Atmospheric
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Supplement of

Variations of ground-level O$_3$ and its precursors in Beijing in summertime between 2005 and 2011
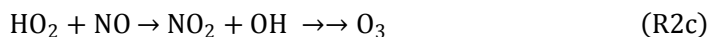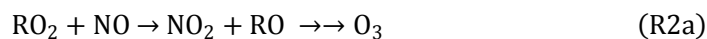
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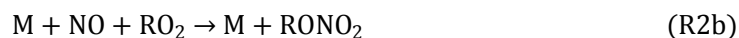
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I. Description of simplified total oxidant production calculation method

The reactions describing HO_x chain propagation and termination are used to derive the equations about ozone production, assuming that these radicals and peroxynitrates are in steady state, which means that $P(HO_x) = L(HO_x)$. The branch reaction producing alkyl nitrates is considered, α is denoted as this production probability (Farmer et al., 2011;Geddes et al., 2009).

Reactions that propagate the HO_x cycle include:

$$VOC + OH \xrightarrow{O2} RO_2 + H_2O \tag{R1}$$

$$RO_2 + NO \rightarrow NO_2 + RO \rightarrow\rightarrow O_3 \tag{R2a}$$

$$HO_2 + NO \rightarrow NO_2 + OH \rightarrow\rightarrow O_3 \tag{R2c}$$

Reactions referred to HO_x chain termination include:

$$M + OH + NO_2 \rightarrow M + HNO_3 \tag{R3}$$

$$M + NO + RO_2 \rightarrow M + RONO_2 \tag{R2b}$$

$$RO_2 + R'O_2 \rightarrow R'OOR + O_2 \tag{R4}$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \tag{R5}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{R6}$$

Considering R2b, R3-R6, terminal loss rate of HO_x can be formulated as:

$$L(HO_x) = k_3[OH][NO_2] + \alpha k_{2b}[RO_2][NO] + 2k_4[RO_2][R'O_2] + 2k_5[RO_2][HO_2]$$

$$+ 2k_6[HO_2][HO_2] \tag{1}$$

Assuming $[HO_2] = [RO_2]$ (this can be acceptable for two radicals over Beijing are at the same magnitude in closure modeling (Liu et al., 2012)) and peroxy radicals are in steady state $P[HO_x] = L[HO_x]$, we can yield that:

$$P(HO_x) = k_3[NO_2][OH] + \alpha k_{2b}[HO_2][NO] + 2(k_4 + k_5 + k_6)[HO_2]^2 \quad (2)$$

Apart from the alkyl nitrates production reaction between NO and RO_2 (R2b), the main reaction (R2a) consumes most RO_2 radicals, thus:

$$[HO_2] = [RO_2] = k_1[VOC][OH] \,/(1-\alpha)k_{2a}[NO] \quad (3)$$

Substituting equation (3) into equation (2) yields:

$$P(HO_x) = k_3[OH][NO_2] + \alpha k_{2b}\frac{k_1[VOC][OH]}{(1-\alpha)}[NO]$$

$$+ \ 2(k_4 + k_5 + k_6)\big[k_1[VOC][OH] \,/(1-\alpha)k_{2a}[NO]\big]^2 \quad (4)$$

$$P(O_x) = k_{2a}[RO_2][NO] + k_{2c}[HO_2][NO] = 2k_1[VOC][OH] \quad (5)$$

HO_x production rate $P(HO_x)$ mainly consist of HONO, OVOCs and ozone photolysis. According to measurement or modeling results of HO_x budget, given a certain value of $P(HO_x)$ and other proper parameters, the instantaneous [OH] and corresponding $P(O_x)$ can be solved through a quadratic equation to indicate the variations of total oxidant:

(6) [OH]

$$= \frac{-\left(k_3[NO_2] + \frac{\alpha k_1[VOC]}{(1-\alpha)}\right) + \sqrt{\left(k_3[NO_2] + \frac{\alpha k_1[VOC]}{1-\alpha}\right)^2 + \frac{8P(HO_x)(k_4+k_5+k_6)(k_1[VOC])^2}{((1-\alpha)k_{2a}[NO])^2}}}{4(k_4+k_5+k_6)(k_1[VOC]/(1-\alpha)k_{2a}[NO])^2}$$

$$= \frac{2P(HO_x)}{\left(k_3[NO_2] + \frac{\alpha k_1[VOC]}{(1-\alpha)}\right) + \sqrt{\left(k_3[NO_2] + \frac{\alpha k_1[VOC]}{1-\alpha}\right)^2 + \frac{8P(HO_x)(k_4+k_5+k_6)(k_1[VOC])^2}{((1-\alpha)k_{2a}[NO])^2}}}$$

(7) $P(O_x) = 2k_1[VOC] * [OH]$

$$= \cfrac{2k_1[VOC] * 2P(HO_x)}{\left(k_3[NO_2] + \cfrac{\alpha k_1[VOC]}{(1-\alpha)}\right) + \sqrt{\left(k_3[NO_2] + \cfrac{\alpha k_1[VOC]}{1-\alpha}\right)^2 + \cfrac{8P(HO_x)(k_4+k_5+k_6)(k_1[VOC])^2}{\left((1-\alpha)k_{2a}[NO]\right)^2}}}$$

$$= \cfrac{4P(HO_x)}{\left(\cfrac{k_3[NO_2]}{k_1[VOC]} + \cfrac{\alpha}{1-\alpha}\right) + \sqrt{\left(\cfrac{k_3[NO_2]}{k_1[VOC]} + \cfrac{\alpha}{1-\alpha}\right)^2 + \cfrac{8P(HO_x)(k_4+k_5+k_6)}{((1-\alpha)k_{2a}[NO])^2}}}$$

In above equations, $k_1[VOC]$ is the total VOC reactivity; $k_{2a}=k_{2b}=k_{2c}$ is the effective reaction constant between NO and RO_2 in the normal atmosphere (Tyndall et al., 2001); k_3 is the reaction constant between OH and NO_2, k_4, k_5 and k_6 are the reaction constants between RO_2 themselves, RO_2 and HO_2, HO_2 and itself, respectively (Farmer et al., 2011).

II. Explanation of inter-comparison of VOC measurements

VOC measurements were done by on-line instruments in three laboratories (Table S1): Peking University (PKU), NOAA Aeronomy lab, and Research Center for Environmental Changes, Academia Sinica of Taiwan (RCEC). During each campaign we conducted calibration of instrument and inter-comparisons when two labs were involved. Two ways of inter-comparisons were preformed: first is a check of VOC standards used by different labs, second is measurement of the same blind samples by different labs. The standard deviations for VOC standard check were less than 10% for all species except for isoprene (which was around 15%), ratios of PKU results and RCEC results varied between 0.87 and 1.11 for all measured species, the inter-comparison between PKU lab and NOAA lab agreed between 0.85-1 (Liu et al., 2008;Shao et al., 2009). Figure S1 and S2 illustrate inter-comparison of measurement results by GC-FID/PID and GC-FID/MSD both in PKU lab in 2010. Different measurements show good consistency in time-series data, regression and bias analysis also demonstrate acceptable ratios between them. We were confident that the VOC data in this work were obtained under reliable QA/QC procedures.

III.Speciated VOC trends from measurements in Beijing between 2005 and 2011

All derived trends of VOC species herein were listed in Table S2 and S3. We treated linear regressions via both means and medians of mixing ratios of VOCs. The regression performances among these species differed largely: Propene, n-butane, i-pentane, n-pentane, benzene, toluene, and o-xylene were likely to show decreasing

trends, whereas the rest showed no clear trends. I-pentane and n-pentane, which decreased at a rate of 8-10%/yr significantly, are usually regarded as trace gases for gasoline evaporation (Liu et al., 2008). Benzene and toluene in the urban atmosphere have various emission sources, in which traffic emissions could also play an important role (Barletta et al., 2005). All these evidences tend to infer that VOC emissions from gasoline vehicles in Beijing were decreasing in the past 7 years.

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Table S1 Summary of information about VOC measurements at PKU site

Year	Instruments	Laboratory	Time resolution
2005	GC-FID/MSD	NOAA	30 min
2006	GC-FID	RCEC	30 min
2007	GC-FID/PID	PKU	30 min
2008	GC-FID/MSD	RCEC	60 min
2009	GC-FID/PID	PKU	30 min
2010	GC-FID/PID	PKU	30 min
2011	GC-FID/MSD	PKU	60 min

Table S2 Linear regression performances of VOC species via means

(Hereafter, CI: confidence interval; AAGR: average annual growth rate, * p<0.05)

Items	Trends, ppbv/yr	95% CI, ±ppbv/yr	r^2	AAGR, %/yr
Propane	-0.09	0.12	0.17	-2.9%
Propene	**-0.06**	**0.02**	**0.65**	**-6.3%**
i-Butane	-0.05	0.08	0.10	-2.6%
n-Butane	**-0.12**	**0.06**	**0.57**	**-5.1%**
i-Pentane	**-0.41**	**0.08**	**0.89***	**-9.9%**
n-Pentane	**-0.13**	**0.03**	**0.84***	**-7.7%**
t-2-Butene	-0.01	0.01	0.19	-5.1%
1-Butene	-0.04	0.03	0.43	-6.6%
c-2-Butene	-0.01	0.01	0.10	-5.1%
t-2-Pentene	-0.01	0.02	0.16	-7.3%
1-Pentene	-0.01	0.01	0.12	-9.8%
n-Hexane	-0.07	0.05	0.37	-11.0%
Benzene	**-0.14**	**0.05**	**0.75**	**-7.9%**
Toluene	**-0.15**	**0.04**	**0.81***	**-4.9%**

Ethyl-benzene	-0.04	0.04	0.27	-4.4%
m/p-Xylene	-0.08	0.16	0.07	-4.8%
o-Xylene	**-0.07**	**0.03**	**0.61**	**-8.6%**
Isoprene	-0.01	0.04	0.03	-1.6%

Table S3 Linear regression performances of VOC species via medians

Items	Trends, ppbv/yr	95% CI, ±ppbv/yr	r^2	AAGR, %/yr
Propane	-0.18	0.12	0.43	-5.5%
Propene	**-0.07**	**0.02**	**0.87***	**-7.5%**
i-Butane	-0.05	0.10	0.09	-2.6%
n-Butane	-0.13	0.08	0.47	-5.5%
i-Pentane	**-0.41**	**0.08**	**0.90***	**-10.3%**
n-Pentane	**-0.14**	**0.04**	**0.81***	**-8.3%**
t-2-Butene	-0.01	0.01	0.12	-6.2%
1-Butene	-0.04	0.03	0.36	-6.9%
c-2-Butene	-0.01	0.01	0.04	-6.4%
t-2-Pentene	-0.01	0.02	0.12	-9.0%
1-Pentene	-0.01	0.01	0.10	-10.0%
n-Hexane	-0.08	0.06	0.37	-13.4%
Benzene	**-0.12**	**0.03**	**0.85***	**-6.7%**
Toluene	**-0.15**	**0.05**	**0.77***	**-5.3%**
Ethyl-benzene	-0.03	0.04	0.20	-3.7%
m/p-Xylene	-0.07	0.16	0.06	-4.3%
o-Xylene	**-0.07**	**0.03**	**0.68**	**-9.4%**
Isoprene	-0.01	0.04	0.03	-1.7%
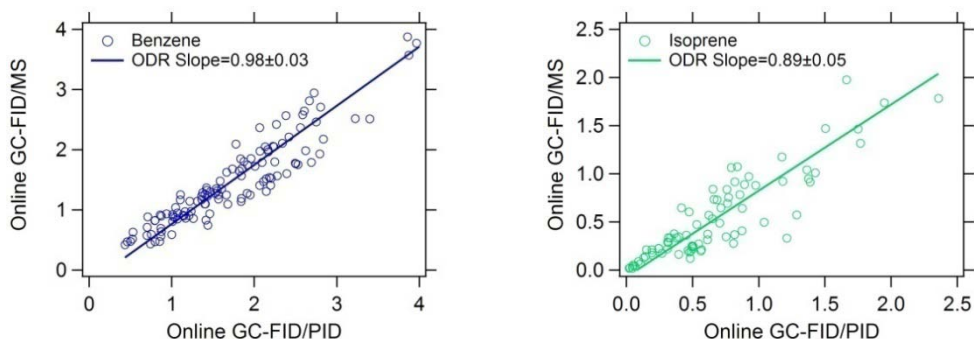
Figure S1 Inter-comparison among GC-FID/PID (GC955 811 or 611 analyzer), GC-MS/FID at PKU site in 2010. Isoprene (right) represents C3-C6 species detected by GC955-811 VOC analyzer and benzene (left) represents C6-C9 species detected by GC955-611 VOC analyzer. Blue and green lines represent slopes of orthogonal distance regression (ODR) between these two instruments in PKU lab.
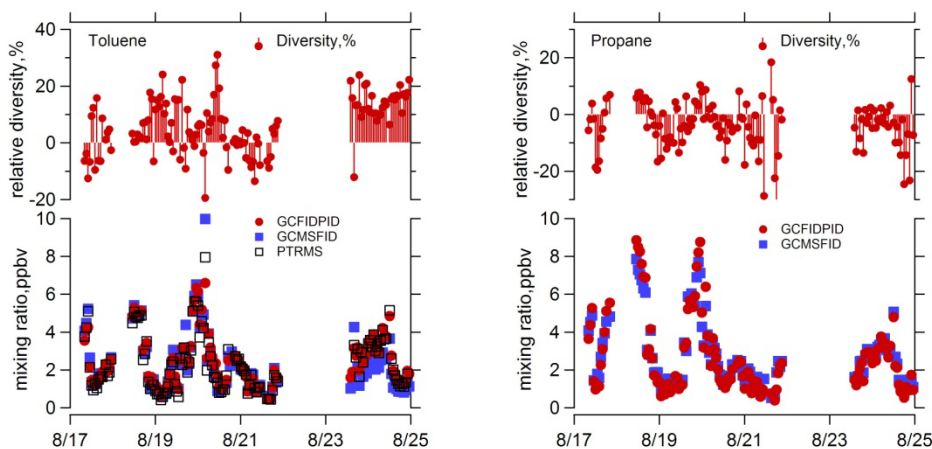
Figure S2 Time-series comparison among GC-FID/PID, GC-MS/FID and PTR-MS (if available) at PKU site in 2010. Toluene (left) and propane (right) are two of most abundant VOC species as examples and red dot and sticks represent relative differences between GC-FID/PID and GC- MS/FID, which appears less than 20% in general.