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Supplement of

A temporally and spatially resolved validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China

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1　Comparisons of anthropogenic NMVOCs emissions
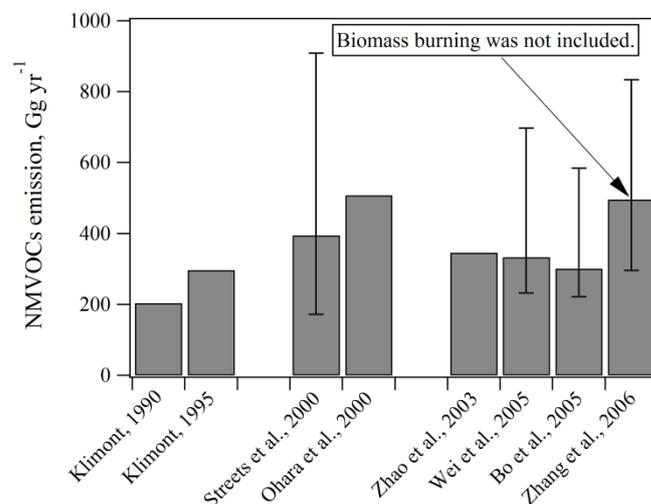
Fig. S1 Comparison of anthropogenic NMVOCs emissions from different emission inventories (Klimont et al., 2002; Streets et al., 2003; Ohara et al., 2007; Bo et al., 2008; Wei et al., 2008; Zhang et al., 2009; Zhao et al., 2012).

2　VOCs sampling and analysis

2.1 Sampling sites for VOCs regional measurements in Beijing

Table S1　Summary of 27 sampling sites for regional VOC measurements in Beijing.

Sites Category (n [a])	Urban (7)	Suburban_South (6)	Suburban_North (9)	Rural (2)	Roadside (3)
	BI1	BOS1	BONE1	BOW1	R1
	BI2	BOS2	BONE2	BOW2	R2
	BI3	BOS3	BONE3		R3
	BI4	BOS4	BONE4		
Sites No.	BI5	BOSE	BOE2		
	BI6	BOE1	BONW1		
	BI7		BONW2		
			BONW3		
			BONW4		

[a] The n is the number of regional sites classified in each site category.

2.2 Sampling periods for regional VOC measurements in Beijing

Table S2　Sampling dates and meteorological conditions for regional VOC measurements in Beijing.

Sampling date	Temperature (°C)		Relative humidity (%)		Wind speed (m·s⁻¹)		Atmospheric pressure (hPa)		Wind direction [a]	
	09:00	13:00	09:00	13:00	09:00	13:00	09:00	13:00	09:00	13:00
Jul. 24, 2009	25	28	70	61	1.9	1.7	999	999	NE	NE
Aug. 7, 2009	24	28	90	74	0.8	1.6	997	996	SSE	NE
Sep. 25, 2009	21	26	83	64	1.1	1.3	1004	1002	S	SW
Oct. 29, 2009	12	20	86	47	0.9	1.0	1005	1003	NW	NW
Nov. 30, 2009	3	10	62	36	1.1	1.9	1012	1010	NW	NW
Dec. 22, 2009	-4	6	39	20	1.0	1.8	1003	1002	NW	NNW
Jan. 14, 2010	-10	-4	52	33	1.3	1.3	1008	1006	NW	NW
Feb. 4, 2010	-5	1	31	21	1.6	1.5	1012	1009	NW	NW
Mar. 19, 2010	3	7	84	67	1.0	1.1	988	986	WNW	NW
Apr. 20, 2010	13	17	74	41	0.8	2	1004	1003	NW	NE
May 20, 2010	26	34	30	15	1.2	2.6	993	992	NW	SW
Jun. 24, 2010	26	31	53	34	1.0	2.2	996	994	NW	SE
Jul. 22, 2010	28	33	76	59	1.0	1.7	995	994	N	S
Aug. 24, 2010	24	28	81	66	1.3	2.2	1001	999	NE	SE
Sep. 14, 2010	21	27	68	48	0.9	2.2	998	995	S	S
Jan. 13, 2011	-7	2	39	18	0.8	2.2	1009	1007	NW	NW

[a] N, E, S, and W means wind from north, east, south, and west, respectively.

2.3 VOCs analysis by online GC-MS/FID

Briefly, two parallel sampling channels collected two separate 300-mL aliquots of ambient samples cryogenically (at approximately -160°C), during the first 5 min of every hour. One channel was designed to measure C2–C5 hydrocarbons. Target compounds were first trapped in a porous layer open tubular (PLOT) capillary column (15 cm, 0.53 mm ID) and then vaporized (110°C) and injected into the GC system, separated using a PLOT (Al$_2$O$_3$/KCl) column (15 m × 0.32 mm ID, J&W Scientific, Folsom, CA, USA), and measured by a flame ionization detector (FID). In the other channel, C5–C12 NMHCs, C3–C6 carbonyl compounds, methanol, C1–C2 halocarbons, and C1–C4 alkyl nitrates were trapped by a deactivated quartz capillary

column (15 cm, 0.53 mm ID), separated using a DB-624 column (30 m × 0.25 mm ID,

J&W Scientific), and measured by a quadrupole mass spectrometer (MSD, QP-2010S,

Shimadzu, Kyoto, Japan). The system was calibrated at multiple concentrations (in

the range of 0.5–8 ppbv) by three gas standards: (1) a mixture of 55 NMHCs (Spectra

Gases, Inc., Newark, NJ, USA) for C2–C12 hydrocarbons; (2) a mixture of 63

chemicals (Spectra Gases, Inc.) for methanol, C1–C2 halocarbons, and C3–C6

carbonyl compounds; and (3) laboratory-prepared $RONO_2$ samples (Earth System

Research Laboratory, NOAA, Boulder, CO, USA) for C1–C4 $RONO_2$. The method

detection limits (MDLs) for C2–C12 NMHCs, C3–C6 carbonyl compounds, and C1–

C4 $RONO_2$ were in the ranges of 0.004–0.013, 0.011–0.015, and 0.001–0.003 ppbv,

respectively.

2.4 Sampling locations and periods for regional VOC measurements in Beijing

To minimize the impact of meteorological conditions on ambient trace gas levels,

16 sampling days, once monthly from July, 2009 to September, 2010 and January

2011, were selected carefully. Most sampling campaigns were conducted on heavy air

pollution days characterized by low wind speed, high relative humidity, and poor

visibility. However, the air quality on July 24th, 2009 and February 4th, 2010 was

excellent, the former because a summer precipitation process had just ended in

Beijing and the latter because of a recent cold winter northwestern airstream.

Sampling was conducted at 09:00, to assess atmospheric pollutant levels during

morning traffic rush hour before the daily photochemical cycle, and 13:00, around the

daily O_3 peak. This allowed temporal comparisons and an examination of the

photochemical removal of reactive NMHC species and secondary production of ground-level O_3 and alkyl nitrates. Details of the sampling periods and meteorological parameters are summarized in Table S2. Backward trajectories (72-h duration) of air masses at an altitude of 500 m arriving in Beijing during the sampling periods were calculated with the NOAA HYSPLIT model (results not shown). Briefly, from October, 2009 to March, 2010 and in January 2011, air masses were transported from the northwest (NW) or west-northwest (WWN) with long transport distances, while during April–September, the air masses originated mainly from the south or southeast, usually traveling short distances. Based on the transport directions and distances of air masses, coupled with surface meteorological conditions, the 16 sampling periods were classified into three types corresponding to different seasons: spring/fall (April–May and September–October), summer (June–August), and winter (November–March).

2.5 VOCs analysis by offline GC-MS/FID

A 500-mL aliquot of air sample from each canister was concentrated using a three-stage cryofocusing pre-concentration system (Entech 7100, Entech Instruments) and analyzed with a GC (HP-7890A, Agilent Technologies, Santa Clara, CA, USA). A PLOT (AL/KCL) column with a FID was used to separate and analyze most of the C2–C4 hydrocarbons. A DB-624 column with a MSD (HP-5975C, Agilent Technologies) was used to measure additional NMHCs.

3　Correlations between VOC species and CO

In order to check whether VOC emission ratios between day and night is different, correlations between several species with long atmospheric lifetime and CO at the PKU site during summer were analyzed. The calculated ratios for ethane, propane, *n*-butane, benzene, and acetone relative to CO using measurement data of 03:00–07:00 LT and all data agrees very well (Fig. S2), suggesting that VOC emission ratios during daytime and nighttime do not change.
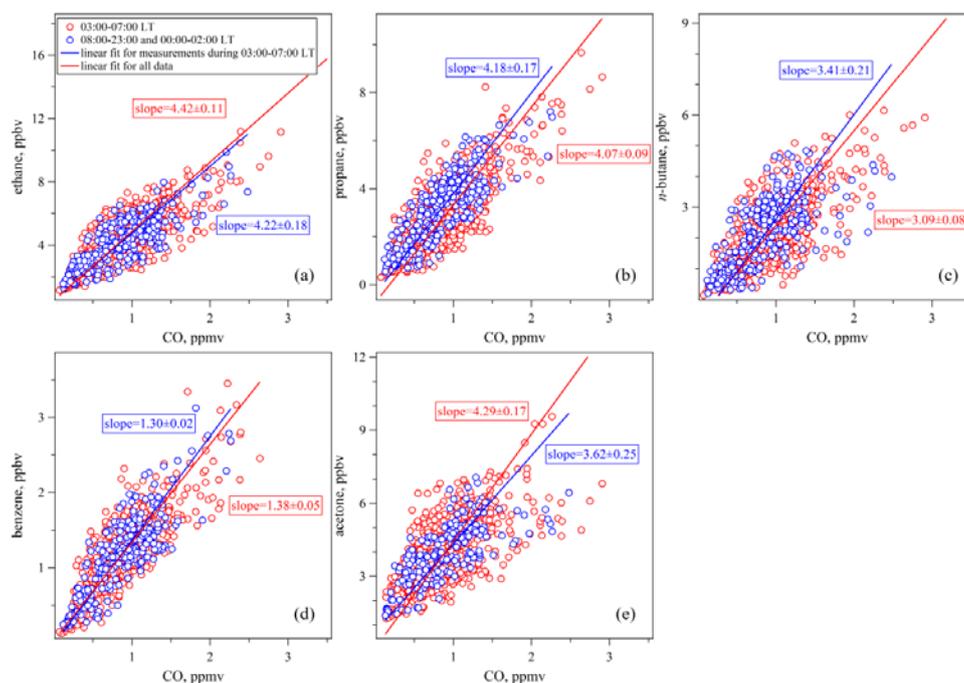
Fig. S2　Scatter plots of ethane, propane, *n*-butane, benzene, and acetone with CO at the PKU site during Aug.–Sep., 2011. The two-sided linear fit (ODR) is applied on measurement data of 03:00–07:00 LT and all data.

4　Average emission ratios of VOC in Beijing

The average emission ratios for VOC at 27 sites in Beijing can be calculated by

two approaches. The first method is to derive the slope of measured VOC mixing ratios to CO levels using the ODR linear regression fit for regional measurement data at 09:00 LT from all sites (the "linear regression" method). The standard deviations of linear regression slopes correspond to the standard deviations of average VOC emission ratios for regional sites. The relative standard deviations (RSD) of emission ratios for most VOC species were lower than 20%. The other method to calculate average value and standard deviation of VOC emission ratios in Beijing is based on the calculated VOC emission ratios at each regional site. For the VOC regional measurements in Beijing, there are two samples (09:00 and 13:00 LT) that were collected at each site during each month. VOC emission ratios at each site were calculated only based on 09:00 data due to the influence of photochemical processing on 13:00 data. Considering the limited data at each site (i.e. 6 data for winter, and 10 data for summer), the VOC emission ratio at each site was estimated as the average value of VOC/CO ratios in each sample (the "average" method). Average VOC emission ratios of Beijing calculated using "average" and "linear regression" methods showed a good agreement, with slope of 1.01 and r of 0.98 (Fig. S3). However, the relative standard deviations of VOC emission ratios calculated using the "average" method were larger than those determined by the "linear regression" method, with values in the range of 23–71%.
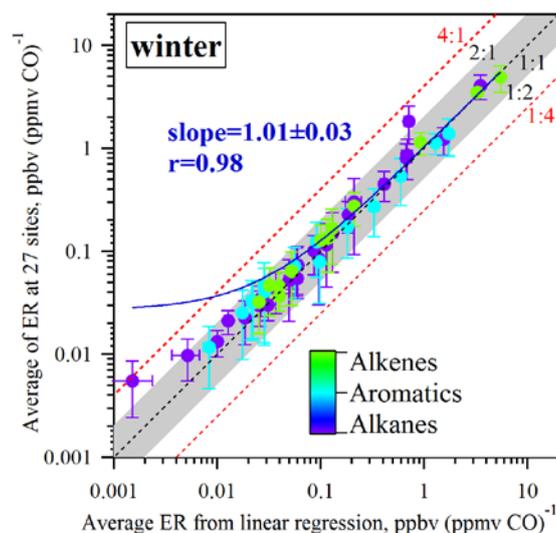
Fig. S3 Comparison of average VOC emission ratios at 27 sites calculated using the "average" and "linear regression" methods. The error bars correspond to the standard deviations of average VOC emission ratios.

Emission ratios for most VOC species determined at the PKU site agreed with average emission ratios of Beijing calculated using both methods within a factor 2 (Fig. S4 and Fig. 8a in the revised manuscript), with *r* of 0.98–0.99 and linear regression slope of 0.91, indicating that VOC emission ratios determined at the PKU site can represent the urban mixture of VOC anthropogenic emissions in Beijing.
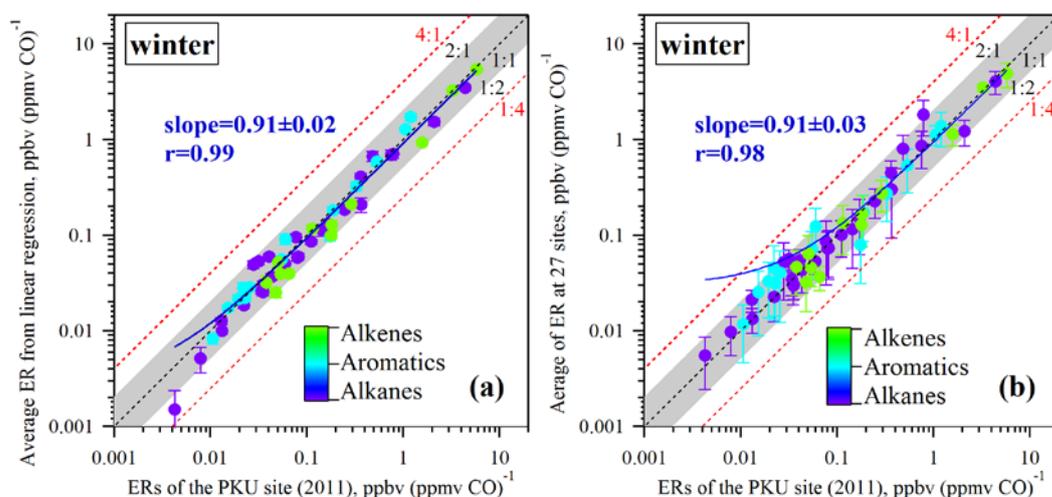
Fig. S4 Comparison of VOC emission ratios determined at the PKU site with average emission ratios in Beijing calculated using (a) "average" and (b) "linear regression"

method. The error bars correspond to the standard deviations of average VOC emission ratios.

5 VOC source apportionment by CMB model

5.1 Fitting species for CMB application in this study

Table S3　Fitting species for CMB application in this study.

Alkanes		unsaturated NMHCs	
ethane	2,2-dimethylbutane	acetylene	styrene[*]
propane	methylcyclopentane	ethene[*, a]	o-xylene[*]
i-butane	2-methylhexane	propene[*]	*i*-propylbenzene[*]
n-butane	3-methylhexane	*trans*-2-butene[*]	*n*-propylbenzene[*]
i-pentane	*n*-heptane	*cis*-2-butene[*]	1,3,5-trimethylbenzene[*]
n-pentane	2-methylheptane	benzene	1,2,4-trimethylbenzene[*]
2-methylpentane	3-methylheptane	toluene	1,2,3-trimethylbenzene[*]
3-methylpentane	*n*-nonane	ethylbenzene[*]	isoprene
n-hexane		*m,p*-xylene[*]	

[a] The species marked by asterisk (*) were used as fitting species for CMB modelling based on emissions, but not for CMB modelling based on measurement data.

5.2 CMB performance

Table S4　CMB performance parameters for three VOC datasets in Beijing.

VOC datasets for CMB model	Number of data (N)	R^{2} [c]	χ^{2} [c]	% Conc. [c]
Regional measurement at 27 sites in Beijing	844	0.65–0.98 (0.85)	0.55–6.01 (2.27)	81–118 (94)
Online measurement at PKU site during summer, 2011	1131 [b]	0.77–0.98 (0.89)	0.68–4.00 (2.00)	82–109 (102)
Online measurement at PKU site during winter, 2011 [a]	369	0.87–0.98 (0.94)	0.52–3.17 (1.64)	92–100 (101)
Total measurement data	2344	0.65–0.98 (0.88)	0.52–6.01 (2.04)	81–118 (99)
Annual emissions of NMHC derived from measurements [a]	1	0.93	0.78	94

[a] Biogenic emission was excluded when running CMB model for wintertime measurement data and NMHC emissions derived from measurements.

[b] VOC measurement data obtained during raining period (August 14, 15, 25 and September 8, 10 during 2011) were excluded when running CMB.

[c] Numbers in parenthesis are the average values of CMB performance parameters (r^2, χ^2, and %

Conc.).

6   The annual emission of individual VOC species

Table S5 listed the derived summertime and wintertime emission ratios and the estimated annual emissions for individual VOC species.

Table S5　Emission ratios and annual emission strengths of anthropogenic VOC species calculated based on measurement data.

Species	ERs, ppbv (ppmv CO)$^{-1}$		Annual Emission*, Gg/year	Species	ERs, ppbv (ppmv CO)$^{-1}$		Annual Emission, Gg/year
	Summer	Winter			Summer	Winter	
Alkanes	--	--	**143.11±66.55**	**Alkenes**	--	--	**50.35±24.73**
ethane	4.34±0.15	4.41±0.15	21.94±12.86	ethylene	4.44±0.07	5.79±0.14	23.86±10.20
propane	3.90±0.07	2.10±0.07	22.21±9.51	Propene	1.39±0.03	1.58±0.05	10.39±5.23
i-butane	2.51±0.04	0.75±0.03	16.03±6.87	*trans*-2-butene	0.42±0.01	0.18±0.01	2.81±1.65
n-butane	2.50±0.05	0.79±0.05	16.15±6.94	1-butene	0.54±0.01	0.29±0.01	3.88±2.27
cyclopentane	0.11±0.01	0.03±0.00	0.84±0.37	*cis*-2-butene	0.37±0.01	0.11±0.01	2.32±1.37
i-pentane	1.98±0.08	0.48±0.02	15.05±6.46	1,3-butadiene	0.16±0.01	0.18±0.01	1.67±1.05
n-pentane	1.20±0.02	0.36±0.02	9.50±4.08	1-pentene	0.10±0.00	0.05±0.00	0.88±0.52
2,2-dimethylbutane	0.04±0.00	0.01±0.00	0.37±0.16	*trans*-2-pentene	0.14±0.01	0.05±0.00	1.11±0.66
2,3-dimethylbutane	0.18±0.02	0.03±0.00	1.58±0.70	*cis*-2-pentene	0.13±0.01	0.05±0.00	1.05±0.62
2-methylpentane	0.61±0.01	0.25±0.01	6.23±2.67	1-hexene	0.10±0.00	0.07±0.00	1.14±0.68
3-methylpentane	0.51±0.02	0.17±0.01	4.95±2.13	isoprene	0.05±0.01	0.06±0.00	0.57±0.46
n-hexane	0.57±0.01	0.37±0.02	6.78±2.91	**Aromatics**	--	--	**98.65±45.47**
2,4-dimethylpentane	0.03±0.00	0.01±0.00	0.38±0.17	benzene	1.24±0.02	1.06±0.03	15.00±6.42
methylcyclopentane	0.30±0.01	0.14±0.01	3.16±1.39	toluene	2.41±0.05	1.20±0.05	27.93±11.97
2-methylhexane	0.14±0.01	0.08±0.00	1.81±0.80	ethylbenzene	0.97±0.08	0.33±0.02	11.63±5.04
cyclohexane	0.14±0.01	0.08±0.00	1.52±0.68	*m,p*-xylene	1.56±0.04	0.53±0.03	18.74±8.05
2,3-dimethylpentane	0.08±0.00	0.04±0.00	1.01±0.45	*o*-xylene	0.59±0.01	0.19±0.01	7.01±3.01
3-methylhexane	0.23±0.01	0.08±0.00	2.64±1.17	styrene	0.41±0.01	0.17±0.03	5.12±3.10
2,2,4-trimethylpentane	0.02±0.00	0.01±0.00	0.24±0.11	*i*-propylbenzene	0.03±0.00	0.01±0.00	0.46±0.28
n-heptane	0.20±0.01	0.11±0.01	2.62±1.16	*n*-propylbenzene	0.06±0.00	0.02±0.00	0.77±0.46
methylcyclohexane	0.11±0.01	0.04±0.00	1.25±0.56	*m*-ethyltoluene	0.23±0.01	0.05±0.00	2.85±1.70
2,3,4-trimethylpentane	0.01±0.00	0.00±0.01	0.11±0.05	*p*-ethyltoluene	0.09±0.00	0.03±0.00	1.15±0.69
2-methylheptane	0.07±0.00	0.03±0.02	1.00±0.62	1,3,5-trimethylbenzene	0.11±0.01	0.02±0.00	1.31±0.79
3-methylheptane	0.05±0.00	0.02±0.03	0.73±0.73	*o*-ethyltoluene	0.09±0.00	0.02±0.00	1.10±0.66
n-octane	0.12±0.01	0.06±0.04	1.74±1.08	1,2,4-trimethylbenzene	0.35±0.01	0.06±0.00	4.22±2.52
n-nonane	0.15±0.01	0.04±0.05	1.97±1.74	1,2,3-trimethylbenzene	0.11±0.01	0.02±0.00	1.35±0.81
n-decane	0.08±0.01	0.03±0.06	1.34±1.68				

continued

Species	ERs, ppbv (ppmv CO)$^{-1}$		Annual Emission, Gg/year	Species	ERs, ppbv (ppmv CO)$^{-1}$		Annual Emission, Gg/year
OVOCs	--	--	111.92±56.98	**Others**			
Methanol	13.75±0.61	7.91±0.39	58.30±29.85	Acetylene	3.67±0.38	3.26±0.2	15.06±6.56
Formaldehyde	2.89±0.22	3.00±0.15	14.52±7.46				
Acetaldehyde	1.50±0.10	0.86±0.04	8.73±4.48				
Propanal	0.11±0.01	0.08±0.01	0.96±0.50				
n-Butanal	0.06±0.01	0.03±0.00	0.49±0.27				
n-Pentanal	0.06±0.01	0.02±0.01	0.52±0.33				
n-Hexanal	0.20±0.03	0.15±0.01	3.36±1.76				
Acetone	2.95±0.13	0.93±0.04	19.07±9.76				
Methylethylketone	0.68±0.05	0.30±0.02	5.97±3.07				

* The standard deviation of VOC emission (U_E) was calculated used the equation: $U_E = \sqrt{U_M{}^2 + U_{OH}{}^2 + U_{ER}{}^2 + U_{CO}{}^2}$. U_M, U_{OH}, U_{ER}, and U_{CO} are the uncertainty of VOC measurements, OH exposure, emission ratio, and CO emission.

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