Supplementary

Table S1. The OH reaction rate constant of each VOC (adapted from Carter, 2010).

Species	K_{VOC} (cm^3 $molecule^{-1}$ s^{-1})	Species	K_{VOC} (cm^3 $molecule^{-1}$ s^{-1})
Ethane	2.54E-13	2,3-Dimethylpentane	7.15E-12
Ethene	8.15E-12	3-Methylhexane	7.17E-12
Propane	1.11E-12	benzene	1.22E-12
Propene	2.60E-11	2,3,4-trimethylpentane	6.60E-12
i-Butane	2.14E-12	Heptane	6.81E-12
n-Butane	2.38E-12	Methylcyclohexane	9.64E-12
Acetylene	7.56E-13	1,2-Dimethylcyclopentane	6.82E-12
t-2-Butene	6.32E-11	2-Methylheptane	8.31E-12
1-Butene	3.11E-11	3-Methylheptane	8.59E-12
c-2-Butene	5.58E-11	Toluene	5.58E-12
Cyclopentane	5.02E-12	n-Octane	8.16E-12
i-Pentane	3.60E-12	Ethylbenzene*	7.10E-12
n-Pentane	3.84E-12	n-Nonane	9.75E-12
1-pentene	3.14E-11	m/p-Xylene*	1.90E-11
Isoprene	1.01E-10	o-Xylene	1.36E-11
2,2-Dimethylbutane	2.27E-12	Styrene	5.80E-11
2,3-Dimethylbutane	5.79E-12	i-Propylbenzene	6.30E-12
2-Methylpentane	5.20E-12	n-Propylbenzene	5.80E-12
3-Methylpentane	5.20E-12	3-Ethyltoluene	1.86E-11
n-Hexane	5.25E-12	4-Ethyltoluene	1.18E-11
2,4-Dimethylpentane	4.77E-12	n-Decane	1.10E-11
Methylcyclopentane	5.68E-12	1,3,5-Trimethylbenzene	5.67E-11
2-Methyhexane	6.89E-12	2-Ethyltoluene	1.19E-11
Cyclohexane	7.02E-12	1,2,4-Trimethylbenzene	3.25E-11

* Atkinson et al., 2006

The comparison between the source apportionment results with and without the adjustment of VOCs

To investigate the photochemical processing on the source apportionments of VOCs, observed VOC data (without the adjustment for photochemical losses) were input into the PMF model. Similar sources profiles and the same four anthropogenic sources (i.e., diesel vehicular emission, solvent usage, biomass burning, and gasoline vehicular emission were identified, however the sources made different contributions to ambient VOC abundance compared to those from the model with the adjustment of VOC concentrations (Fig. S1b). In the scenario without adjustment, gasoline vehicular emission contributed the most (32 ± 5%) to ambient VOCs, with the total concentrations of ~27 μg/m^3, followed by biomass burning (28 ± 4 %, ~24 μg/m^3), solvent usage (24 ± 5 %, ~21 μg/m^3), and diesel vehicular emission (15 ± 5 %, ~13 μg/m^3), which indicated the higher contributions of solvent usage and biomass burning and lower contributions of diesel vehicular emission in the scenario without adjustments than the scenario with adjustments. The main species of diesel vehicular emission (i.e., C_2-C_4 alkenes, styrene) had higher photochemical reactivity than those of solvent usage (i.e., heptane, methylcyclohexane, 2-methylheptane, and 3- methylheptane) and biomass burning (i.e., ethane, propane, cyclopentane) (Carter, 2010). Thus, VOCs emitted from diesel vehicular emission would be consumed faster than those emitted from solvent usage and biomass burning, which might result in different contributions of a particular source between the two scenarios. This indicates the importance of considering the influence of photochemical processing on VOCs, especially for species with high photochemical reactivity.

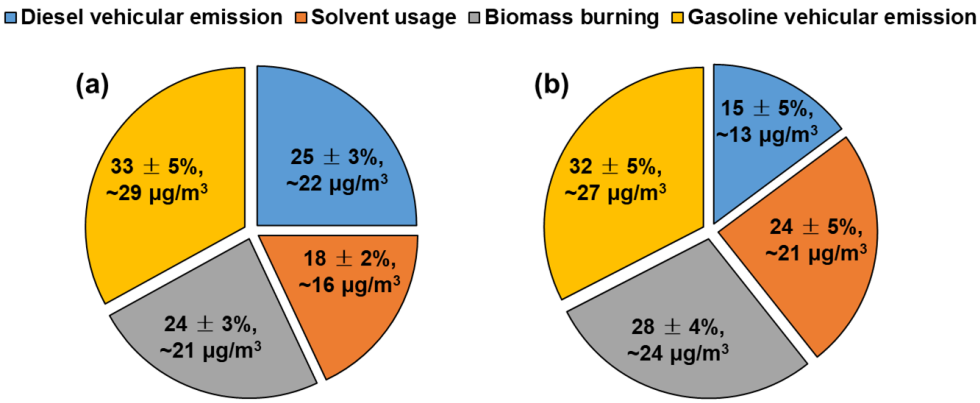

Figure S1. Contributions of different sources to ambient volatile organic compounds (VOCs) extracted from positive matrix factorization (PMF) in; (a) the scenario with adjustment, and (b) the scenario without adjustment.

Investigation on the potential source areas for VOCs at the Heshan site by backward trajectory analysis

To roughly identify the potential source areas of VOCs, 24-h air masses backward trajectories in 3-h intervals were calculated, and 7 main types of backward trajectories were obtained through cluster analysis (Fig. S2), which were mostly passing through the center cities of PRD before arriving at the Heshan site. As the air mass age was calculated as about 3 hours by the photochemical-aged-based parameterization method, the position of 3-h backward trajectories of each type was extracted to determine the source areas. It was found that ~70% air masses were from the center cities of PRD (i.e., Foshan and Guangzhou), while ~30% were from the southeast of Jiangmen city and from the center of Zhongshan city, indicating that the air masses at the Heshan site were from or through the urban areas with significant anthropogenic emissions.

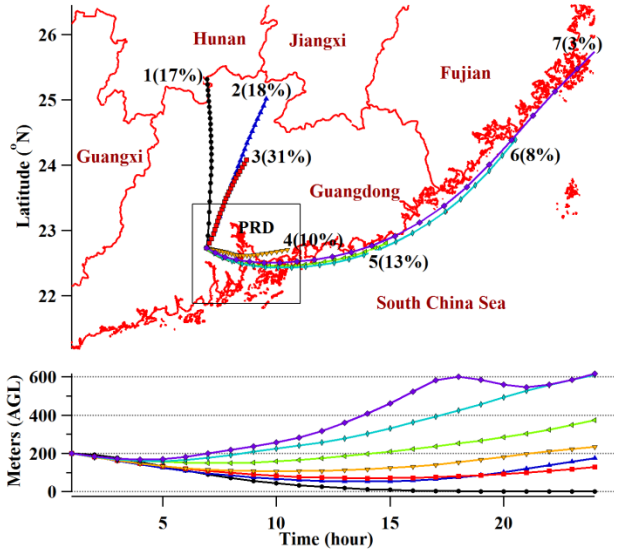

Figure S2. The seven clusters of 24-h air masses backward trajectories with Heshan as the ending point (the trajectories were simulated for 3-h intervals at the ending point of 200 m above sea level) (Ling et al., 2013).