Quality Control and Quality Assurance

Before sampling, all canisters were flushed at least five times by repeatedly filling and evacuating humidified zero air. In order to check if there was any contamination in the canisters, all canisters were evacuated after the cleansing procedures, re-filled with pure nitrogen, stored in the laboratory for at least 24 h, and then analyzed the same way as field samples to make sure that all the target VOC compounds were not present.

Target compounds were identified based on their retention times and mass spectra, and quantified by external calibration method. C_4–C_{12} hydrocarbons were determined based on MSD signals, while C_2 and C_3 hydrocarbons were determined based on FID signals. The calibration standards were prepared by dynamically diluting the 100 ppbv Photochemical Assessment Monitoring Stations (PAMS) standard mixture (57 NMHCs) and TO-14 standard mixture (39 compounds) from Spectra Gases Inc., NJ, USA to 0.5, 1, 5, 15 and 30 ppbv. The calibration curves were obtained by running the five diluted standards plus humidified zero air the same way as the field samples. The analytical system was challenged daily with a one-point (typically 1 ppbv) calibration before running air samples. If the response was beyond +/−10% of the initial calibration curve, recalibration was performed. The method detection limits (MDLs) for each NMHC species were presented in Table S2. The measurement accuracy and precision for C_2–C_4 alkenes are within 5% and 3%, respectively.

Table S1. Weather information during the sampling periods

Sampling Site	Sampling Date	Temperature (° C)	Relative Humidity (%)	Wind Speed (m/s)	Air Pressure (hpa)	Rainfall (mm)	Cloud Amount (%)
Guangzhou	2012.09.03	27.0	83	1.9	1001	0	74
	2012.09.10	28.4	81	1.0	1002	0	65
	2012.09.19	25.3	72	2.1	1003	0	94
	2012.09.20	25.4	80	1.5	1004	0	100
	2012.09.21	27.0	77	2.1	1003	0	79
Shenzhen	2012.10.11	25.9	48	2.3	1006	0	9
	2012.10.12	25.0	71	2.0	1006	0	19
	2012.10.13	25.0	74	2.0	1005	0	23
	2012.10.14	25.6	80	1.8	1006	0	21
	2012.10.15	26.5	74	1.5	1008	0	50
	2012.10.16	26.0	78	1.8	1007	0	45
Chengdu	2012.09.13	20.3	70	1.0	956	0	90
	2012.09.14	20.1	77	0.9	954	0.3	100
	2012.09.15	17.4	92	1.6	952	6.3	100
	2012.09.16	16.4	93	1.5	954	9.0	100
	2012.09.17	17.9	82	0.6	955	0	78
	2012.09.18	17.9	82	0.5	952	0	83
	2012.09.19	18.3	84	0.8	950	0	88
	2012.09.20	18.9	88	0.9	949	3.0	100

Table S2. The method detection limit (MDL, pptv) for each NMHC species

Alkanes	MDL	Alkenes	MDL	Aromatics	MDL
ethane	39	Ethene	41	Benzene	14
propane	31	Propene	31	Toluene	9
n-Butane	21	1-Butene	17	Ethylbenzene	6
i-Butane	17	trans-2-Butene	13	o-Xylene	4
n-Pentane	8	cis-2-Butene	11	m/p-Xylene	9
i-Pentane	14	1,3-Butadiene	20	Isopropylbenzene	4
2,2-dimethylbutane	14	2-methyl-1-Butene	12	n-Propylbenzene	4
2,3-dimethylbutane	12	3-methyl-1-Butene	12	2-Ethyltoluene	3
Cyclopentane	12	2-methyl-2-Butene	12	3-Ethyltoluene	3
2-Methylpentane	8	1-Pentene	20	4-Ethyltoluene	3
3-Methylpentane	7	trans-2-Pentene	10	1,3,5-Trimethylbenzene	3
n-Hexane	6	cis-2-Pentene	6	1,2,4-Trimethylbenzene	6
2,3-Dimethylpentane	9	Isoprene	13	1,2,3-Trimethylbenzene	5
2,4-Dimethylpentane	4	Cyclopentene	14	p-Diethylbenzene	4
Methylcyclopentane	9	4-methyl-1-Pentene	12	m-Diethylbenzene	4
2-Methylhexane	6	1-Hexene	12	1,3-Diethylbenzene	4
3-Methylhexane	6	3-Hexene	12	Styrene	8
Cyclohexane	6	α- Pinene	9	**Alkynes**	**MDL**
Methylcyclohexane	5	β- Pinene	5	Ethyne	57
2,2,4-Trimethylpentane	9				
2,3,4-Trimethylpentane	6				
n-Heptane	10				
2-Methylheptane	4				
3-Methylheptane	5				
n-Octane	6				
n-Nonane	6				
n-Decane	6				
n-Undecane	7				
n-Dodecane	7				

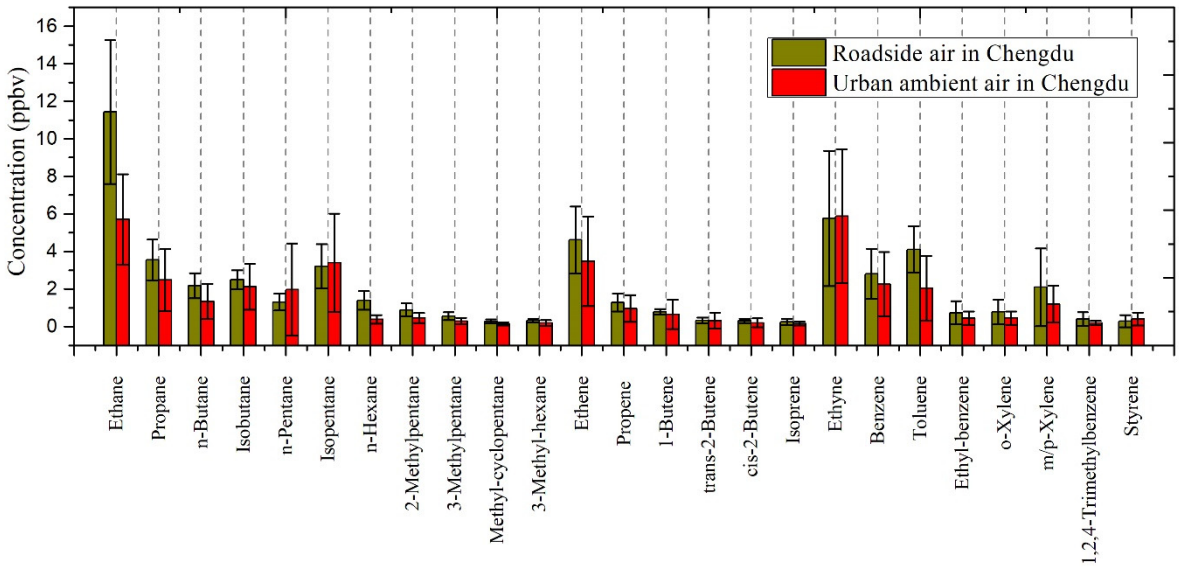

Fig. S1. Comparison of major NMHCs species of roadside and urban ambient air in Chengdu.