., 2012), which was probably related to transport of photochemical plumes from the surrounding areas (such as Hebei Province and Tianjin) to Beijing. As the emission reductions were implemented within the Beijing area, i.e. in a range of about 150 km radius, acetone background should be hardly affected by the emission controls. So, it seems to be difficult to reduce the concentrations of acetone in Beijing if relying solely on the control of local emissions.

Except acetonitrile and acetone, the deviation for all other species between the full control period and the uncontrolled days is statistically significant from Student's T test

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at the 95 % level ($P(t) < 0.05$). By contrast, the reference data from the uncontrolled period were well predicted by the MLP simulations, with correlation coefficients ranging from 0.79 to 0.94 and successful T tests for all the species (presented in Table S1). Thus, the emission restrictions implemented in Beijing had significant effects on the NMHCs dominated by vehicular emissions, which is consistent with those results in B. Wang et al. (2010). The reductions in OVOCs species are moderate in comparison to their precursors (e.g. NMHCs), which are subject to the combined influence of controlled direct emissions, local production from reduced precursors and regional formation processes (transport). In subsequent model analysis, the changes of secondary OVOCs produced from local NMHCs oxidation will be discussed.

3.3 Emission ratios for anthropogenic NMHCs

As NMHCs play significant roles on the formation of ozone and secondary OVOCs, the reduction in NMHCs affects the production of secondary pollutants to some extent. Thus, it is essential to understand the changes of NMHCs source patterns in Beijing before and during the controlled period in 2008, and this also provide a case study for establishing a long-term regulatory strategy on secondary pollutants in the near future. From previous studies on VOCs source apportionment in Beijing (Liu et al., 2005; Song et al., 2007; Lu et al., 2007; B. Wang et al., 2010), vehicle exhaust is the largest contributor to ambient NMHCs with a percentage of 40–58 %, followed by solvent usage and painting processes (18–30 %), gasoline evaporation (7–13 %) and chemical plants (3–15 %). Here, the emission ratios (ERs) for NMHCs before and during the control period are used to examine the potential changes of fresh emitted NMHCs.

The emission ratios were determined using a photochemical-age based method presented in de Gouw et al. (2005), Warneke et al. (2007) and Borbon et al. (2013). The degradation of NMHCs by their reactions with OH is described as Eq. (1), where $\mathrm{ER_{NMHC}}$ represents emission ratio of NMHC species relative to CO, k_{NMHC} and k_{CO} are the OH rate coefficients for NMHC and CO, respectively. The ERs reflect the comprehensive effect of all emission sources on ambient NMHCs at the site. Here, the photochemical age of the sampled air masses was calculated by the measured ratio of toluene/benzene (T/B) using Eq. (2), and the initial T/B was set to 2.8 ± 0.7. The 24 h averaged concentration of OH was taken as 2.5×10^6 molecules cm^{-3} that was from OH measurements at a suburban site near Beijing during CAREBEJING 2006 campaign (Lu et al., 2013). The ratio of NMHCs (e.g., toluene, m,p-xylene) to CO decreases with the photochemical age (Fig. 4). The yellow line in Fig. 4a is the linear fit between ln([toluene]/[CO]) and the photochemical age. The emission ratio of toluene relative to CO ($\mathrm{ER_{toluene}}$) is determined by the intercept of the linear fit. It is noted that CO data used for the fitting was subtracted by a constant background of 120 ppbv, which was determined from the minimum concentrations when prevailing wind were from northeast and relatively clean air were measured.

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

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

Since the GC-MS/FID data was only available for the full control period of 2008, VOCs data measured at PKU site in August 2005 (Liu et al., 2009) were used as a reference for uncontrolled situations. The emission ratios for all measured hydrocarbons vs. CO in Beijing for August 2008 and August 2005 are compared in Fig. 5, and the values are tabulated in Table S2 together with some ER results from two US cities in previous work (Warneke et al., 2007; Borbon et al., 2013). In general, the ERs for all groups of NMHCs in the two years agree with each other within a factor of 1.5 (indicated by the shaded area in Fig. 5). For traffic-related NMHCs including most of alkenes, acetylene, benzene, toluene and ethylbenzene, the difference of the ERs between 2005 and 2008 ranged from ±6.5 to ±29 %, within the range of combined error (30 %) for ER calculations (Warneke et al., 2007). This suggests that the pollution control measures did not change the emission composition of the species closely related to vehicular emissions, although the absolute concentrations of those species did drop by half (e.g., toluene/CO in Fig. 4a). A newly published work by Wang et al. (2014) also reported a good agreement of emission ratios for most NMHCs at PKU site in the summertime of 2008, 2010 and 2011. These results reflect that the similarity of NMHCs composition for typical urban emissions of Beijing.

Some alkanes (ethane, *n*-butane, *i*-butane, *n*-pentane) and aromatics (m,p-xylene and o-xylene, labeled in Fig. 5) showed a larger variability (35–50 %) in the two ER datasets for 2005 and 2008. For example, the emission ratio for m,p-xylene in August 2008 was observed to be 38 % lower than the value in August 2005, shown in Fig. 4b. Besides an additional error (5–10 %) by subtracting a constant CO background in ER estimation, one possible reason for the larger difference is that above species also come from "other" emission sources in addition to vehicles. C_8-aromatics were observed as the main components from solvent usage in Beijing (Yuan et al., 2010b). The 2008 control measures included temporary closures of chemical plants, painting process and constructions involving evaporation emissions. If the influence of the control measures on emissions of solvent usage and of automobile source occurred to different degrees, the averaged emission profiles of the city would be changed for the characteristic species (i.e., xylenes) of solvent usage.

The ERs of hydrocarbons related to vehicle emissions (acetylene, ethylene, propene, benzene and toluene) in Beijing generally agree with those in two US cities (in Table S2). It indicates that the emission pattern of automobile source is of similarities in those species for different cities. Greater deviations of lighter alkanes, some C_4–C_5 alkenes and higher aromatics were found, probably because of unique characteristics of emission sources (e.g. fuel types, vehicle fleet ages, solvent and paint types, industrial procedures and etc.) for each city.

4 Modeling analysis for the changes of OVOCs

To better understand the relationship between reduced precursors (NMHCs) and OVOCs concentrations during CAREBEIJING-2008 experiment, a box model using the recent version of MCM was applied in this study. According to the source apportionments of OVOCs in Beijing (Liu et al., 2009; Yuan et al., 2012), 60–70 % of aldehydes are attributed to hydrocarbon oxidation (secondary formation), the contributions from primary sources are more important for ketones (38–80 %) and alcohols (48–74 %), and the contribution of secondary formation was not detected in methanol. Therefore, the following sections will focus on the formation of aldehydes and ketones. The direct emissions of aldehydes from anthropogenic and biogenic sources are neglected in all model scenarios. The primary emissions for acetone and MEK will not be included in the base model, but added to subsequent scenarios for comparison.

4.1 Description of model scenarios and OH simulation results

Four model scenarios for OVOCs simulation are summarized in Table 3. M0 is the base case model with the settings described in Sect. 2.3. In M1, the variation of the boundary layer height (BLH) at a suburban site near Beijing taken from Liu et al. (2011) was included in model run. The dry deposition rate in M1 was set to 1.2 $\mathrm{cm\,s^{-1}}$, as used in the model scenario M0. The primary sources for acetone and MEK were estimated by employing the emission ratios of ketones relative to CO and measured CO. In M2, different dry deposition rates were applied to the simulated species. The values were taken from Emmerson et al. (2007) for HNO_3 (2 $\mathrm{cm\,s^{-1}}$), organic peroxides (0.5 $\mathrm{cm\,s^{-1}}$), H_2O_2 and organic nitrates (1.1 $\mathrm{cm\,s^{-1}}$), from Li et al. (2013) for HCHO and other aldehydes (1 $\mathrm{cm\,s^{-1}}$). Also the vertical dilution rates that represent entrainment of a growing boundary layer were introduced to all modelled species in M2. It is estimated from the growth rate of boundary layer heights (Riemer et al., 2009), described by the equation given in Table 2.

As OH concentrations were not directly measured in August 2008, the modelled OH by the box model were compared with the concentrations calculated by an observed dependence of OH on ozone photolysis frequency ($J(O^1D)$) that was obtained from OH measurements in CAREBEIJING-2006 (Lu et al., 2013). Figure 6a shows the average diurnal profiles of modelled and calculated OH, indicating that the modelled OH in the daytime shows a broader peak and it was overestimated by ∼ 30 % compared to the calculations from the empirical relation. Relatively higher nighttime concentrations were determined from the OH-$J(O^1D)$ calculations, probably due to unknown OH production at night (Lu et al., 2014). As such strong relations between observed OH concentrations and $J(O^1D)$ were also found at some rural sites located in Germany (Rohrer et al., 2014), it makes sense to estimate OH radicals using the empirical OH-$J(O^1D)$ relations when lacking of direct measurements of OH. Considering the uncertainty of OH measurements and the linear fitting between OH and $J(O^1D)$, the difference between modelled and calculated concentrations of OH is acceptable, which give a hint that the model employed here provides a reasonable explanation of radical chemistry in the urban environments.

4.2 OVOCs simulation

Unlike OH, a large difference of a factor of 2–4 was found between the measured and modelled concentrations of aldehydes by the base model (M0), as summarized in Table S3. After modifying deposition rates or/and vertical dilution, the averaged concentrations of HCHO and acetaldehyde in M1 and M2 were decreased by 30–37 % compared to the base case. But the modelled concentrations of the two aldehydes are still higher (> 1.4 times) than the measured values. As shown in Fig. 6b and c, the maximum of modelled HCHO occurred at 3.00–4.00 p.m., which was about 3 h delayed from the observations. The diurnal pattern of simulated acetaldehyde was well matched with the observed variation for most of the time. Thus, the box model overestimated the mixing ratios of aldehydes. The considerations of dry deposition and vertical dilution can help to explain 40–50 % of the large discrepancy. Those results are in consistence with recent study on modelling of formaldehyde and glyoxal in PRD (Li et al., 2013). Li et al. (2013) also pointed out that the uptake of formaldehyde and glyoxal by aerosols had the largest contribution (∼ 50 %) to aldehydes sinks in the presence of high acidic aerosols. Therefore, the loss of aldehydes on aerosol particles should be more important in the polluted areas with high emissions and/or production rates of aerosols. Further research on OVOCs sinks, particularly for heterogeneous uptake processes, is still needed in future studies.

The model overpredicted the overall concentrations of MVK + MACR by 25 % (Table S3). The diurnal cycle of modelled MVK + MACR is similar in shape and magnitude to the measurements for early morning and nighttime, while the model overestimated the midday peak by a factor of 1.5 in the afternoon (Fig. 6d). It suggests that the box model is able to predict MVK + MACR nocturnal productions, but cannot fully explain the daytime mechanisms of isoprene oxidation. Missing sinks are also important for the MVK + MACR simulations.

The modelled concentrations of MEK in M0 underestimated the measurements by 56 % (given in Table S3), implying that current mechanisms are not sufficient to explain the observed MEK. The underestimation is possibly caused by the absence of direct anthropogenic emissions of MEK in the model. Sommariva et al. (2011) also found the underprediction of ketones using box model in the ICARTT campaign. So, the primary ketones were added in subsequent model scenarios (M1–M3) by using CO concentrations and the emission ratios of ketones (acetone/CO = 2.23, MEK/CO = 1.22). The ERs of OVOCs were calculated from the multivariate regression results for OVOCs data at PKU site in Yuan et al. (2012). The modelled ketones in M1 and M2 were comparable to the measurements, as listed in Table S3. For diurnal variations, the agreement between modelled and measured MEK concentrations is generally good (shown in Fig. 6f). Figure 7 indicates the simulated contributions of primary and secondary sources to MEK at PKU site. Primary sources dominated the ambient MEK concentration (∼ 77 %) on a 24 h basis, and the contribution of secondary MEK increased to 25 % at noon and early afternoon. However, the model cannot reproduce the observed variations of acetone. The acetone peak occurred at noon was probably attributed to fresh emission, as the direct emissions of acetone have not always kept pace with CO, the primary acetone derived from acetone/CO ratio cannot explain it. Thus, more detailed measurements on primary sources of acetone need to be investigated in further studies.

In summary, the box model overestimated the concentrations of aldehydes by a factor of 1.4–1.7. This discrepancy is mainly attributed to missing sinks, such as vertical dilution, transport, and heterogeneous uptake on aerosols. In the presence of fresh emissions, the box model predicted the concentrations and variations of MEK well, but it cannot explain observed acetone, likely to be affected by unidentified primary emissions or high backgrounds. Despite the existence of drawbacks on the estimation of sinks, the box model still can give an overview of the relative importance of different precursors on the production of secondary OVOCs. It also can be used as a tool to quantify the relative changes in OVOCs production due to the reduced precursors and other pollutants during the emission control period.

4.3 Secondary production of OVOCs

Figure. 8a–c illustrates averaged diurnal variations of the production of formaldehyde, acetaldehyde and acetone from different groups of NMHCs in M2 during the full control period. As a average, the photooxidation of alkenes contributed most to secondary HCHO production with a percentage of 54 %, followed by the oxidation of isoprene (30 %) and aromatics (15 %), the contributions of pinenes and alkanes were negligible (< 1 %). The contributions of C_2–C_4 alkenes and isoprene were well-matched, accounting for 39.7 and 37.5 % of the total of averaged HCHO production, respectively (listed in Table S4). For acetaldehyde production, it was found to be dominantly through alkenes oxidation (91 %), and the contributions of alkanes and aromatics were minor (7 and 1 %, respectively). For acetone, 60 % of its production was from alkenes, 29 % from alkanes, 10 % from pinenes, and the resting 1 % was attributed to aromatics and isoprene. Secondary MEK was predominantly produced from the oxidation of alkanes (> 95 %). The averaged results show that the oxidation of anthropogenic precursors is the dominant production pathway for secondary OVOCs in Beijing.

The NMHCs oxidation for all OVOC compounds displays an obvious diurnal pattern with a peak at noon. Table 5 summarizes the averaged production rates and corresponding percentages of HCHO from different NMHCs groups. For the full control period (M2), the pathway of isoprene oxidation accounted for up to 40 % of the total production in the daytime, comparable to that of anthropogenic alkenes (46 %). And the rests (13 %) of HCHO production was attributed to aromatics. The contribution of biogenic source decreased to 23 % during the night, accordingly anthropogenic source became the dominant contributor to HCHO production with a combined percentage of 76 % (alkenes + aromatics). The differences in contributions between day and night are closely related to different diurnal patterns of anthropogenic and biogenic NMHCs.

4.4 Changes in secondary OVOCs responding to the control measures

As indicated above, ambient concentrations of NMHCs were decreased by 30–45 % due to cutting the city's emissions from 21 July to 27 August. Here, the effect of the reduced precursors together with other gas pollutants (CO, NO, NO_2 and O_3) on secondary OVOCs has been estimated using the box model.

Since the whole group of NMHCs were not measured by online GC-MS before the full control (3–20 July), the model scenario M3 ran with increased concentrations of alkanes, alkenes, aromatics and isoprene by 30, 35, 40 and 15 %, respectively, according to the results from this work and a previous study on NMHCs by B. Wang et al. (2010), in order to simulate the situation of the uncontrolled period. The concentrations of NO, NO_2 and CO in M3 were increased by 35, 25 and 17 %, while O_3 was decreased by 16 %, taken from the observed changes in T. Wang et al. (2010) and Chou et al. (2011). Then, the relative changes of secondary OVOCs responding to the control measures were determined by the difference between the model run of M3 (the uncontrolled period) and M2 (the full control period).

The modelled reductions in HCHO and MVK + MACR from M3 to M2 agree quite well with the corresponding results from the MLP network (given in Table 4), suggesting the measurable changes of these two species can be reasonably represented by the photochemical production from the oxidation of reduced precursors in the model. For acetaldehyde, the modelled change is about 5 % larger than those from the MLP network. Considering the uncertainties of the two methods (box model and MLP network) and measurements, the above results are acceptable, indicating that the box model is helpful to understand the chemical processes of aldehydes formation and isoprene oxidation in the urban circumstances. For MEK, the relative change from box model is 4 % lower than the MLP results, likely related to the uncertainty of primary emissions. However, it is found a large discrepancy of acetone changes in the two methods; the modelled changes (13.5 %) of acetone were much larger than MLP result (1 %). As discussed in Sect. 3.2, there is no significant change in acetone during the full control period due to high backgrounds in the region around Beijing. It is difficult for the box model to evaluate the effect of background or transport. More improvements need to be done on the model to eliminate this influence.

The HCHO production rates from most of the precursors have been lowered during the full control period, but the ranks of different precursors did not change much, details listed in Table S4. Due to the emission restrictions the total production rate of HCHO decreased from 7.50 to 6.75 ppb h^{-1}, and the daytime production of HCHO from the oxidation of alkenes, aromatics and isoprene were reduced by 13, 12 and 6 %, respectively (from Table 5). The relative contribution of alkene oxidations in the daytime was decreased by 1.5 % from the uncontrolled days (M3) to the full control period (M2), and accordingly the contribution of isoprene was increased by 1.7 %. Here, it should be aware that the relative importance of isoprene chemistry has been enhanced when the NMHCs precursors from anthropogenic sources were reduced by 30–40 %. This would affect the relative potentials of reactive NMHCs for the formation of secondary pollutants (such as OVOCs and ozone).

5 Conclusion

In the summer of 2008 the pollution control measures implemented in Beijing provides a unique opportunity for studying how the primary and secondary air pollutants react to the reductions of anthropogenic emissions. Using a neural network analysis, we concluded that the emission controls taken in Beijing had a notable effect on reducing the ambient concentrations of formaldehyde, acetaldehyde, MEK and methanol. The influence of emission restrictions on OVOCs (except acetone) was found to be statistically significant when the variations due to meteorological conditions have been excluded by the MLP network analysis. However, the effect of local emission controls on acetone seems to have been submerged in high background levels, and no obvious changes were detected in acetone during the full control period. This highlights the complexity of secondary air pollutants (like OVOCs and O_3), which needs to be treated as a regional issue.

The chemical production and degradation of OVOCs in Beijing under the emission controlled conditions have been determined quantitatively using a box model constrained with measurements of OVOCs precursors, gas pollutants and other physical parameters. The most important precursor of HCHO is isoprene, accounting for 30 % of the total HCHO production. While, as a whole, anthropogenic source is still the main contributor to secondary HCHO formation, with alkene oxidation accounting for 54 % and aromatics for 15 %. Unlike HCHO, anthropogenic NMHCs were found to play predominant roles on the chemical production of acetaldehyde, acetone and MEK. Over 90 % of acetaldehyde production can be attributed to the oxidation of alkenes. Anthropogenic alkenes and alkanes contributed 60 and 29 % of acetone formation, respectively; and biogenic precursors (pinenes) contributed the rest 10 %. The relative changes in the modelled aldehydes and MVK + MACR due to the emission restrictions are shown to be consistent with the estimated results from the neural network, reflecting that the current chemical mechanisms can largely represent the realistic formation processes of aldehydes and MVK + MACR in the high NO_x urban conditions.

Compared to measurements of OVOCs, the box model overestimated the measured aldehydes by a factor of 1.4–1.7, while it was able to roughly explain diurnal variations of acetaldehyde for most of time. The model-measurement discrepancy for aldehydes is mostly caused by missing sinks in the model, including physical dilution, transport and heterogeneous processes on the surface of aerosols. After adding the primary concentrations of ketones to the box model, the concentrations and diurnal cycles of MEK can be well represented by the model simulations. However, the model was not able to predict acetone because of transport effect or local emissions. These results demonstrate the importance of further investigating fresh emissions of OVOCs in Beijing and its surrounding areas.

The analysis of the summer 2008 situation in Beijing improves our understanding of the complicated relationship between anthropogenic emissions and pollution levels of primary and secondary VOCs. The concentrations of NMHCs were reduced by 30–40 % due to the emission controls. As vehicular emissions is the most important emitter of VOCs in the city, the emission ratios of the traffic-related species (C_2–C_3 alkenes and lighter aromatics) in the controlled days are found to be fairly similar to the values before the controls and other urban areas. The relatively stable emission ratios for reactive hydrocarbons in cities will help to provide a general idea of the photochemical evolution of gas-phase organic carbons in urban plumes based on model simulations. As China is currently in the midst of a sustained effort to improve air quality in megacities, the results presented in this study can be served as a case for further understanding of the atmospheric chemistry not only for Beijing but also for large regions, and it is also important for aiding policymakers in considering ways to reduce pollution more efficiently in the long term.

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

Time period		T (°C)	RH (%)	Precipitation (mm)	WS ($\mathrm{m\,s^{-1}}$)	UVA ($\mathrm{W\,m^{-2}}$)
Before the full control	3–20 Jul	28.9 ± 4.5	66.9 ± 20.0	0.04 ± 0.37	1.1 ± 0.9	6.6 ± 8.7
During the full control	21 Jul–27 Aug	28.0 ± 4.1	67.9 ± 17.5	0.05 ± 0.51	0.9 ± 0.8	5.3 ± 7.1

Table 2. Comparison of the observed and predicted values of median ln(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.

	Median_ln(VOC)			Concentration (ppbv)		Deviation of	
	observation	prediction	*P*(*t*)	observation	prediction	concentrations (%)	*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
C_8-aromatics	0.12	0.73	0.00	1.12	2.08	−46.0	0.44
C_9-aromatics	−0.63	−0.17	0.00	0.53	0.84	−37.0	0.26
C_{10}-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, $\tau_D = 24\,\mathrm{h}$, the boundary layer height (BLH) was assumed to 1000 m, i.e. $v_{\mathrm{depo.}} = 1.2\,\mathrm{cm\,s^{-1}}$;
M1	as M0, (1) the variation of BLH was taken into consideration, $\tau_D = v_{\mathrm{depo}}/\mathrm{BLH}$, and $v_{\mathrm{depo.}}$ was set to $1.2\,\mathrm{cm\,s^{-1}}$ as what was in M0; (2) using emission ratios of ketones relative to CO ($\mathrm{ER_{OVOC}}$) and measured CO, the primary ketones were added to the model run;
M2	as M1, $\tau_D = v_{\mathrm{depo}}/\mathrm{BLH}$, but v_{depo} were different for calculated species, vertical dilution rates ($\lambda_{\mathrm{dil,vert}}$) were added, $\lambda_{\mathrm{dil,vert}} = \max\left(0, \frac{1}{H(t)}\frac{\mathrm{d}H(t)}{\mathrm{d}t}\right)$;
M3	as M2, the concentrations of NMHCs, CO, $\mathrm{NO_x}$, $\mathrm{O_3}$ were increased in order to simulate the scenario without traffic restrictions.

Table 4. The average of relative changes in OVOCs concentrations from the scenario without pollution control measures (M3) to the control period (M2), compared to the corresponding values from MLP network. Modelled change % = (M2 – M3)/M3 · 100.

Compounds	Reduction from MLP %	Modelled changes (%) average ± SD
Formaldehyde	−12.9	−13.2 ± 2.7
Acetaldehyde	−15.8	−20.4 ± 2.7
MVK + MACR	−11.3	−12.3 ± 3.6
Acetone	−1.0	−13.5 ± 1.6
MEK	−17.0	−13.6 ± 0.7
OH		9.9 ± 5.6
HO_2		20.2 ± 8.0

Table 5. The average of production rates and corresponding percentages of formaldehyde from different precursors in the model simulations for the full control period (M2) and the scenario without the control measures (M3). All the values are presented in "average ± SD".

	9:00–17:00 LT		18:00–8:00 LT	
	M2	M3	M2	M3
P_{alkanes} (ppb h^{-1})	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
P_{alkenes} (ppb h^{-1})	3.08 ± 1.65	3.53 ± 1.93	0.75 ± 0.72	0.87 ± 0.82
$P_{\text{aromatics}}$ (ppb h^{-1})	0.88 ± 0.50	1.00 ± 0.58	0.20 ± 0.18	0.23 ± 0.20
P_{isoprene} (ppb h^{-1})	2.77 ± 1.76	2.95 ± 1.97	0.35 ± 0.45	0.37 ± 0.48
P_{pinenes} (ppb h^{-1})	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
P_{total} (ppb h^{-1})	6.75 ± 3.68	7.50 ± 4.22	1.31 ± 1.32	1.47 ± 1.46
P_{alkanes} (%)	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	0.2 ± 0.2
P_{alkenes} (%)	46.5 ± 8.1	48.0 ± 8.3	59.2 ± 5.5	60.3 ± 5.5
$P_{\text{aromatics}}$ (%)	13.2 ± 1.9	13.3 ± 2.0	16.8 ± 2.6	16.7 ± 2.7
P_{isoprene} (%)	40.0 ± 8.5	38.4 ± 8.6	23.1 ± 6.2	22.1 ± 6.0
P_{pinenes} (%)	0.2 ± 0.1	0.1 ± 0.1	0.8 ± 0.6	0.6 ± 0.5

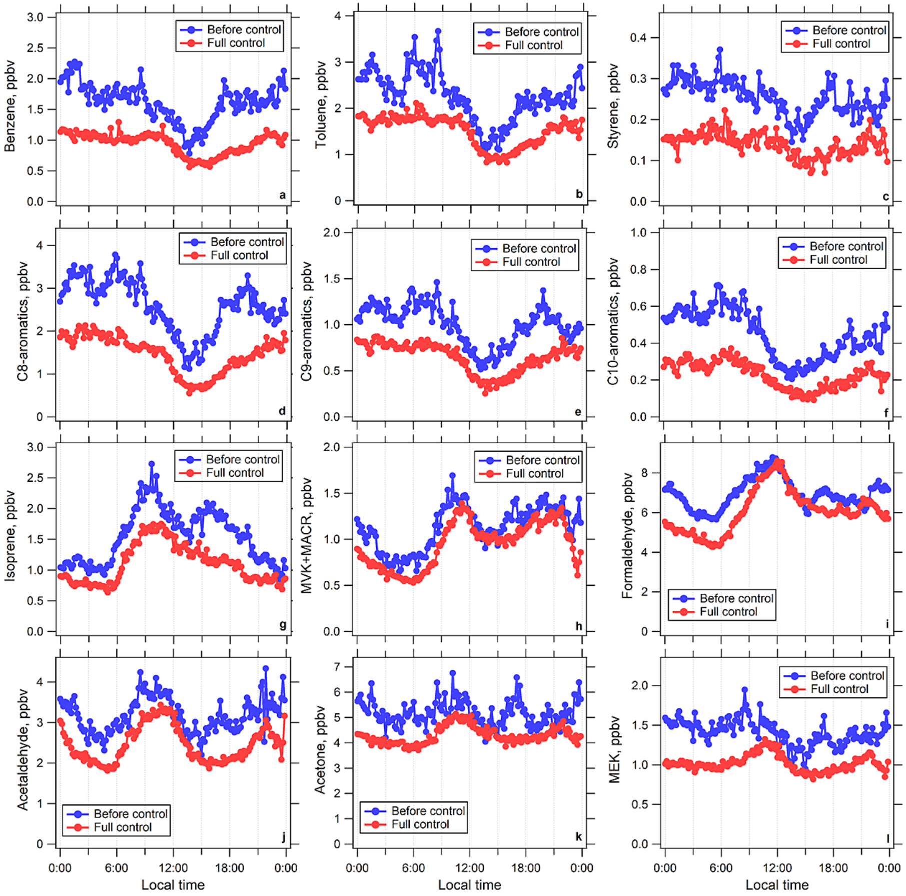

Figure 1. 10 min-average diurnal variations of some NMHCs and OVOCs measured by PTR-MS at PKU site before (1–20 July, blue) and during (21 July–27 August, red) the full control, respectively. **(a)** benzene; **(b)** toluene; **(c)** styrene; **(d)** C_8-aromatics; **(e)** C_9-aromatics; **(f)** C_{10}-aromatics; **(g)** isoprene; **(h)** MVK + MACR; **(i)** HCHO; **(j)** acetaldehyde; **(k)** acetone; **(l)** MEK.

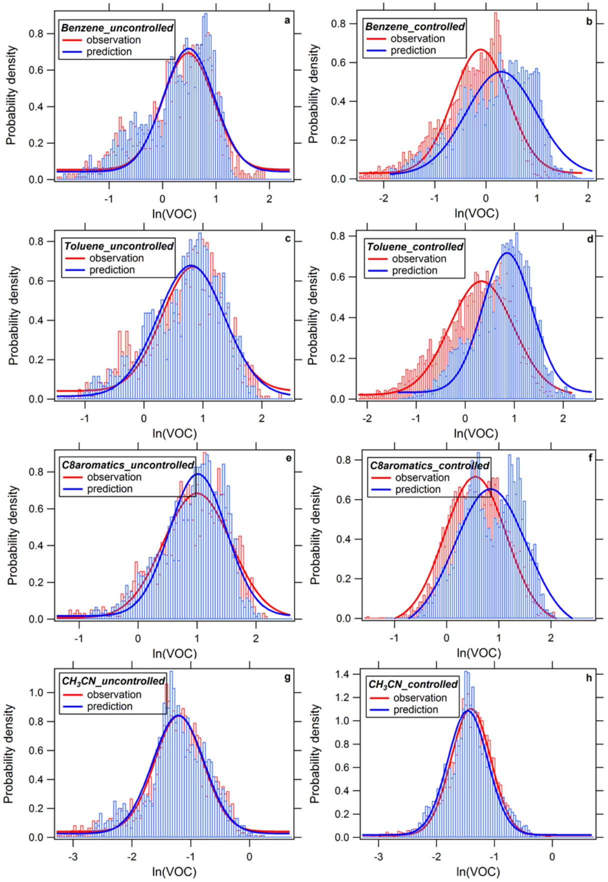

Figure 2. Probability density distribution of the observed ln(VOC) (red) and the predicted values (blue) before the full control (left column) and after the full control (right column) for NMHCs species: **(a, b)** benzene, **(c, d)** toluene, **(e, f)** C_8-aromtics, **(g, h)** acetonitrile.

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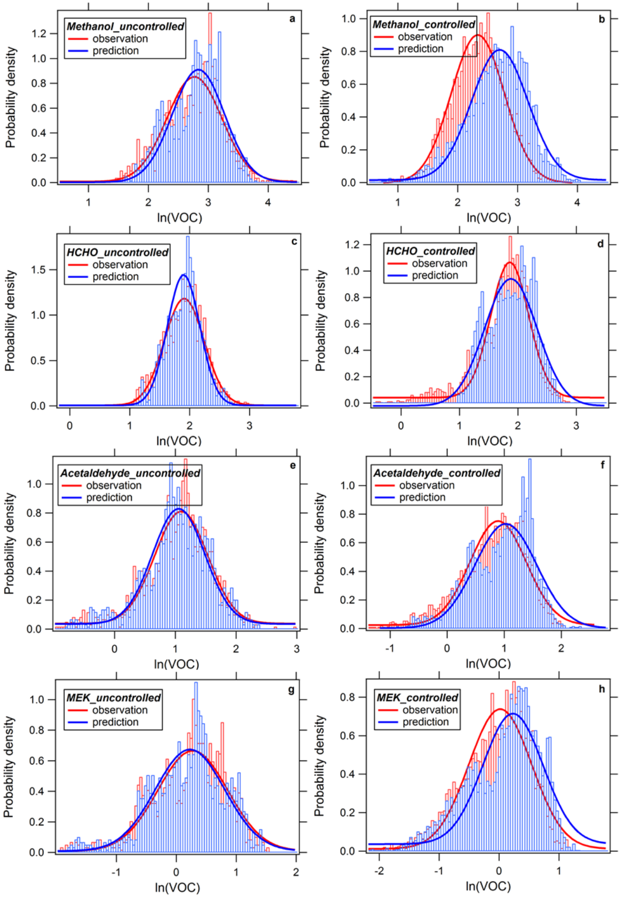

Figure 3. Probability density distribution of the observed ln(VOC) (red) and the predicted values (blue) before the full control (left column) and after the full control (right column) for OVOCs species: **(a, b)** methanol, **(c, d)** HCHO, **(e, f)** acetaldehyde, **(g, h)** MEK.

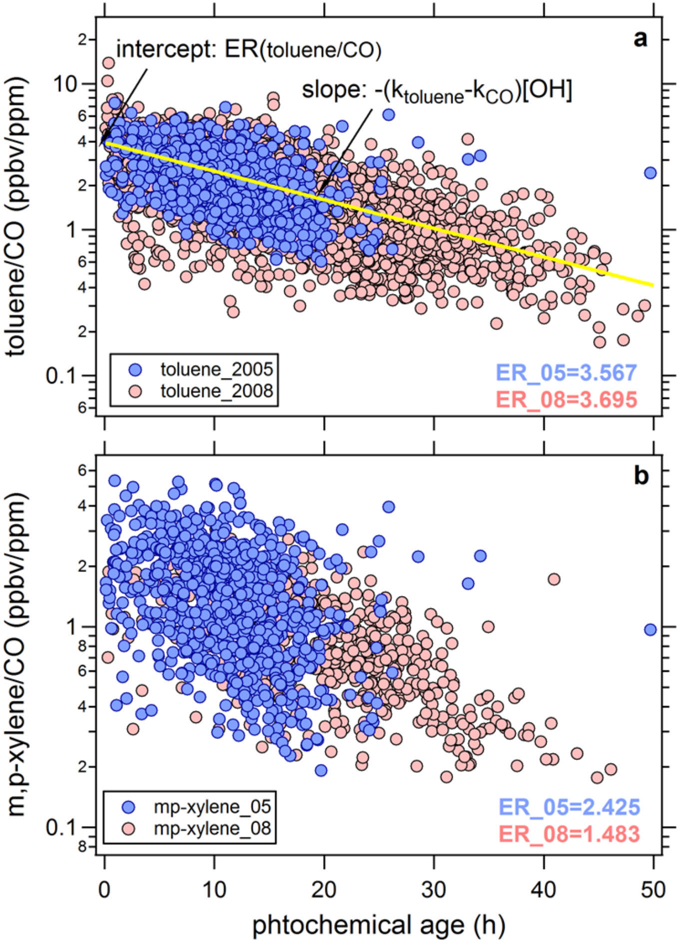

Figure 4. The ratios of toluene/CO **(a)** and m,p-xylene/CO **(b)** vs. the photochemical age of the sampled air mass in Beijing for August 2008 (pink) and August 2005 (blue).

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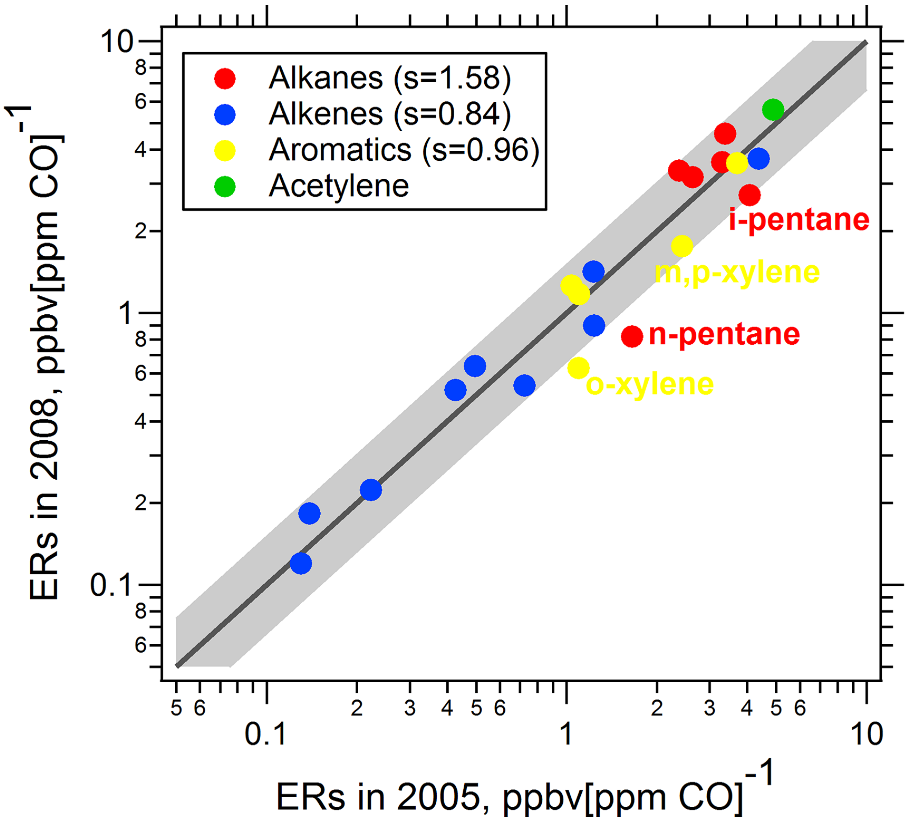

Figure 5. Comparison of the emission ratios (ERs) of NMHCs relative to CO in the 2008 and 2005 summer at PKU site, where each point represents one compounds and different colors indicate the classes of NMHCs. The black line represents 1 : 1 line and the shaded area shows the agreements within a factor of 1.5.

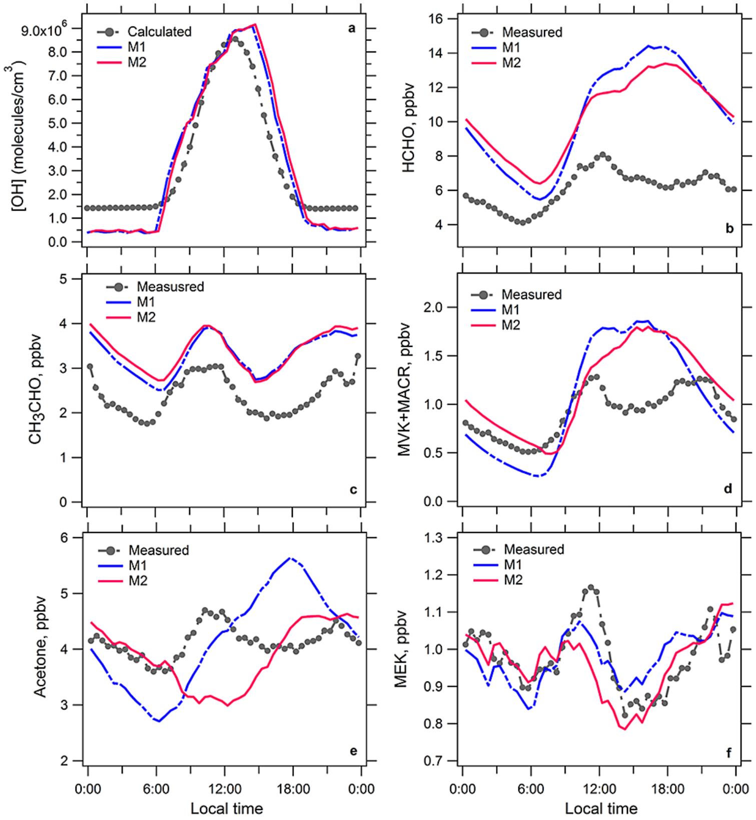

Figure 6. 30 min-average modelled and measured (or calculated) concentrations of **(a)** OH radical, **(b)** HCHO, **(c)** acetaldehyde, **(d)** MVK + MACR, **(e)** acetone and **(f)** MEK plotted as diurnal patterns from 26 July to 27 August The dashed black lines with solid dots indicates measured (or calculated) data, dash-dotted blue lines and solid magenta lines represent the modelled concentrations by simulation M1 and M2, respectively.

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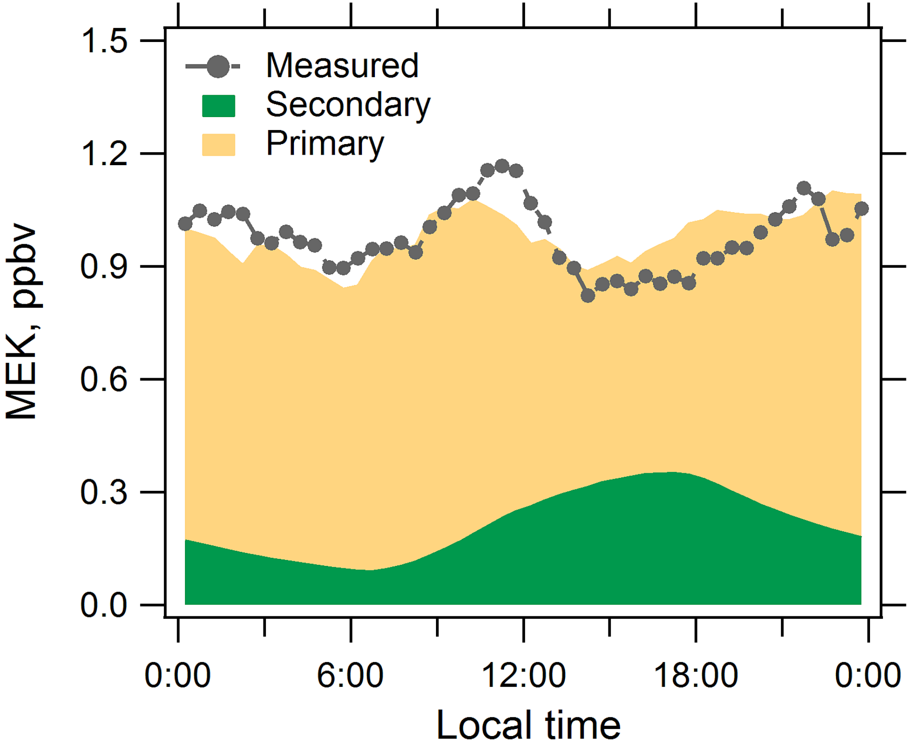

Figure 7. Partitioning of MEK to primary emissions (yellow area) and secondary chemical formation (green area) at PKU site, and the dashed black lines with solid dots represents measured concentrations.

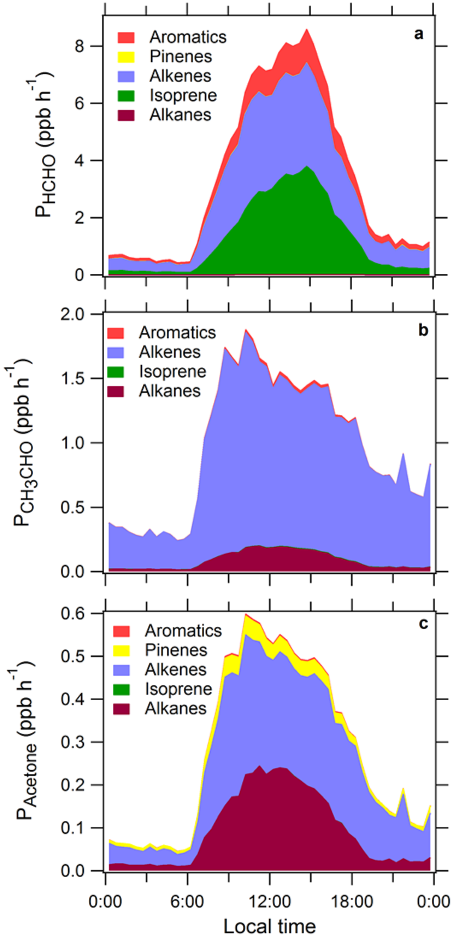

Figure 8. Averaged production of **(a)** formaldehyde, **(b)** acetaldehyde and **(c)** acetone during the full control period in the simulation of M2.