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Supplement of

Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013

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1. NMHC species measured at the PKU site

Table S1 NMHC species measured at the PKU site during 2004–2012.

Species	Species
Alkanes	*Aromatics*
ethane	benzene
propane	toluene
i-butane	ethylbenzne
n-butane	*m,p*-xylene
i-pentane	*o*-xylene
n-pentane	*Alkenes*
n-hexane	ethylene
Alkynes	propylene
acetylene	1-butene

2. NMHC emission standards for vehicle exhaust and paint & solvent use

Table S2 The implementation dates of tail pipe emissions regulations (Euro Ⅰ to Euro Ⅴ) for new vehicles in Beijing.

Vehicles	Euro Ⅰ	Euro Ⅱ	Euro Ⅲ	Euro Ⅳ	Euro Ⅴ
LDGV*	1999/1/1	2003/1/1	2005/12/30	2008/3/1	2013/2/1
HDGV*	2002/7/1	2003/9/1	2009/7/1	2010/7/1	--
HDDV*	2000/1/1	2003/1/1	2005/12/30	2008/7/1	2013/2/1
MC*	2001/1/1	2004/1/1	2008/7/1	--	--

* LDGV: light-duty gasoline vehicles; HDGV: high-duty gasoline vehicles; HDDV: high-duty gasoline vehicles; MC: motorcycles.

Table S3 The emission limits of total hydrocarbon (THC) for vehicles from Euro Ⅰ to Euro Ⅴ standards.

Vehicles	Euro Ⅰ	Euro Ⅱ	Euro Ⅲ	Euro Ⅳ	Euro Ⅴ
LDGV (g/km)	0.97*	0.5*	0.2	0.1	0.1
HDGV (g/kW h)	14*	4.1*	0.35	0.29	--
HDDV (g/kW h)	1.1	1.1	0.66	0.46	0.46
MC (g/km)	4	1.2	0.8	--	--

Table S4   Limits of benzene and other aromatics in national standards for paint and solvents in China.

| Standard No.	National standard name	Limits of benzene	Limits for aromatics	Implementation Date
GB 24613-2009	Limit of harmful substances of coatings for toys	≤ 0.3%	TEX ≤ 30%	2010.10.01
GB 18581-2009	Indoor decorating and refurbishing materials-Limit of harmful substances of solvent based coatings for woodenware	≤ 0.3%	TEX ≤ 30%	2010.06.01
GB 24408-2009	Limit of harmful substances of exterior wall coatings	≤ 0.3%	TEX ≤ 40%	2010.06.01
GB 24409-2009	Limit of harmful substances of automobile coatings	≤ 0.3%	TEX ≤ 40%	2010.06.01
GB/T 23446-2009	Spray polyurea waterproofing coatings	≤ 200 mg/kg	TEX ≤ 1.0 g/kg	2010.01.01
GB/T 22374-2008	Floor coatings	≤ 0.1 g/kg (water based) ≤ 1.0% (solvent based)	TX ≤ 10 g/kg (water based) TX ≤ 200 g/kg (solvent based)	2009.05.01
HJ 457-2009	Technical requirement for environmental labeling products-Waterproof coatings	≤ 0.5 g/kg	TEX ≤ 80 g/kg (Epoxy and polyurethane coatings) TEX ≤ 50 g/kg (Polyurea coating)	2009.05.01
GB 18582-2008	Indoor decorating and refurbishing materials-Limit of harmful substances of interior architectural coatings	--	BTEX ≤300 mg/kg	2008.10.01
HG/T 3950-2007	Antibacterial coating	≤ 0.5%	TX ≤ 45% (Nitrocellulose); TX ≤ 40% (polyurethane); TX ≤ 5% (Alkyd paint)	2008.01.01
JC 1066-2008	Limit of harmful substances of building waterproof coatings	-- (water based) ≤ 200 mg/kg (reactive waterproof coating) ≤ 2 g/kg (solvent based)	BTEX ≤ 300 mg/kg (water based) TEX ≤ 1.0 g/kg (reactive coating A) TEX ≤ 5.0 g/kg (reactive coating B) TEX ≤ 400 g/kg (solvent based)	2008.07.01
HJ/T 414-2007	Technique requirement for Environmental labelling products-Solvent based wood coatings for indoor decoration and refurbishing	≤ 0.05%	TEX ≤ 25% (Nitrocellulose and polyurethane coatings); TEX ≤ 5% (Alkyd paint)	2008.04.01
	Cleaner production standard–Automobile manufacturing (Painting)	=0		2006.12.01
HJ/T 201-2005	Technical requirement for environmental labeling products-Water based coatings	--	TEX ≤ 300 mg/kg	2006.01.01
GB 50325-2001	Code for indoor environmental pollution control of civil building engineering	5 g/L	--	2002.01.01
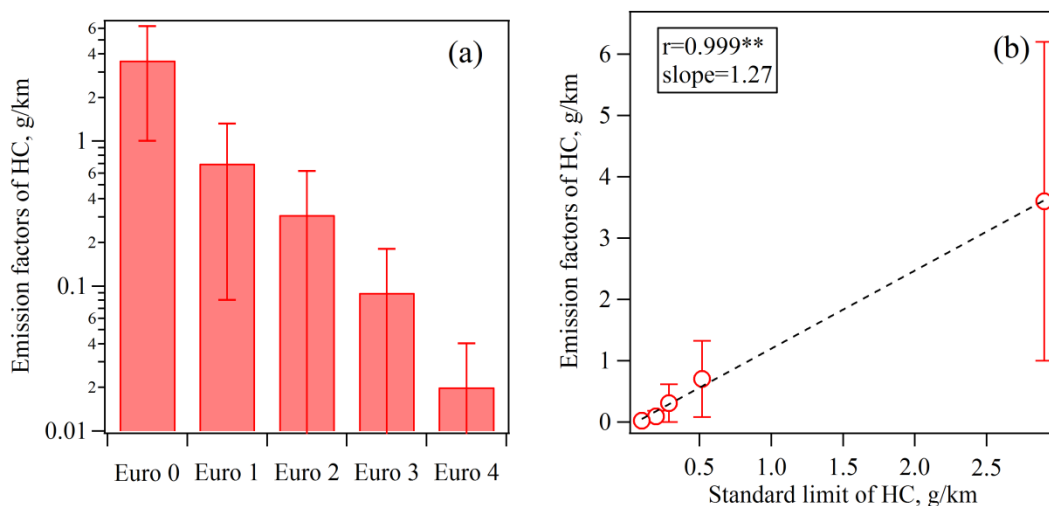
Fig. S1 (a) Emission factors of hydrocarbons for Euro 0–Euro 4 vehicles and (b) their relationship with hydrocarbon limits in vehicular emission standards.

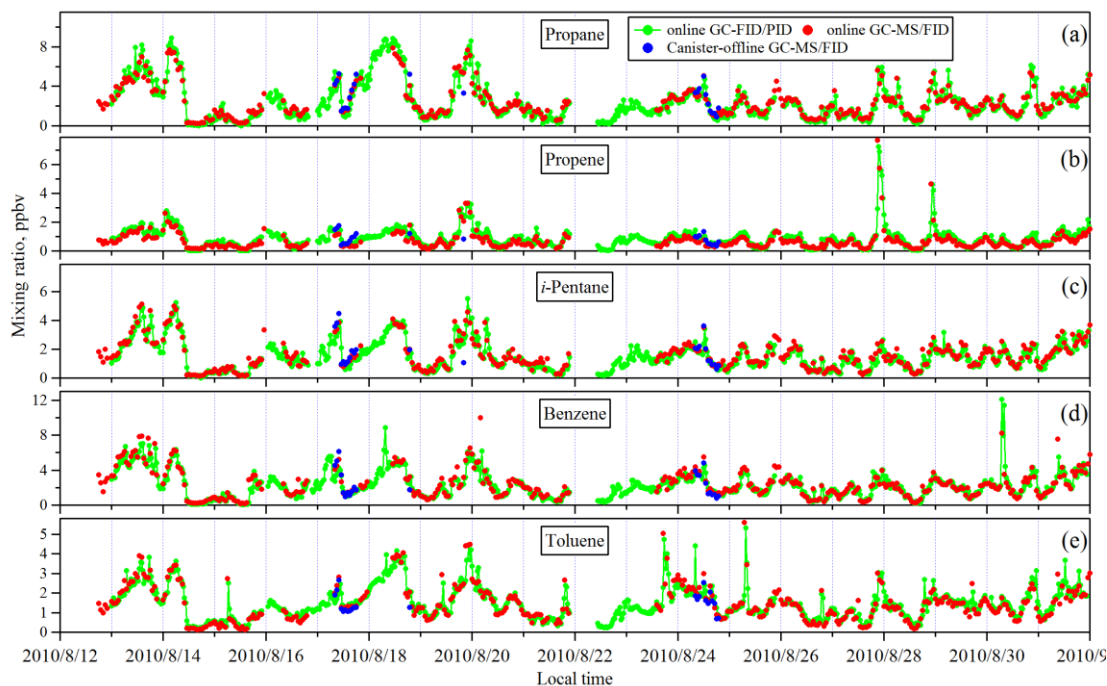## 3. Inter-comparison of NMHC measurements

Fig. S2 Inter-comparisons of (a) propane, (b) propene, (c) *i*-pentane, (d) benzene, and (e) toluene measurements among online GC-MS/FID, online GC-FID/PID, and canister-offline GC-MS/FID systems.

4. Temporal changes in wintertime NMHC mixing ratios

Figure S3 compares average mixing ratios of ethane, acetylene, 1,3-butadiene,

benzene, and toluene measured in urban areas of Beijing during January–February 2001 (Barletta et al., 2005), December 2002 (Liu et al., 2005) and December 2011–January 2012 (Wang et al., 2014). Average mixing ratios of ethane and acetylene during December 2011–January 2012 were 11.5 ± 6.8 and 7.9 ± 5.5 ppbv, lower than measured values during January–February 2001 by 30% and 77%, respectively. Average level of 1,3-butadiene during December 2011–January 2012 was 0.25 ± 0.23 ppbv, significantly lower than the values of 1.3–1.4 ppbv in 2001 and 2002. Compared with ambient levels in January–February 2001, average mixing ratios of benzene in December 2002 and December 2011–January 2012 decreased by 28% and 59%, respectively. For toluene, the percentages of decline for these two years were 34% and 64%, respectively. It can be found that the relative decline percentages for mixing ratios of these NMHC species except ethane during the past decade were all greater than 50%. Additionally, we found that the relative decline rates for wintertime acetylene (7.0% yr^{-1}), benzene (5.5% yr^{-1}), and toluene (5.8% yr^{-1}) levels were similar with those for summertime observations (6.3% yr^{-1} for acetylene, 5.6% yr^{-1} for benzene, and 4.6% for toluene).
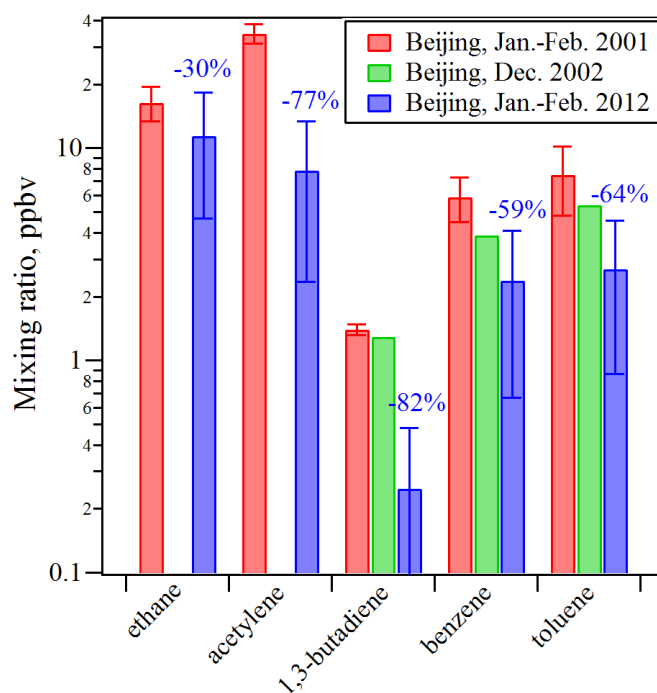

Fig. S3 Comparisons of mixing ratios for ethane, acetylene, 1,3-butadiene, benzene, and toluene measured during January–February 2001 (Barletta et al., 2005), December 2002 (Liu et al., 2005), and December 2011–January 2012 (Wang et al.,

2014) in Beijing.

5. Temporal trend of oxidizing capacity in Beijing

The daytime average mixing ratios of O_3 measured at the PKU site increased rapidly at an annual rate of 2.6 ppbv yr^{-1}, around 5% yr^{-1} between August 2005 and August 2011 (Zhang et al., 2014). The photo-dissociation of ozone is a primary pathway to form hydroxyl (OH) radical in the atmosphere, and thus the rising O_3 levels will possibly result in the increase of OH abundance. Although there are no direct measurements of OH radical over long time periods in Beijing and its surrounding regions, the average abundance of OH radical ([OH]) can be estimated based on ratios of two hydrocarbons that have similar sources but different reaction rates with OH radical using the following equation (McKeen et al., 1990; Ehhalt et al., 1998):

$$[OH] = \frac{1}{(k_{HC_2} - k_{HC_1})\Delta t} \times \left(\ln\left(\frac{[HC_2]_{t_0}}{[HC_1]_{t_0}} \right) - \ln\left(\frac{[HC_2]_{t_0+\Delta t}}{[HC_1]_{t_0+\Delta t}} \right) \right) \tag{S1}$$

where k_{HC_2} and k_{HC_1} are rate constants for the oxidation of HC_1 and HC_2 by OH radical, respectively. $[HC_2]_{t_0}/[HC_1]_{t_0}$ and $[HC_2]_{t_0+\Delta t}/[HC_1]_{t_0+\Delta t}$ are the ratios of HC_2 with HC_1 measured at the time of t_0 and $t_0+\Delta t$, respectively. Δt is the reaction time of hydrocarbons. In this study, the ratio of propene/ethene was selected to estimate [OH] for the following reasons: (1) ethene and propene are both mainly emitted from vehicular exhaust during summer of Beijing (Song et al., 2007; Liu et al., 2009), and therefore variations in measured ratios of propene/ethene were mainly associated with photochemical processing; (2) the rate constant of propene with OH radical ($k_{OH} = 3.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) is significantly higher than that for ethene ($k_{OH} = 9.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) (Atkinson et al., 2006); (3) mixing ratios of propene and ethene in Beijing were high enough to be accurately quantified by VOC analysis systems.

Figure S4 shows the average diurnal variations of propene/ethene during August

2005 and August 2011. The relative decline of propene between 6:00 and 14:00 LT for August 2005 was 30.6%, significantly lower that for August 2011 (62.1%). This indicates that the average photochemical removal degree of these two hydrocarbons significantly increased from August 2005 to August 2011.
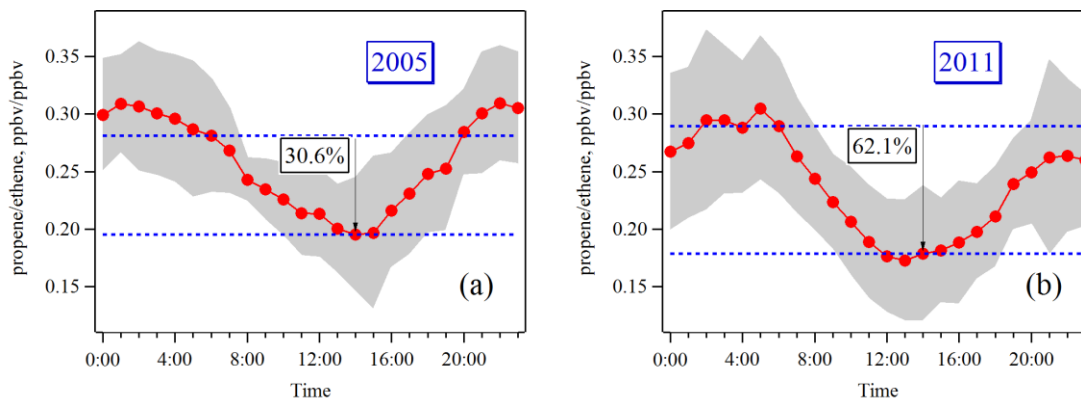

Fig. S4 Diurnal variations in hourly averaged ratios of propene to ethene (propene/ethene) during (a) August 2005 and (b) August 2011, respectively.

Assuming that the difference of average reaction time (Δt) between August 2005 and August 2011 was negligible (i.e. $\Delta t_{2005} = \Delta t_{2011}$), the relative change of average OH abundance (RC) between these two years can be described by the following equation:

$$
\begin{aligned}
\mathrm{RC} &= \frac{[\mathrm{OH}]_{2011} - [\mathrm{OH}]_{2005}}{[\mathrm{OH}]_{2005}} \times 100\% \\
&= \frac{[\mathrm{OH}]_{2011}\,\Delta t_{2011} - [\mathrm{OH}]_{2005}\,\Delta t_{2005}}{[\mathrm{OH}]_{2005}\,\Delta t_{2005}} \times 100\%
\end{aligned}
\tag{S2}
$$

Appling Eq. (S1) to calculate average OH abundance during 6:00–14:00 LT, then the RC was estimated to be 32.3% based on propene/ethene ratios using the following equation:

$$
\mathrm{RC} = \frac{\left(\ln\left(\frac{\mathrm{propene}}{\mathrm{ethene}}\right)_{6:00,2011} - \ln\left(\frac{\mathrm{propene}}{\mathrm{ethene}}\right)_{14:00,2011}\right) - \left(\ln\left(\frac{\mathrm{propene}}{\mathrm{ethene}}\right)_{6:00,2005} - \ln\left(\frac{\mathrm{propene}}{\mathrm{ethene}}\right)_{14:00,2005}\right)}{\left(\ln\left(\frac{\mathrm{propene}}{\mathrm{ethene}}\right)_{6:00,2005} - \ln\left(\frac{\mathrm{propene}}{\mathrm{ethene}}\right)_{14:00,2005}\right)} \times 100\%
\tag{S3}
$$

This means the average OH abundance during 6:00-14:00 LT at the PKU site increased by 32.3% between August 2005 and August 2011, with speed of 5.4% yr^{-1},

close to the rising rate of O_3 levels (5% yr^{-1}) at the same site reported by Zhang et al. (2014).

The influence of rising OH abundance on temporal trend of acetylene levels was considered to be negligible, due to the low reactivity of acetylene ($k_{OH} = 1.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}). The rate constants of OH oxidation for ethene ($k_{OH} = 9.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}) and propene ($k_{OH} = 3.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) were significantly higher than that for acetylene, but the relative declines of ethene and propene levels measured at the PKU site were close to that for acetylene (Fig. 4a-c). This indicates that the rise of atmospheric oxidizing capacity was not an important cause for the decline of hydrocarbon levels measured at the PKU site.

6. Spatial distribution of NMHC levels and chemical compositions in Beijing

In order to investigate the spatial distribution characteristic of NMHC levels in Beijing, sixteen regional measurement campaigns were conducted at 27 sites across the whole city from September 2009 to January 2011. Detailed descriptions on these regional sites and sampling strategies were provided by Wang et al. (2014). Figure S5 shows the spatial distribution of annual average NMHCs levels at 27 sites in Beijing from September 2009 to January 2011. It can be found that the mixing ratios of NMHCs in downtown and southern areas of Beijing were significantly higher than those for suburban/rural sites in northern and western regions. However, as shown in Fig. S6, the emission ratios for most NMHC species showed good agreements between the PKU site and the 27 regional sites in Beijing, with *r* of 0.99 and linear regression slope of 0.91±0.02 (Wang et al., 2014).
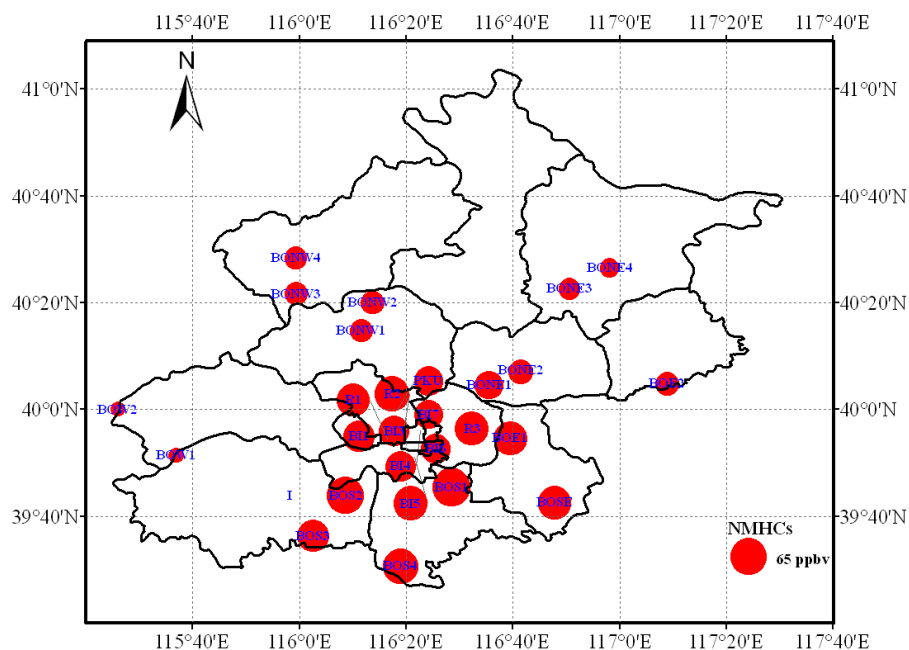
Fig. S5 Spatial distribution of annual averaged mixing ratios of NMHCs measured at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).
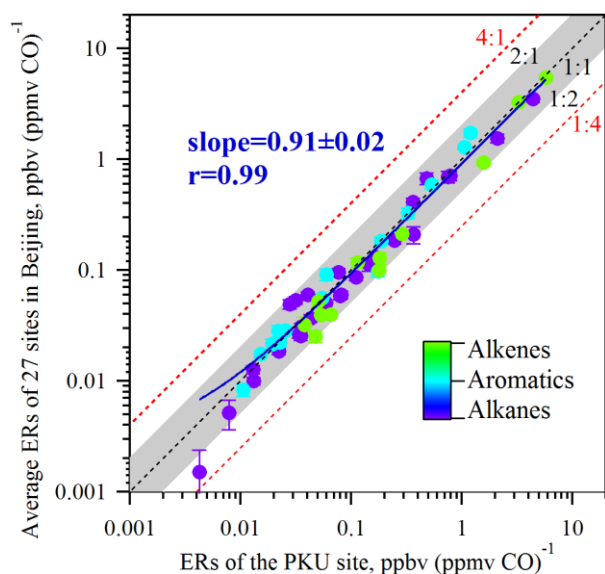

Fig. S6 Comparisons of VOC emission ratios determined at the PKU site with those determined from regional measurements at 27 sites in Beijing from September 2009 to January 2011 (Wang et al., 2014).

In fact, the spatial distribution of industry and urbanization level in Beijing has been evolving during the last two decades (Wang et al., 2014). High pollution industries have gradually moved out of the urban center of Beijing; meanwhile, industrial clusters have been developed in southern suburban areas. Accompanied by

the rapid economic development, southern suburban areas of Beijing have become more urbanized during these years. Although we can not obtain NMHC measurement data during the last decade for southern regions of Beijing, the Beijing government have selected 5 routine monitoring sites, two of them are located in southern regions, to measure the levels and speciation of HMHCs in entire Beijing since 2012. This will provide an opportunity for us to investigate the temporal trends of NMHCs at more sites of Beijing in the near future.

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