Supplementary material:

Ozone formation potential related with release of volatile organic compounds (VOCs) and nitrogen oxide (NO_X) from a typical industrial park in the Pearl River Delta

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Text S1

Measurement of VOCs

The collected VOC samples were detected using an Entech 7100 pre-concentrator (Entech Instruments Inc., CA, USA) and gas chromatography-mass spectrometer (7890A GC-5975C MS, Agilent Technologies, USA) based on the USEPA TO-15 method. Briefly, a volume of 200 mL sample was firstly extracted from each Summa canister to concentrate in the module 1 at -40 °C with liquid nitrogen. After baking at 150 °C, the sample escaped to module 2 and was trapped at -50 °C. Then the concentrated compounds were transferred to module 3 though baking at 220 °C and concentrated again at -180 °C. After 2.5 min, the VOCs were highly focused with quickly desorbed at 120 °C/min and swept into the column for the separation.

The GC oven temperature program used a DB-5 column (60 m × 0.32 mm × 0.25 μm, Agilent Technologies, USA) as followed: initially 35°C for 5 min, programmed to 150°C at a rate of 5 °C/min, and then to 250°C at a rate of 15 °C/min which was maintained for 2 min. The carrier gas is ultrahigh purity helium at a constant flow rate of 1.2 mL/min. Mass spectrometer conditions were set as follows: Ion source: EI source; ionizing energy: 70 eV; scan range: 45 − 260 amu; temperature of the transfer line: 290 °C. We used internal standard calibration to quantify the concentrations of VOCs, which was determined by standard samples Photochemical Assessment Monitoring Stations (PAMS) and TO-15 (Linde Spectra Environment Gases, USA). Bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 and 4-bromofluorobenzene were used as internal standards. The detailed steps of the pre-concentration GC-MS method can be found in previous works [1, 2]. Before measurement, all experimental instruments were calibrated. All steps were in accordance with the analytical procedures and the requirements of the TO-15 method compiled by US Environmental Protection Agency, including method detection limits (Table S2), field blanks, retention time, accuracy, accuracy repeats and reference sample analysis.

Text S2

The O_3 production in the AtChem Online model can be represented by (R1)-(R3):

$$HO_2 + NO \rightarrow NO_2 + OH \quad (R1)$$

$$RO_2 + NO \rightarrow NO_2 + HO_2 \quad (R2)$$

$$NO_2 + h\upsilon \rightarrow NO + O_3 \quad (R3)$$

The removed O_3 in the AtChem Online model can be represented by (R4)-(R8):

$$(O_3 + h\upsilon \rightarrow)\ O^1D + H_2O \rightarrow 2OH \quad (R4)$$

$$O_3 + \text{alkenes} \rightarrow \text{products} \quad (R5)$$

$$O_3 + OH \rightarrow HO_2 + O_2 \quad (R6)$$

$$O_3 + HO_2 \rightarrow OH + O_2 \quad (R7)$$

$$NO_2 + OH \rightarrow HNO_3 \quad (R8)$$

The net photochemical production rate of O_3 $P(O_3)$ can be expressed as follows:

$$P(O_3)=k_1[HO_2][NO]+k_2[RO_2][NO]-k_4[O^1D][H2O]-k_5[O_3][\text{alkenes}]-k_6[O_3][OH]-k_7[O_3][HO_2]-k_8[NO_2][OH]$$

where the k values in the equation represent the reaction rate coefficients of the reactions.

Table S1 The description of sampling sites

Site	Longitude	Latitude	Characteristics
1	113°31′28″	23°9′30″	Electronic and machine manufacturing, traffic
2	113°31′39″	23°9′23″	Electronic and machine manufacturing, village
3	113°31′52″	23°8′55″	Comprehensive utilization of waste resources, textiles, raw material manufacturing, machinery manufacturing, traffic
4	113°31′52″	23°9′08″	Printing
5	113°31′53″	23°9′16″	Village, machinery manufacturing
6	113°31′46″	23°9′24″	Village
7	113°31′47″	23°9′34″	Village, hill, traffic
8	113°32′04″	23°9′26″	Village, transportation
9	113°32′16″	23°9′29″	Hill, electronic and machine manufacturing
10	113°32′25″	23°9′24″	Hill, electronic and machine manufacturing
11	113°32′26″	23°9′13″	Hill, research and experimental development, transportation
12	113°32′15″	23°9′25″	Electronic and machine manufacturing, research and experimental development, transportation
13	113°32′15″	23°9′15″	Transportation, research and experimental development
14	113°32′03″	23°9′10″	Electronic and machine manufacturing, pharmaceutical manufacturing, village
15	113°32′07″	23°9′03″	Pharmaceutical manufacturing, electronic and machine manufacturing, raw material manufacturing
16	113°32′18″	23°9′03″	Transportation, machinery manufacturing
17	113°32′26″	23°8′53″	Pharmaceutical manufacturing, research and experimental development, hill
18	113°32′14″	23°8′54″	Research and experimental development, machinery manufacturing, pharmaceutical manufacturing, transportation
19	113°32′03″	23°8′55″	Machinery manufacturing, raw material manufacturing, traffic
20	113°31′37″	23°8′55″	Comprehensive utilization of waste resources, textiles
21	113°31′27″	23°8′56″	Transportation, highway
22	113°31′20″	23°9′06″	Chemical process, traffic
23	113°31′18″	23°9′17″	Chemical process, traffic, pharmaceutical manufacturing
24	113°31′19″	23°9′30″	Research and experimental development, traffic

Table S2 R^2, MDL, MIR and OFP (ppb) of all identified compounds

	Compounds	Mean	SD	MDL	R^2	MIR	OFP
HHs (33)	Dichloromethane	3.19	1.82	0.01	0.997	0.04	3.14
	1,2,4-Trichlorobenzene	0.78	0.96	0.48	0.994	0.00	NA
	Trichloroethylene	0.54	1.58	0.02	0.991	0.64	8.32
	Benzyl chloride	0.44	0.32	0.09	0.998	0.00	NA
	hexachloro-1,3-Dutadiene	0.39	0.91	0.03	0.996	0.32	3.01
	p-Dichlorobenzene	0.39	0.83	0.12	0.997	0.18	1.67
	Freon12	0.36	0.23	0.21	0.998	0.00	NA
	1,2-Dichloroethane	0.35	0.32	0.14	0.996	0.21	1.78
	1,3-Dichlorobenzene	0.30	0.70	0.07	0.996	0.00	NA
	o-Dichlorobenzene	0.27	0.60	0.19	0.998	0.18	1.15
	1,2-Dibromoethane	0.22	0.64	0.08	0.995	0.10	0.55
	cis-1,3-Dichloropropene	0.20	0.36	0.13	0.998	3.70	18.15
	Freon11	0.19	0.08	0.19	0.99	0.00	NA
	Chlorobenzene	0.12	0.31	0.01	0.991	0.32	0.94
	cis-1,2-Dichloroethylene	0.10	0.15	0.10	0.998	1.70	4.17
	1,1,2,2-Tetrachloroethane	0.10	0.32	0.07	0.992	0.00	NA
	Ethylidene chloride	0.08	0.04	0.03	0.995	0.07	0.13
	Tribromomethane	0.07	0.23	0.04	0.995	0.00	NA
	Carbon tetrachloride	0.07	0.04	0.06	0.998	0.00	NA
	Perchlorethylene	0.06	0.11	0.02	0.999	0.03	0.04
	trans-1,2-Dichloroethylene	0.05	0.17	0.01	0.998	1.70	2.22
	1,1,2-Trichloroethane	0.05	0.15	0.02	0.993	0.09	0.10
	Chloroform	0.05	0.08	0.01	0.995	0.02	0.02
	Dibromochloromethane	0.04	0.12	0.03	0.998	0.00	NA
	Bromdichlormethan	0.04	0.09	0.03	0.998	0.00	NA
	1,2-Dichloropropane	0.03	0.04	0.02	0.996	0.29	0.23
	Freon113	ND	ND	0.12	0.995	0.00	NA

	Freon114	ND	ND	0.40	0.993	0.00	NA
	Chloroethane	ND	ND	0.41	0.994	0.29	NA
	1,1,1-Trichloroethane	ND	ND	0.19	0.999	0.00	NA
	Methyl bromide	ND	ND	0.66	0.997	0.02	NA
	Chloroethylene	ND	ND	0.25	0.997	2.83	NA
	1,1-Dichloroethene	ND	ND	0.20	0.993	1.79	NA
Alkanes (19)	Undecane	3.84	14.89	1.97	0.997	0.61	56.25
	Isopentane	3.34	3.08	0.30	0.998	1.45	116.32
	n-Hexane	1.77	3.27	0.92	0.996	1.24	52.53
	3-Methylpentane	1.34	1.70	0.15	0.995	1.80	57.80
	Decane	0.53	0.73	0.46	0.996	0.68	8.67
	2,3-Dimethylbutane	0.40	0.24	0.29	0.994	0.97	9.28
	3-Methylhexane	0.37	0.15	0.22	0.994	1.61	14.20
	2,2,4-Trimethylpentane	0.32	0.30	0.32	0.998	1.26	9.60
	Methylcyclohexane	0.31	0.08	0.29	0.995	1.70	12.46
	n-Heptane	0.30	0.08	0.19	0.999	1.07	7.78
	2-Methylheptane	0.30	0.12	0.28	0.995	1.07	7.76
	2,4-Dimethylpentane	0.26	0.23	0.23	0.994	1.55	9.77
	Cyclohexane	0.26	0.08	0.17	0.996	1.25	7.81
	n-Octane	0.22	0.06	0.21	0.996	0.90	4.86
	3-Methylheptane	0.21	0.02	0.20	0.997	1.24	6.39
	Methylcyclopentane	0.19	0.16	0.06	0.996	2.19	10.15
	2,3-Dimethylpentane	0.19	0.07	0.02	0.99	1.34	6.21
	2,3,4-Trimethylpentane	0.18	0.05	0.11	0.999	1.03	4.40
	2,2-Dimethylbutane	0.09	0.08	0.01	0.997	1.17	2.53
Alkenes (8)	Isoprene	1.83	1.27	0.45	0.995	10.61	466.80
	1-Hexene	1.57	3.01	0.62	0.998	5.49	206.23
	1-Pentene	0.73	0.43	0.36	0.998	7.71	134.81
	trans-2-Butene	0.70	0.59	0.52	0.995	15.16	254.69

	cis-2-Butene	0.39	0.39	0.28	0.996	14.24	134.28
	cis-2-Pentene	0.17	0.12	0.11	0.996	10.38	43.20
	trans-2-Pentene	0.15	0.16	0.06	0.995	10.56	37.23
	Butadiene	ND	ND	0.29	0.998	12.61	25.48
AHs (18)	Toluene	1.52	0.96	0.53	0.993	4.00	145.79
	Naphthalene	1.15	1.00	0.93	0.999	3.34	91.88
	m-Xylene	0.83	0.67	0.16	0.998	9.75	195.33
	p-Xylene	0.69	0.32	0.04	0.998	5.84	96.29
	p-Diethyl benzene	0.64	1.54	0.31	0.997	4.43	68.23
	Ethylbenzene	0.54	0.28	0.18	0.997	3.04	39.72
	1,2,4-Trimethylbenzene	0.53	0.34	0.15	0.995	8.87	112.52
	1,3-Diethylbenzene	0.52	1.18	0.21	0.991	7.10	88.26
	o-Xylene	0.47	0.32	0.22	0.998	7.64	86.61
	1,2,3-Trimethylbenzene	0.35	0.67	0.36	0.995	11.97	101.95
	Styrene	0.34	0.34	0.09	0.992	1.73	14.16
	m-Ethyltoluene	0.33	0.30	0.35	0.992	7.39	59.00
	o-Ethyltoluene	0.33	0.32	0.31	0.997	5.59	44.50
	p-Ethyltoluene	0.33	0.28	0.19	0.996	4.44	34.64
	1,3,5-Trimethylbenzene	0.28	0.27	0.36	0.996	11.76	79.54
	Benzene	0.28	0.09	0.16	0.997	0.72	4.82
	n-Propylbenzene	0.21	0.13	0.14	0.995	2.03	10.24
	Isopropylbenzene	0.14	0.07	0.30	0.993	2.52	8.34
OVOCs (3)	Tetrahydrofuran	0.17	0.25	0.05	0.991	4.31	17.75
	MTBE	0.73	0.51	0.34	0.99	0.73	12.74
	2-Butanone	1.45	1.65	0.24	0.993	6.01	209.15
Other (1)	Carbon disulfide	0.20	0.25	0.10	0.997	0.25	1.19

Note: MDL: method detection limitation; R^2: the correlation coefficient for linear fitting of standard curve; ND: Not detected; NA: Not available.

Table S3 Concentrations of VOCs in the Pearl River Delta

Sites	Category	Period	Concentration	species Number	Top 10 species
Guangzhou [a]	Industrial	June 2020	41 ± 24 ppb	81	Undecane, isopentane, dichloromethane, isoprene, 1-Hexene, Toluene, 2-Butanone, 3-Methylpentane, naphthalene, m-Xylen
PRD [b]	Urban	April 2005	88.8 ± 38.6 ppbv	56	Ethane, propane, i-Butane, n-Butane, i-Pentane, ethene, ethyne, benzene, toulene, m/p-Xylene
	Suburban		60.8 ± 31.5 ppbv	56	Toulene, ethyne, ethane, propane, i-Butane, n-Butane, i-Pentane, wthene, benzene, ethylbenzene, m/p-Xylene
	Rural		23.4 ± 9.8 ppbv	56	Ethane, propane, i-Butane, n-Butane, i-Pentane, ethene, toulene, ethyne, benzene, m/p-Xylene
PRD [c]	Suburban	July 2006	19.6 ± 12.0 ppbv	56	Propane, n-Butane, ethene, isoprene, acetylene, benzene, toluene, m,p-Xylene, formaldehyde, acetaldehyde.
Wanqingsha [d]	Suburban	September-November 2017	36.3 ± 27.9 ppb	56	Ethane, propane, n-butane, i-butane, i-pentane, n-pentane, ethyne, toluene, ethylbenzene, m/p -xylene.
Guangzhou [e]	Urban	March and May 2017	55.0 ppb	80	Toluene，methanol，ascetic acid，propionic acid, benzene, ethylbenzene and Σ(o/m/p)-xylene, n-hexane, isopentane, dichloromethane
	Suburban		24.5 ppb	80	Propene，butene，methanol，acetaldehyde，methyl ethyl ketone, benzene, toluene, ethylbenzene and Σ(o/m/p)-xylene, n-hexane

N.A.: not available. a, this study; b [3]; c [4]; d [5]; e [2]

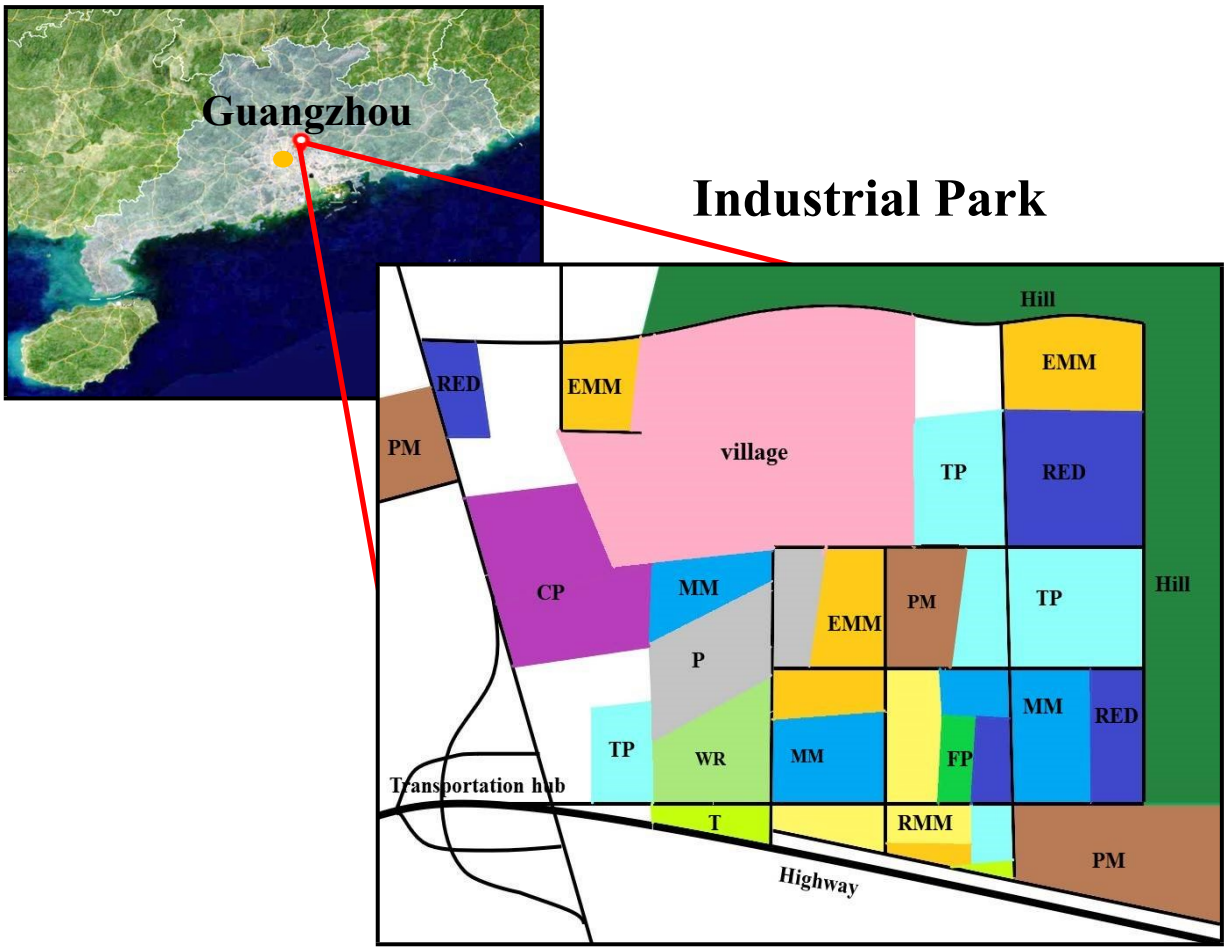

Fig. S1 Geographical location of the industrial park: Raw material manufacturing (RMM), machinery manufacturing (MM), chemical process (CP), comprehensive utilization of waste resources (WR), printing (P), textiles (T), food processing (FP), pharmaceutical manufacturing (PM), transportation (TP), electronic and machine manufacturing (EMM), research and experimental development (RED). The lines represent the roadways.

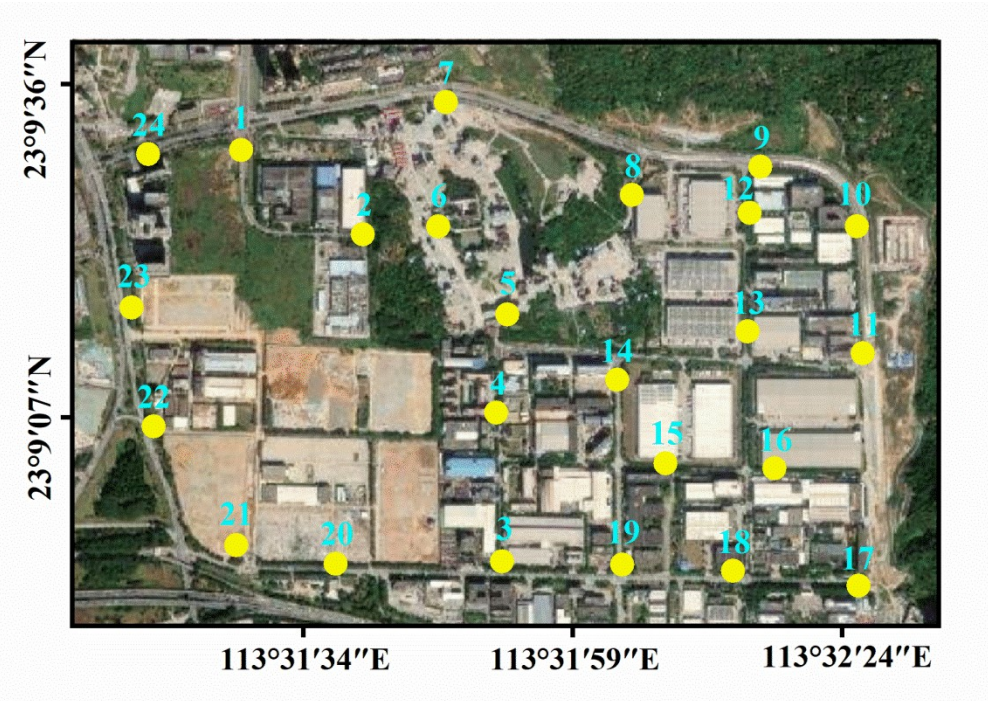

Fig. S2 Geographical location and layout of sampling points.

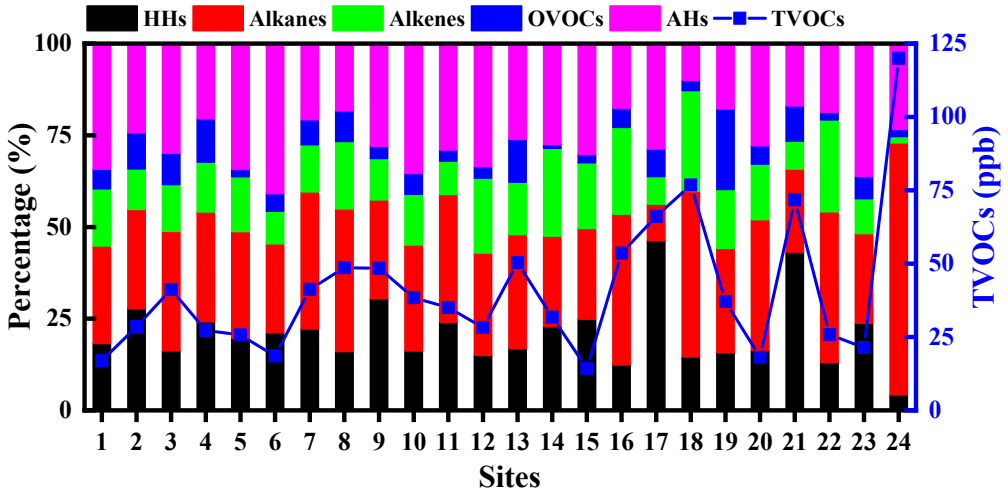

Fig. S3 The concentration level of total VOCs and the ratio of VOC composition.

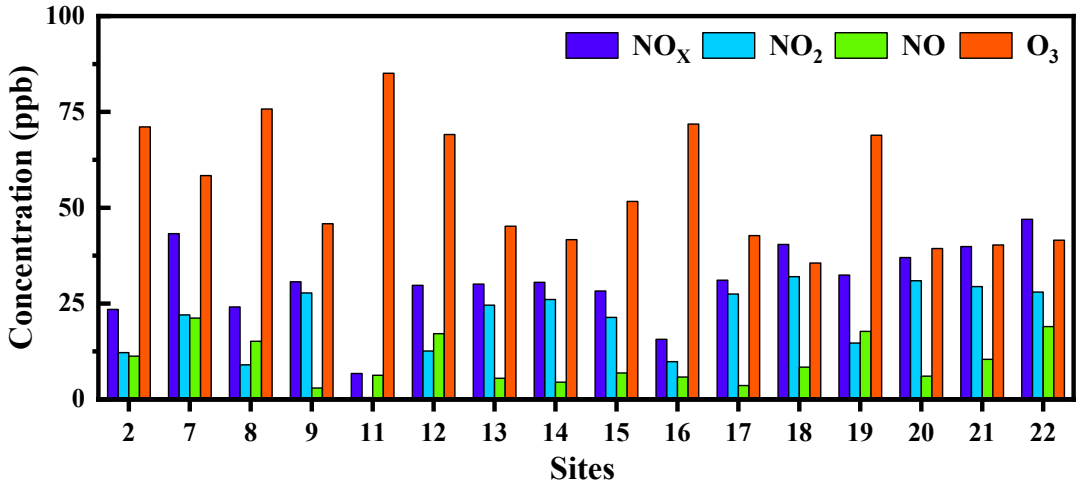

Fig. S4 The concentrations of NO_X and ozone.

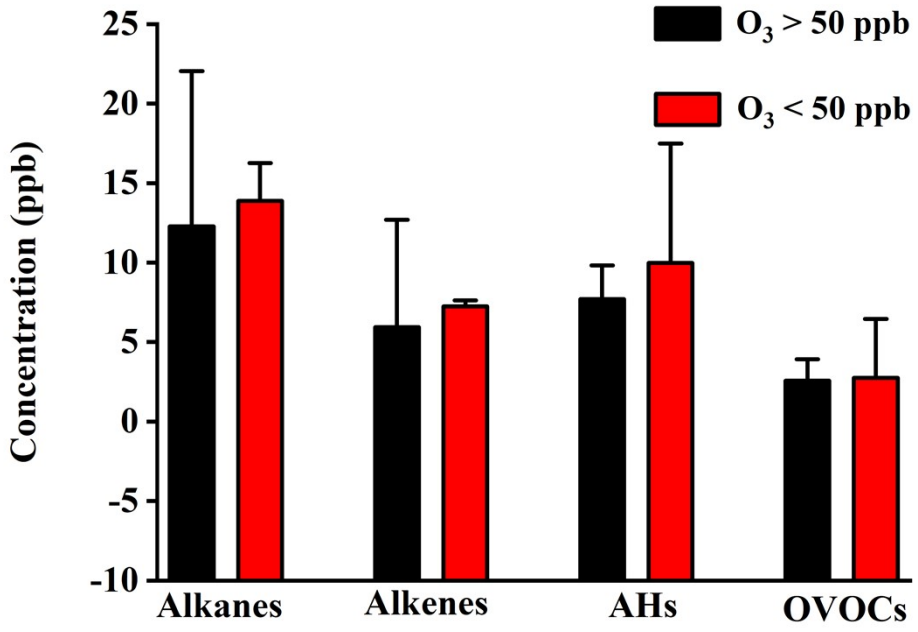

Fig. S5 The concentrations of alkanes, alkenes, AHs and OVOCs in the high and low O_3 regions.

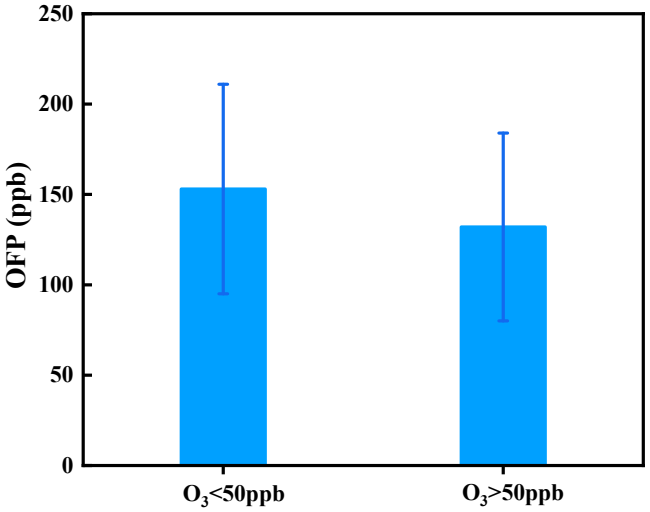

Fig. S6 The description of the values of Ozone formation potential (OFP) in the high O_3 region and the low O_3 region.

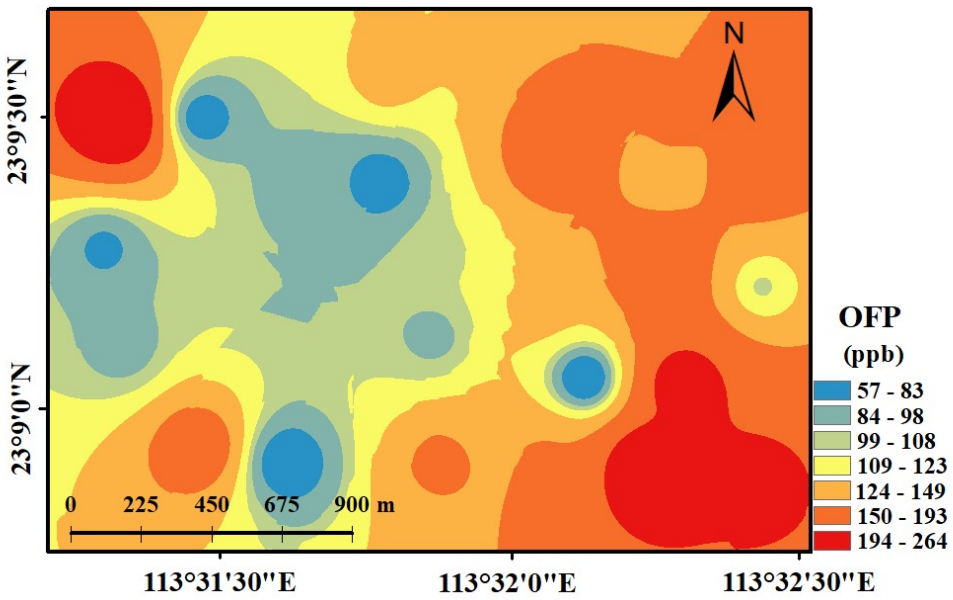

Fig. S7 The distribution of the values of Ozone formation potential (OFP). The blue to the red represents a gradual increase in concentration.

References:

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