

26 respectively.

27 **Table S1.** Weight percentage (wt.%) of individual VOC from different vehicle types and gas
 28 evaporation.

VOC species	LDGV	Taxi	HDDT	Bus	Motorcycle	Gas evaporation
Ethane	0.45±0.07	0.41±0.03	0.82±0.51	0.46±0.15	2.88±1.20	ND
Propane	0.03±0.03	0.04±0.02	2.35±1.55	1.26±1.19	1.09±0.75	19.59±2.68
n-butane	0.53±0.08	0.48±0.06	0.25±0.14	0.27±0.13	1.33±0.45	7.89±3.41
n-pentane	2.31±0.23	2.52±0.27	0.51±0.21	0.34±0.05	0.87±1.24	5.27±1.54
n-hexane	3.04±0.55	2.97±0.17	0.53±0.19	0.98±0.74	2.88±1.22	1.32±0.56
n-heptane	1.60±0.21	1.47±0.09	1.04±0.33	0.92±0.38	2.33±1.21	0.54±0.50
n-octane	2.51±0.31	3.06±1.11	1.69±0.62	1.20±1.08	0.58±0.30	ND
n-nonane	0.96±0.12	0.98±0.18	3.79±1.11	3.56±1.17	0.25±0.23	ND
n-decane	3.95±0.47	3.51±0.71	6.62±1.27	7.10±2.66	0.15±0.14	ND
n-undecane	0.38±0.08	0.52±0.41	9.78±3.27	7.60±0.44	0.06±0.10	ND
n-dodecane	0.16±0.02	0.29±0.07	11.36±2.61	15.94±11.44	0.06±0.09	ND
Isobutene	0.24±0.05	0.27±0.03	0.35±0.12	0.59±0.72	1.47±0.43	11.73±5.85
Isopentane	2.97±0.20	2.85±0.29	2.02±0.67	1.60±1.30	2.54±2.32	14.27±2.94
2,2-dimethylbutane	0.72±0.40	0.86±0.44	ND	ND	0.43±0.15	1.30±0.98
2,3-dimethylbutane	1.02±0.17	1.16±0.10	1.41±1.57	ND	1.29±0.48	0.60±0.18
2-methylpentane	2.27±0.15	1.9±0.31	0.52±0.33	ND	1.90±0.97	1.96±0.50
3-methylpentane	2.05±0.51	1.84±0.41	1.43±0.50	0.58±0.73	2.00±0.83	0.90±0.30
2-methylhexane	1.26±0.38	1.31±0.31	0.52±0.40	0.43±0.10	23.43±10.72	1.28±0.88
3-methylhexane	1.10±0.23	0.90±0.10	0.89±0.86	0.68±0.22	1.55±0.29	0.35±0.10
2,4-dimethylpentane	0.02±0.01	0.05±0.01	ND	0.35±0.26	0.61±0.30	0.13±0.16
2,3-dimethylpentane	1.02±0.32	0.68±0.08	0.61±0.41	0.18±0.00	1.36±0.51	0.06±0.07
2,3,4-trimethylpentane	0.11±0.04	0.16±0.02	ND	0.60±0.57	0.48±0.64	0.07±0.14
3-methylheptane	1.61±0.19	1.61±0.23	1.01±0.32	1.01±0.58	0.68±0.46	ND
2,2,4-trimethylpentane	1.39±0.52	1.03±0.17	1.04±0.67	0.60±0.01	0.91±0.85	0.87±0.88
2-methylheptane	1.96±0.18	1.96±0.23	1.00±0.24	1.04±0.90	0.55±0.31	ND
Cyclopentan	1.36±0.44	1.28±0.14	0.03±0.01	0.04±0.02	1.17±0.33	0.04±0.04
Cyclohexane	0.48±0.12	0.35±0.04	ND	ND	0.98±0.70	1.41±1.74
Methylcyclopentane	2.63±0.15	2.62±0.82	0.07±0.02	0.10±0.06	1.31±0.48	0.68±0.20
Methylcyclohexane	1.68±0.66	0.95±0.17	0.24±0.06	0.34±0.26	0.77±0.48	0.07±0.09
Ethene	0.40±0.08	0.37±0.05	0.75±0.47	0.43±0.13	3.13±1.49	2.94±2.07
Propene	1.18±0.68	1.92±0.34	9.78±1.33	11.92±0.18	0.79±0.42	2.05±0.15
1,3-butadiene	0.01±0.00	0.02±0.02	ND	ND	0.04±0.02	0.04±0.02
1-butene	2.05±0.25	2.03±0.34	1.17±0.61	0.88±0.10	1.76±0.65	3.90±1.09
trans-2-butene	0.19±0.13	0.24±0.05	0.24±0.10	0.22±0.08	0.40±0.53	3.64±0.84
cis-2-butene	0.27±0.01	0.86±1.27	0.15±0.06	0.16±0.06	0.54±0.36	1.79±0.72
isoprene	0.03±0.01	0.03±0.02	ND	ND	0.05±0.02	0.06±0.08
trans-2-pentene	0.95±0.24	0.53±0.07	0.16±0.11	0.13±0.01	0.36±0.22	0.64±0.09
cis-2-Pentene	0.38±0.18	0.76±0.13	0.08±0.04	0.07±0.00	0.27±0.27	2.68±0.22

1-pentene	0.35±0.12	0.27±0.02	1.10±0.77	0.72±0.02	0.65±0.33	10.13±2.77
1-hexene	0.74±0.21	1.26±0.59	1.78±1.51	1.32±0.27	1.59±0.98	1.10±0.59
Ethyne	0.40±0.05	0.36±0.02	0.74±0.46	0.42±0.15	2.54±1.23	ND
Benzene	2.90±0.53	2.88±0.33	3.37±0.75	2.92±0.55	1.34±0.33	0.09±0.02
Toluene	7.37±0.1	7.72±0.71	3.02±0.61	2.3±2.11	2.50±0.81	0.34±0.09
Styrene	2.09±0.23	2.21±0.31	0.12±0.02	0.24±0.13	0.23±0.10	0.01±0.01
Ethylbenzene	4.3±0.23	4.53±0.37	0.95±0.13	0.94±0.79	5.53±5.26	0.03±0.01
m,p-Xylene	7.53±0.56	5.88±0.52	2.13±0.33	2.44±0.78	9.34±6.48	0.02±0.02
o-Xylene	5.55±0.46	4.85±0.38	0.74±0.07	0.91±0.26	4.37±5.00	0.02±0.00
1,3,5-trimethylbenzene	1.82±0.07	1.91±0.31	0.35±0.06	0.45±0.14	0.55±0.49	0.01±0.01
1,2,4-trimethylbenzene	3.48±0.26	3.55±0.32	1.15±0.31	1.56±0.73	0.65±0.53	ND
isopropylbenzene	0.49±0.11	0.63±0.04	0.08±0.02	0.10±0.02	0.12±0.07	ND
n-propylbenzene	0.71±0.09	0.72±0.08	0.24±0.04	0.30±0.10	0.30±0.16	ND
m-ethyltoluene	0.49±0.19	0.57±0.15	0.55±0.24	0.93±0.44	0.37±0.32	ND
p-ethyltoluene	2.32±0.99	3.52±0.40	0.32±0.09	0.49±0.22	0.20±0.15	ND
o-ethyltoluene	1.15±0.34	1.49±0.37	0.20±0.14	0.20±0.07	0.31±0.23	ND
1,2,3-trimethylbenzene	1.77±0.24	2.11±0.43	0.73±0.15	1.04±0.43	0.29±0.3	ND
m-diethylbenzene	0.69±0.16	0.79±0.47	0.22±0.06	0.42±0.26	ND	ND
p-diethylbenzene	0.87±0.18	1.11±0.18	0.56±0.84	2.58±3.26	ND	ND
Acetone	0.63±0.12	0.42±0.07	7.53±4.57	6.47±1.26	0.55±0.54	ND
isopropanol	0.06±0.03	0.04±0.01	ND	1.09±1.17	0.01±0.01	ND
methyl-ethyl-ketone	0.05±0.01	0.05±0.03	1.83±1.24	1.42±0.64	ND	ND
Tetrahydrofuran	0.07±0.01	0.07±0.01	0.21±0.07	0.19±0.04	ND	ND
Vinylacetate	0.01±0.01	0.01±0.01	2.32±0.81	1.41±0.04	ND	ND
Dioxane	0.01±0.00	0.02±0.01	ND	ND	ND	ND
Ethylacetate	0.09±0.01	0.10±0.02	0.87±0.21	1.07±0.06	1.12±0.47	ND
Methyl-tertbutyl-ether	0.08±0.00	0.11±0.03	0.28±0.06	0.46±0.28	3.96±1.96	ND
4-methyl-2-pentanone	0.14±0.03	0.10±0.02	0.2±0.04	0.25±0.01	ND	ND
2-hexanone	0.03±0.02	0.10±0.02	0.55±0.21	0.39±0.11	ND	ND

29 2. Observation data of meteorological condition and air pollutant concentration

30 Fig. S1 shows the location of the monitoring site in this study. The site was on
31 the roof of a 5-floor building (15 m high above the ground) at Shanghai Academy of
32 Environmental Science (31.17°N, 121.43°E), which was located southwest of the
33 urban area of Shanghai. The site was mostly surrounded by commercial properties
34 and residential dwellings. Vehicle exhaust was a major source of pollutants near this
35 site.

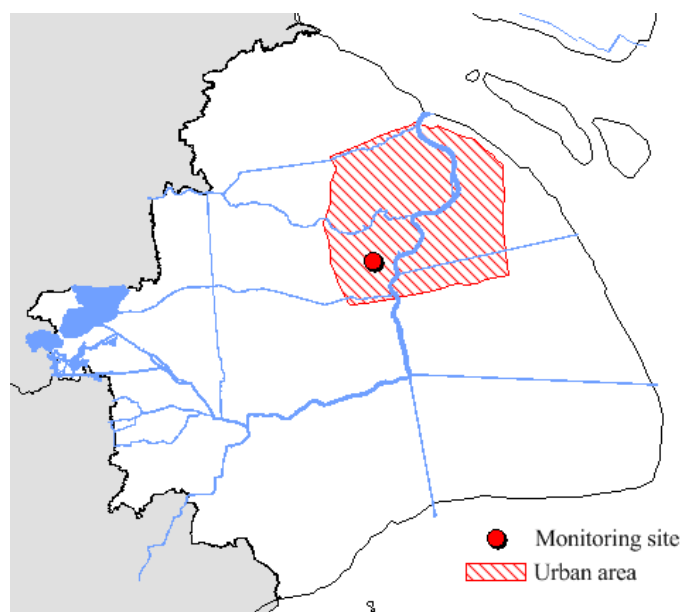


Fig. S1. Location of the monitoring site.

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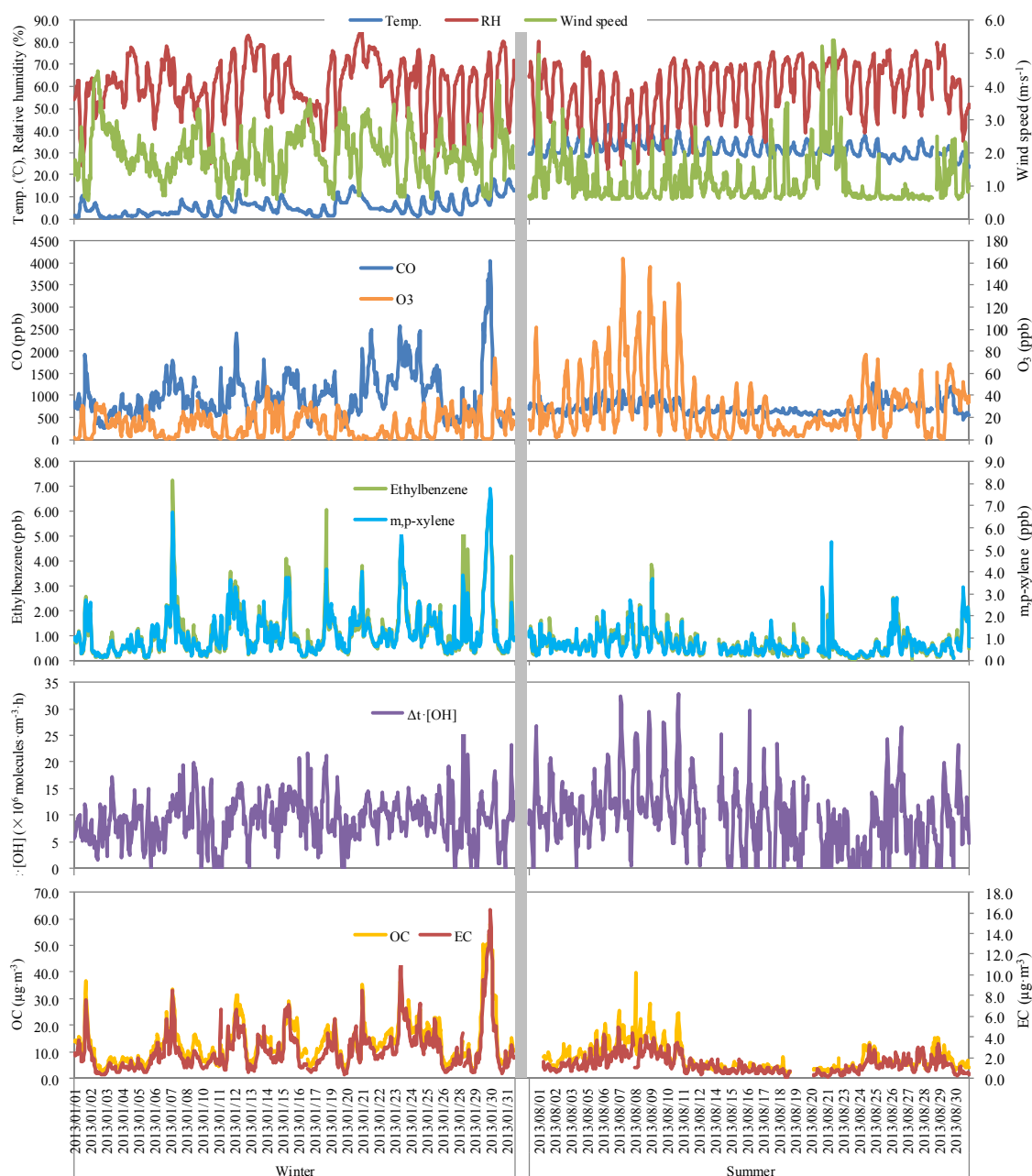
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38 Fig. S2 shows time series observation data of meteorology parameters and CO,
 39 O₃, VOCs species, OC, and EC concentration in summer (from January 1 to January
 40 31) and winter (from August 1 to August 31) in the atmosphere of Shanghai urban in
 41 2013. Detail information of the monitoring site was introduced by Qiao et al. (2014).
 42 During the winter observation, air temperature varied in the range of -0.8-18.0°C and
 43 the average temperature was 5.5±3.8°C. Relative humidity (RH) fluctuated in the
 44 range of 23.3-84.9% and the average RH was 59.8±12.9%. Wind speed was in the
 45 range of 0.6-4.5m·s⁻¹ and the average wind speed was 2.0±0.7m·s⁻¹. The average
 46 concentrations of CO, ethylbenzene, and m,p-xylene in winter were 993±544ppb,
 47 1.16±1.09ppb, and 1.27±1.11ppb. The maximum O₃ concentration was 74ppb. The
 48 average concentrations of OC and EC were 13.40±8.68μg·m⁻³ and 2.72±2.17μg·m⁻³.

49 During the summer observation, air temperature varied in the range of
 50 23.7-43.0°C and the average temperature was 31.9±3.8°C. Relative humidity (RH)
 51 fluctuated in the range of 22.6-80.4% and the average RH was 58.2±12.8%. Wind
 52 speed was in the range of 0.6-5.4m·s⁻¹ and the average wind speed was 1.2±0.8 m·s⁻¹.
 53 The average concentrations of CO, ethylbenzene, and m,p-xylene in summer were
 54 721±140ppb, 0.73±0.57ppb, and 0.26±0.21ppb. The maximum O₃ concentration was
 55 164ppb. The average concentrations of OC and EC were 7.44±4.81μg·m⁻³ and

56 $1.37 \pm 0.86 \mu\text{g} \cdot \text{m}^{-3}$.

57 Concentrations of CO, ethylbenzene, xylene, OC and EC showed good
58 consistency in the observation period. The photochemical exposure ($\Delta t \cdot [\text{OH}]$) was
59 calculated using Eq. (1). The figure indicates during the period with high ozone, the
60 OC/EC ratio and $\Delta t \cdot [\text{OH}]$ is much higher than during the other periods. More
61 secondary formation of OC can be expected during the high ozone period.



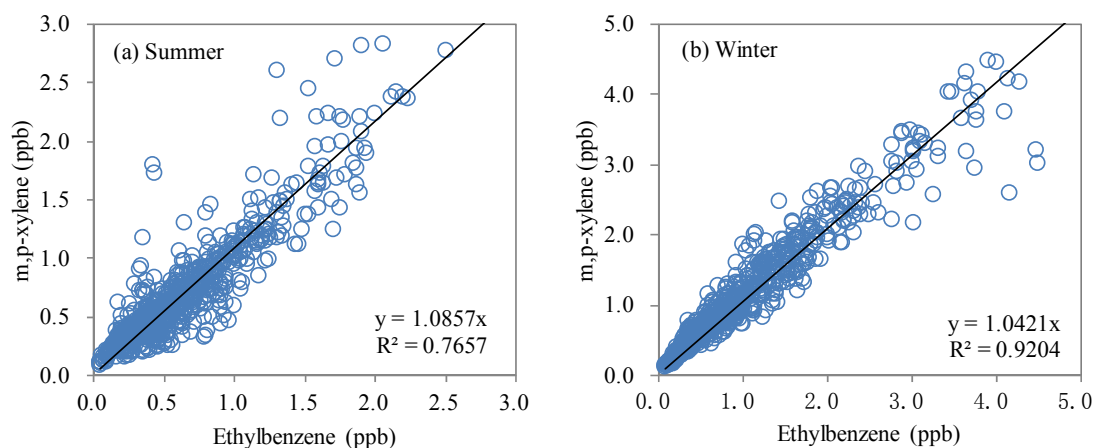
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63 **Fig. S2.** Time series observation data of meteorological condition and CO, O₃, ethylbenzene,

64 m,p-xylene, OC, and EC concentration in Shanghai urban in 2013.

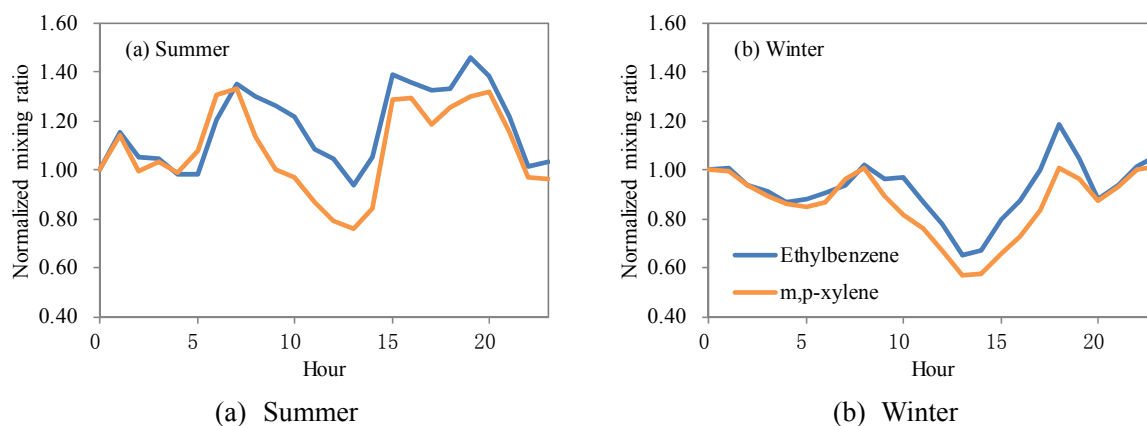
65 3. Correlation of ethylbenzene and m,p-xylene during the observation period

66 Fig. S3 shows the correlation of hourly ethylbenzene and m,p-xylene
67 concentration in the urban atmosphere during the observation period in Shanghai. It
68 was indicated that these two species presented strong correlation whether in
69 summer or winter. The ratios of m,p-xylene to ethylbenzene were 1.09 and 1.04, and
70 the correlation coefficients were 0.88 and 0.96 in summer and winter, respectively.
71 The correlation implied that two species mainly came from the same source.
72 According to the measured VOCs profiles from vehicle exhaust, vehicle emission
73 could be the major source of m,p-xylene to ethylbenzene.



74 **Fig. S3.** Correlation between ethylbenzene and m,p-xylene mixing ratios in summer and winter in
75 2013.

76 Fig. S4 shows the diurnal distribution of average concentrations of ethylbenzene
77 and m,p-xylene in summer and winter during the observation period. The average
78 concentrations of ethylbenzene and m,p-xylene were normalized to 1 at 0:00 am. It
79 was indicated that there was an obvious depletion of m,p-xylene compared with
80 ethylbenzene in daytime. And more m,p-xylene depletion was observed in summer
81 than in winter. On this account, we used the ratios of m,p-xylene to ethylbenzene to
82 characterize the photochemical age.

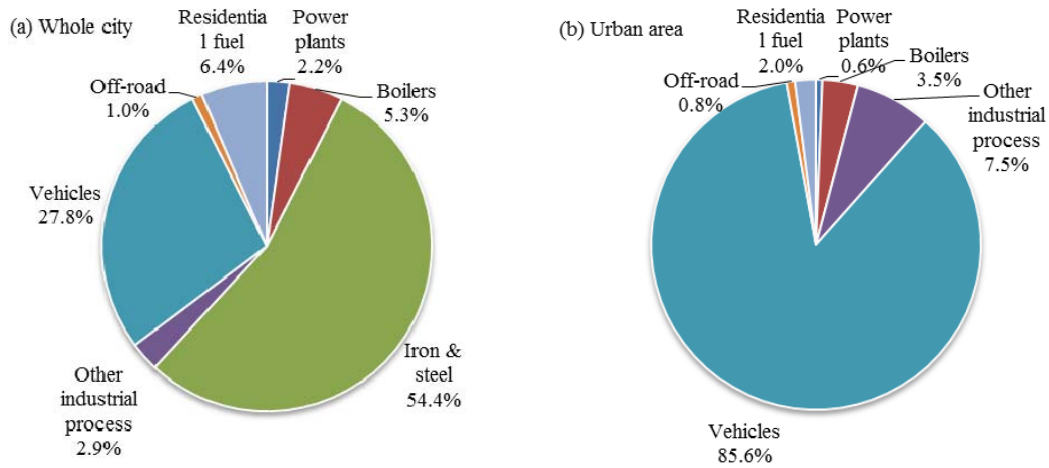


83 **Fig. S4.** Diurnal distribution of average concentrations of ethylbenzene and m,p-xylene in summer
 84 and winter in 2013.

85 **4. CO emission inventory in Shanghai**

86 Fig. S5 shows CO emission contribution of different sources in the whole city (a)
 87 and the urban area (b) of Shanghai in 2012. The methodology of CO emission
 88 inventory compilation has been introduced by Huang et al. (2011). The emission
 89 sources covered power plants, boilers, industrial processes including iron and steel
 90 manufacturing, oil refining, cement producing, etc., vehicles, off-road mobile sources,
 91 and residential fuel combustion. The activity data were updated to the year of 2012
 92 from the pollution source census data, national key pollution source list, and statistical
 93 yearbook. Total CO emission amount was 1236.1 tons for the whole city of Shanghai
 94 in 2012. Iron & steel manufacturing was the major source of CO emission, which
 95 accounted for 55% of the total. The sector produced 19.7×10^6 and 18×10^6 tons of pig
 96 irons and crude steels, and consumed more than 10×10^6 tons of coal in 2012. Vehicle
 97 was the second major source, taking up 27.8% of the total CO emission. In the urban
 98 area of Shanghai, vehicle dominated CO emission, comprising 85% of the total.

99



100

101 **Fig. S5.** CO emission contribution of different sources in the whole city (a) and the urban area (b)

102 of Shanghai in 2012.

103 **References**

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