Validation of emission inventories by measurements of ambient volatile organic compounds in Beijing, China

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1 Comparisons of anthropogenic NMVOCs emissions

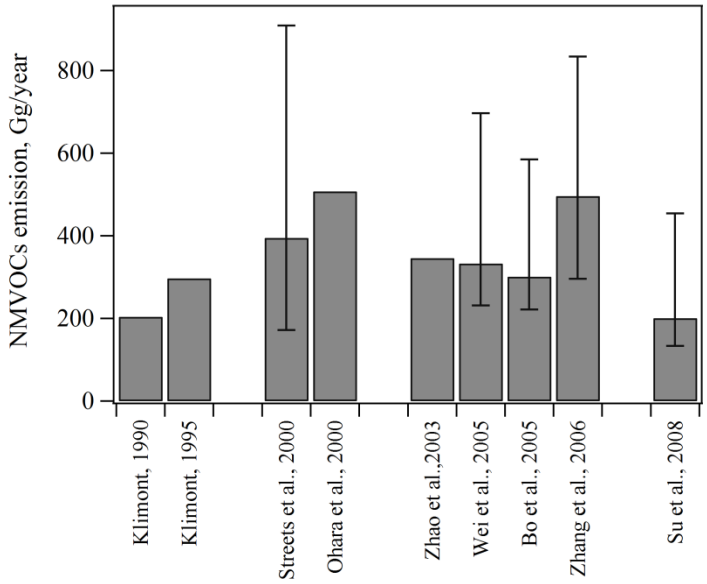

Fig. S1 Comparison of anthropogenic NMVOCs emissions from different emission inventories (Klimont et al., 2002; Streets et al., 2003; Ohara et al., 2007; Bo et al., 2008; Wei et al., 2008; Zhang et al., 2009; Su et al., 2011; Zhao et al., 2012).

2 VOCs sampling and analysis

2.1 The sampling sites of VOCs grid study in Beijing

Table S1 Summaries of sampling sites in this campaign

Sites Category	Urban	Suburban_South	Suburban_North	Rural	Roadside
Sites Count	8	6	8	2	3
Sites No.	BI1	BOE1	BONE2	BOW1	R1
	BI2	BOS1	BONE3	BOW2	R2
	BI3	BOS2	BONE4		R3
	BI4	BOS3	BOE2		
	BI5	BOS4	BONW1		
	BI6	BOSE	BONW2		
	BI7		BONW3		
	BONE1		BONW4		

2.2 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_2O_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.

2.3 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 The annual emission of individual VOC species

Table S2 listed the derived summertime and wintertime emission ratios and the estimated annual emissions for individual VOC species.

Table S2 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	*t*-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	*c*-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	*t*-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	*c*-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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