Supporting Information

In total, 108 target species, including 29 alkanes, 11 alkenes, 18 aromatic hydrocarbons, 1 alkyne, 34 chlorocarbons, and 15 oxygenated volatile organic compounds, are listed in Table S1. Due to the detection limit of the laboratory analytical method, not all species could be detected in every sample, so the number of species detected at each point was different.

Table S1. The targeting species.

Alkane	Alkene	Chlorocarbon	OVOCs
Ethane	Ethylene	Chloromethane	Ethanol
Propane	Propylene	Chloroethane	Isopropanol
iso-Butane	1,3-Butadiene	Dichloromethane	Acrolein
n-Butane	1-Butene	Bromomethane	Acetone
Cyclopentane	trans-2-Butene	1,2-Dichloroethane	2-Butanone
n-Pentane	cis-2-Butene	1,1-dichloroethane	4-Methyl-2-pentanone
iso-Pentane	Isoprene	1,2-Dichloropropane	2-Hexanone
Cyclohexane	trans-2-Pentene	Trichloromethane	Tetrahydrofuran
Methylcyclopentane	cis-2-Pentene	Dichlorodifluoromethane	Methyl tert-butyl ether
2,3-Dimethylbutane	1-Pentene	1,1,1-Trichloroethane	Ethenyl ethanoate
n-Hexane	1-Hexene	1,1,2-Trichloroethane	Ethyl acetate
2,2-Dimethylbutane	**Alkyne**	Fluoro trichloro methane	Methyl methacrylate
2-Methylpentane	Acetylene	Bromodichloromethane	Carbon tetrachloride
3-Methylpentane	**Aromatic hydrocarbon**	1,1,2,2-tetrachloroethane	Carbon disulfide
Methylcyclohexane	Benzene	1,2-Dichlorotetrafluoroethane	1,4-dioxane
n-Heptane	Toluene	1,1,2-Trichlorotrifluoroethane	
2,4-Dimethylpentane	Styrene	1,2-Dibromoethane	
2-Methylhexane	Ethylbenzene	Chlorodibromomethane	
2,3-Dimethylpentane	m,p-Xylene	Tribromomethane	
3-Methylhexane	o-Xylene	Vinyl chloride	
2,2,4-Trimethylpentane	1,3,5-Trimethylbenzene	Vinylidene chloride	
2,3,4-Trimethylpentane	1,2,4-Trimethylbenzene	trans-1,2-Dichloroethylene	
2-Methylheptane	Isopropylbenzene	cis-1,2-Dichloroethene	
3-Methylheptane	n-Propylbenzene	cis-1,3-Dichloropropene	
n-Octane	m-Ethyltoluene	trans-1,3-Dichloropropene	
n-Nonane	p-Ethyltoluene	Trichloroethylene	
n-Decane	o-Ethyltoluene	Tetrachloroethylene	
Undecane	1,2,3-Trimethylbenzene	Hexachlorobutadiene	
Dodecane	4-Ethyltoluene	Chlorobenzene	
	m-Diethylbenzene	Benzyl chloride	
	p-Diethylbenzene	1,3-Dichlorbenzene	
	Naphthalene	1,4-Dichlorbenzene	
		1,2-Dichlorobenzene	
		1,2,4-trichlorobenzene	

The relatively high concentration of TFT-A was mainly due to the high concentrations of styrene, ethylbenzene, m,p-xylene, o-xylene, etc. at 8:00 (Fig. S1). Some studies have found that species such as styrene, ethylbenzene, m,p-xylene, and o-xylene are mainly related to emissions from solvent use (Liu *et al.*, 2008; Mo *et al.*, 2016), which indicates that the relatively high values at TFT-A at 8:00 can be attributed to contamination by sources in addition to traffic emission. To eliminate this possible contamination, the 8:00 TFT-A sample was not included in subsequent calculations.

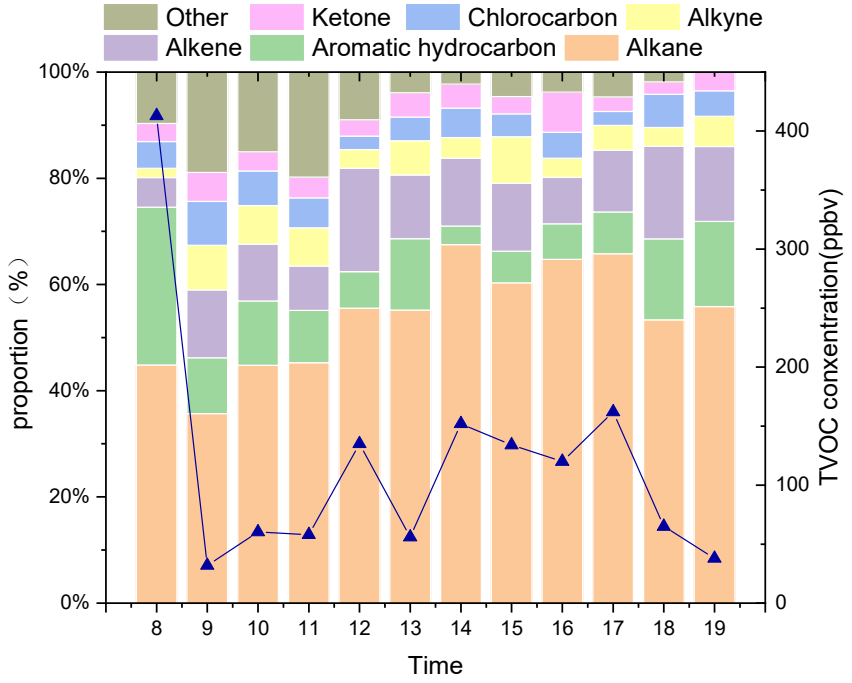

Figure S1. Temporal pattern of VOCs at the inlet of the Tianfu tunnel (TFT-A).

Quality Control and Quality Assurance

Each SUMMA canister was cleaned in the laboratory five times using a can cleaning system and then repeatedly rinsed with high-purity nitrogen to remove interfering substances before sampling. After cleaning, each SUMMA canister was placed under vacuum for 24 hours, and a pressure gauge was used to perform a leak check to ensure that the seal was intact. All tests were performed based on the EPA method. The measured VOCs were calibrated within a calibration range of 0.1-10 $\mu g \cdot L^{-1}$, and the calibration curve had an R^2 higher than 0.99. To control the background contamination generated during sampling, transport and analysis, field blanks were prepared during sampling and analysis. To control the interference introduced by laboratory reagents and other factors during analysis, high-purity nitrogen was injected into a clean sample canister as a laboratory blank. At least two blank samples and laboratory blank samples were measured for each batch of samples, and no target compounds or substances above the method detection limit were detected in any of the blank samples. In addition, to ensure the stability of the experimental analysis process, blank samples were analysed every 10 samples, and the relative deviation of parallel samples was less than 15%.