Supplementary Material

Exploring the Crucial Role of Atmospheric Carbonyl Compounds in Regional Ozone heavy Pollution: Insights from Intensive Field Observations and Observation-based modelling in the Chengdu Plain Urban Agglomeration, China

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Table S1. Information of off-line sampling points of atmospheric carbonyl compounds.

Sites location	Sites abbreviation	Latitude and longitude (° E, ° N)	Type of sites	Sampling details
Mianyang	MY	104.67, 31.47	urban	**Measurement periods**: 2019/08/04 0:00-2019/08/18 22:00 **Sampling time for one day** 0:00-2:00, 2:00-4:00,4:00-6:00, 6:00-8:00, 8:00-10:00, 10:00-12:00, 12:00-14:00, 14:00-16:00, 16:00-18:00, 18:00-20:00, 20:00-22:00, 22:00-24:00. **Sampling volume**: Sampling 96 L for each sample
Deyang	DY	104.41,31.13	urban	
Chengdu	CDHKY	104.05, 30.66	urban	
Xinjin, Chengdu	XJ	103.85, 30.40	suburban	
Suining	SN	105.56, 30.57	urban	
Ziyang	ZY	104.63, 30.14	urban	
Meishan	MS	103.85, 30.08	urban	
Yaan	YA	102.99,29.97	urban	
Leshan	LS	103.75, 29.60	urban	

Table S2. Detection information for 15 kinds of carbonyl compounds by HPLC/UV/MS.

Species (measured by DNPH derivatization)	Retention Time (min)	Resolution	Linear Range (ng/mL)	Correlation Coefficient (R^2)	Detection Limit (ng/mL)	Quantification Limit (ng/mL)
formaldehvde	4.97	---	15-600	1.0000	0.56	1.87
acetaldehyde	6.24	4.74	15-600	1.0000	0.83	2.77
acetone	8.13	0.85	15-600	1.0000	1.28	4.25
propionaldehyde	8.70	1.63	15-600	1.0000	1.37	4.57
crotoraldehyde	10.55	4.85	15-600	1.0000	1.84	6.13
butyaldehyde	12.00	3.43	15-600	0.9998	2.14	6.42
benzaldehyde	13.31	2.83	15-600	0.9994	3.29	9.89
isovaleraldehyde	16.20	5.24	15-600	0.9996	3.63	12.10
valeraldehyde	17.13	1.52	15-600	0.9980	3.53	11.75
o-Tolualdehyde	18.32	1.93	15-600	0.9992	5.13	17.10
m-Tolualdehyde	18.95	0.98	15-600	0.9982	5.12	17.07
p-Tolualdehyde	19.76	1.23	15-600	0.9978	5.57	18.56
hexaldehyde	24.21	8.18	15-600	0.9998	2.93	9.78
2,5-diemthybenzaldehyde	24.75	1.35	15-600	0.9998	3.51	11.71
MACR	11.67	2.09	15-450	0.9994	2.00	6.60

Table S3. VOCs Species of Anthropogenic and Biogenic VOCs Considered in the Formation of Formaldehyde, Acetaldehyde, and Acetone

No.	Category	CAS	Species
1	Alkanes	75-28-5	Isobutane
2	Alkanes	106-97-8	n-Butane
3	Alkanes	74-84-0	Ethane
4	Alkanes	78-78-4	Isopentane
5	Alkanes	109-66-0	n-Pentane
6	Alkanes	74-98-6	Propane
7	Alkanes	75-83-2	2,2-dimethylbutane
8	Alkanes	79-29-8	2,3-dimethylbutane
9	Alkanes	107-83-5	2-Methylpentane
10	Alkanes	287-92-3	Cyclopentane
11	Alkanes	96-14-0	3-Methylpentane
12	Alkanes	110-54-3	n-Hexane
13	Alkanes	108-08-7	2,4-Dimethylpentane
14	Alkanes	96-37-7	Methylcyclopentane
15	Alkanes	591-76-4	2-Methylhexane
16	Alkanes	565-59-3	2,3-Dimethylpentane
17	Alkanes	110-82-7	Cyclohexane
18	Alkanes	589-34-4	3-Methylhexane
19	Alkanes	540-84-1	2,2,4-trimethylpentane
20	Alkanes	142-82-5	n-Heptane
21	Alkanes	108-87-2	Methylcyclohexane
22	Alkanes	123-91-1	1,4-Dioxane
23	Alkanes	565-75-3	2,3,4-trimethylpentane
24	Alkanes	592-27-8	2-Methylheptane
25	Alkanes	589-81-1	3-Methylheptane
26	Alkanes	111-65-9	Octane
27	Alkanes	111-84-2	n-Nonane
28	Alkanes	124-18-5	n-Decane
29	Alkanes	1120-21-4	Undecane
30	Alkanes	112-40-3	Dodecane
31	Alkenes	74-85-1	Ethylene
32	Alkenes	106-98-9	1-Butene
33	Alkenes	106-99-0	1,3-Butadiene
34	Alkenes	624-64-6	trans-2-Butene
35	Alkenes	590-18-1	cis-2-Butene
36	Alkenes	109-67-1	1-Pentene
37	Alkenes	646-04-8	trans-2-Pentene
38	Alkenes	78-79-5	Isoprene
39	Alkenes	627-20-3	cis-2-Pentene

40	Alkenes	115-07-1	Propylene
41	Alkenes	592-41-6	1-Hexene
42	Alkynes	74-86-2	Acetylene
43	Aromatic hydrocarbons	71-43-2	Benzene
44	Aromatic hydrocarbons	108-88-3	Toluene
45	Aromatic hydrocarbons	100-41-4	Ethylbenzene
46	Aromatic hydrocarbons	106-42-3	m/p-Xylene
47	Aromatic hydrocarbons	95-47-6	o-Xylene
48	Aromatic hydrocarbons	100-42-5	Styrene
49	Aromatic hydrocarbons	98-82-8	Isopropylbenzene
50	Aromatic hydrocarbons	103-65-1	n-Propylbenzene
51	Aromatic hydrocarbons	620-14-4	3-Ethyltoluene
52	Aromatic hydrocarbons	622-96-8	4-Ethyltoluene
53	Aromatic hydrocarbons	108-67-8	1,3,5-Trimethylbenzene
54	Aromatic hydrocarbons	611-14-3	2-Ethyltoluene
55	Aromatic hydrocarbons	95-63-6	1,2,4-Trimethylbenzene
56	Aromatic hydrocarbons	100-52-7	Benzaldehyde
57	Aromatic hydrocarbons	526-73-8	1,2,3-Trimethylbenzene
58	Aromatic hydrocarbons	141-93-5	1,3-Diethylbenzene
59	Aromatic hydrocarbons	105-05-5	1,4-Diethylbenzene
60	Aromatic hydrocarbons	95-50-1	1,2-dichloro-benzene
61	Aromatic hydrocarbons	620-23-5	3-methyl-benzaldehyde
62	Aromatic hydrocarbons	120-82-1	1,2,4-trichloro-benzene
63	Aromatic hydrocarbons	91-20-3	Naphthalene

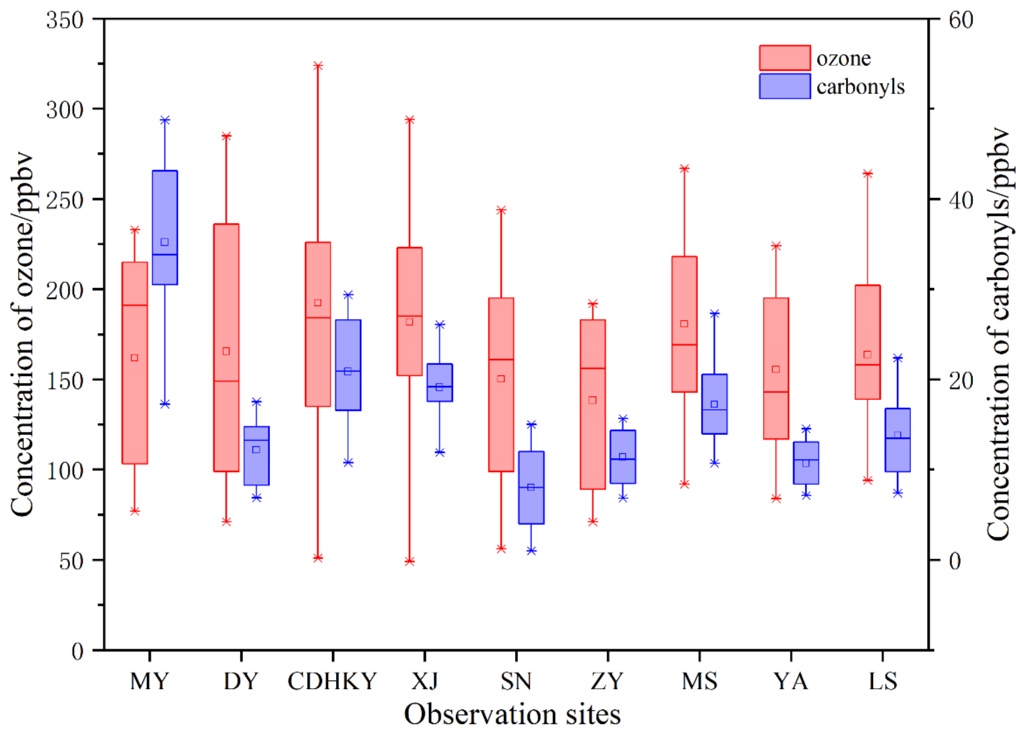

Figure S1. Average concentrations of ozone and carbonyl compounds at each site in the CPUA during the observation period.

Table S4. Daily average value and proportion of volume concentration of carbonyl compounds at each site in the CPUA during the observation period.

Sites	Total volume concentration daily average （ppbv）	Carbonyl compounds daily average value (ppbv) and percentage (%)			
		Formaldehyde	Acetaldehyde	Acetone	others
MY	35.18	12.82 （36.4%）	16.65 （47.3%）	4.36 （12.4%）	1.35 （3.84%）
DY	12.16	6.06 （49.9%）	1.54 （12.7%）	2.80 （23.1%）	1.75 （14.4%）
CDHKY	20.84	10.09 （48.4%）	3.65 （17.5%）	4.51 （21.7%）	2.60 （12.5%）
XJ	19.04	8.87 （46.5%）	2.33 （12.2%）	3.70 （19.4%）	4.15 （21.8%）
SN	16.05	6.98 （43.5%）	2.62 （16.3%）	3.14 （19.5%）	3.32 （20.7%）
ZY	11.47	5.84 （51.0%）	1.40 （12.2%）	3.23 （28.1%）	1.00 （8.7%）
MS	17.19	8.47 （49.3%）	3.24 （18.8%）	2.15 （12.5%）	3.33 （19.4%）
YA	10.70	6.36 （59.4%）	0.88 （8.2%）	2.18 （20.4%）	1.29 （12.0%）
LS	13.46	6.55 （48.7%）	1.63 （12.1%）	2.91 （21.6%）	2.37 （17.6%）
CPUA	17.34	8.00 （48.1%）	3.37 （17.5%）	3.22 （19.9%）	2.35 （17.6%）

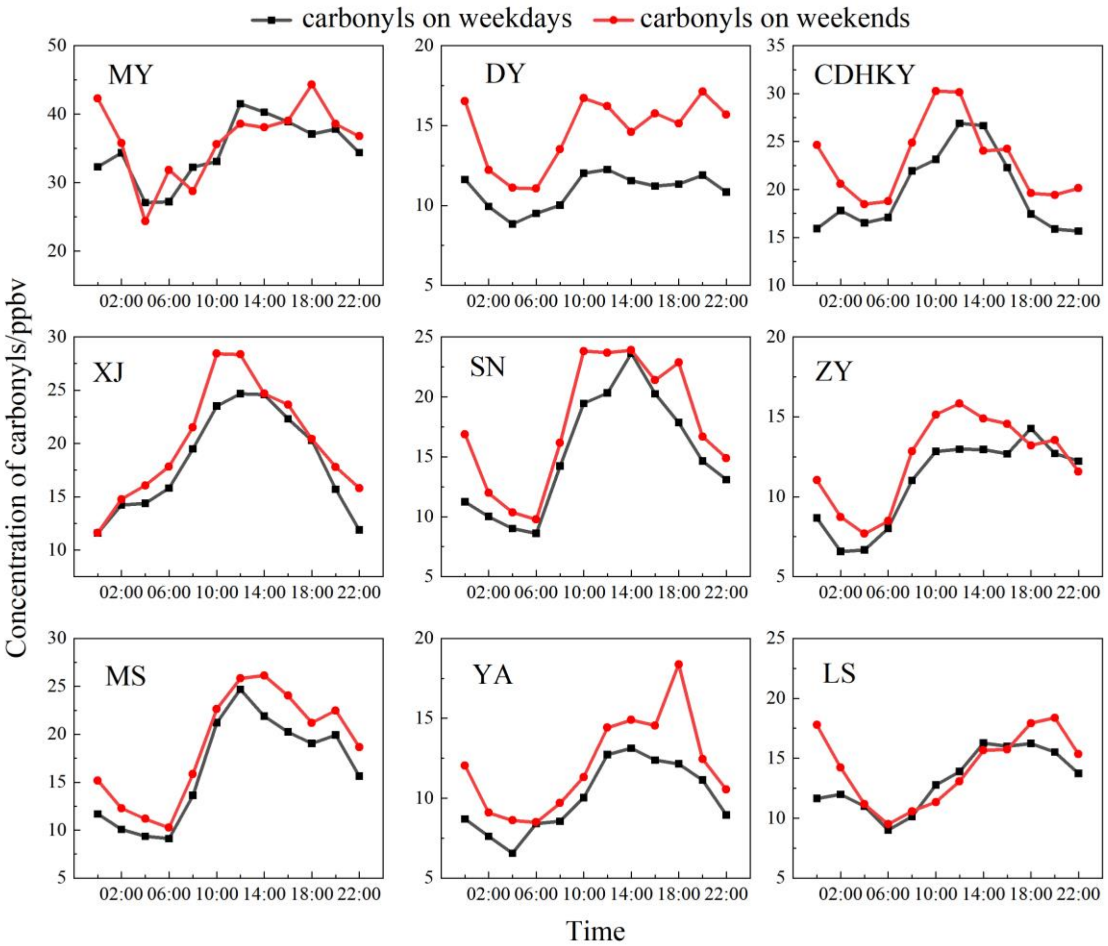

Figure S2 Comparison of daily changes in volumetric concentrations of carbonyl compounds at each site in the CPUA at different time periods during the observation period.. The black line represents the daily changes of aldehydes and ketones on weekdays and the red line represents the daily changes of aldehydes and ketones on weekends.

Table S5. Atmospheric photochemical reactivity of carbonyl compounds L_{OH} and OFP at sites in the CPUA during the observation period.

Sites	L_{OH}/s^{-1}						OFP/（$\mu g \cdot m^{-3}$）					
	Σ15carbonyls	C1	C2	C3	C3	≥C4	Σ15carbonyls	C1	C2	C3	C3	≥C4
MY	5.92	2.18	3.48	0.14	0.05	0.06	238.11	121.24	108.91	4.82	1.50	1.64
DY	1.67	1.03	0.32	0.08	0.08	0.15	76.13	57.36	10.08	2.63	2.13	3.94
CDHKY	2.98	1.72	0.76	0.15	0.15	0.19	133.41	95.42	23.85	4.93	3.93	5.29
XJ	2.84	1.51	0.49	0.09	0.49	0.26	121.70	83.87	15.23	3.30	11.90	7.41
SN	2.36	1.19	0.55	0.14	0.13	0.36	100.67	65.98	17.15	4.60	3.10	9.83
ZY	1.50	1.00	0.29	0.12	0.07	0.03	71.12	55.29	9.17	3.83	1.54	1.29
MS	2.76	1.44	0.68	0.12	0.20	0.31	118.31	80.14	21.17	4.28	5.19	7.54
YA	1.56	1.08	0.18	0.15	0.12	0.03	74.63	60.12	5.75	4.82	2.94	1.00
LS	1.97	1.12	0.34	0.10	0.23	0.19	86.61	61.98	10.64	3.29	5.01	5.70

Table S6. Contribution Values of Various VOC Compounds to Ozone Formation Potential (OFP) at Five Sites in the Chengdu Plain Urban Agglomeration during the Observation Period.

OFPs ($\mu g/m^3$)	**ZY**	**YA**	**SN**	**LS**	**MY**
Alkanes	63.91	52.65	49.17	77.30	41.22
Alkenes	170.74	165.97	113.79	169.46	168.85
Alkynes	5.92	0.76	1.54	3.03	2 22
Aromatic hydrocarbons	53.90	24.02	46.17	71.21	41.95
Carbonyl compounds	71.12	74.63	100.67	86.61	238.11
Sum	365.59	318.03	311.34	407.61	490.13
Contribution	19.5%	23.5%	32.3%	21.2%	48.6%

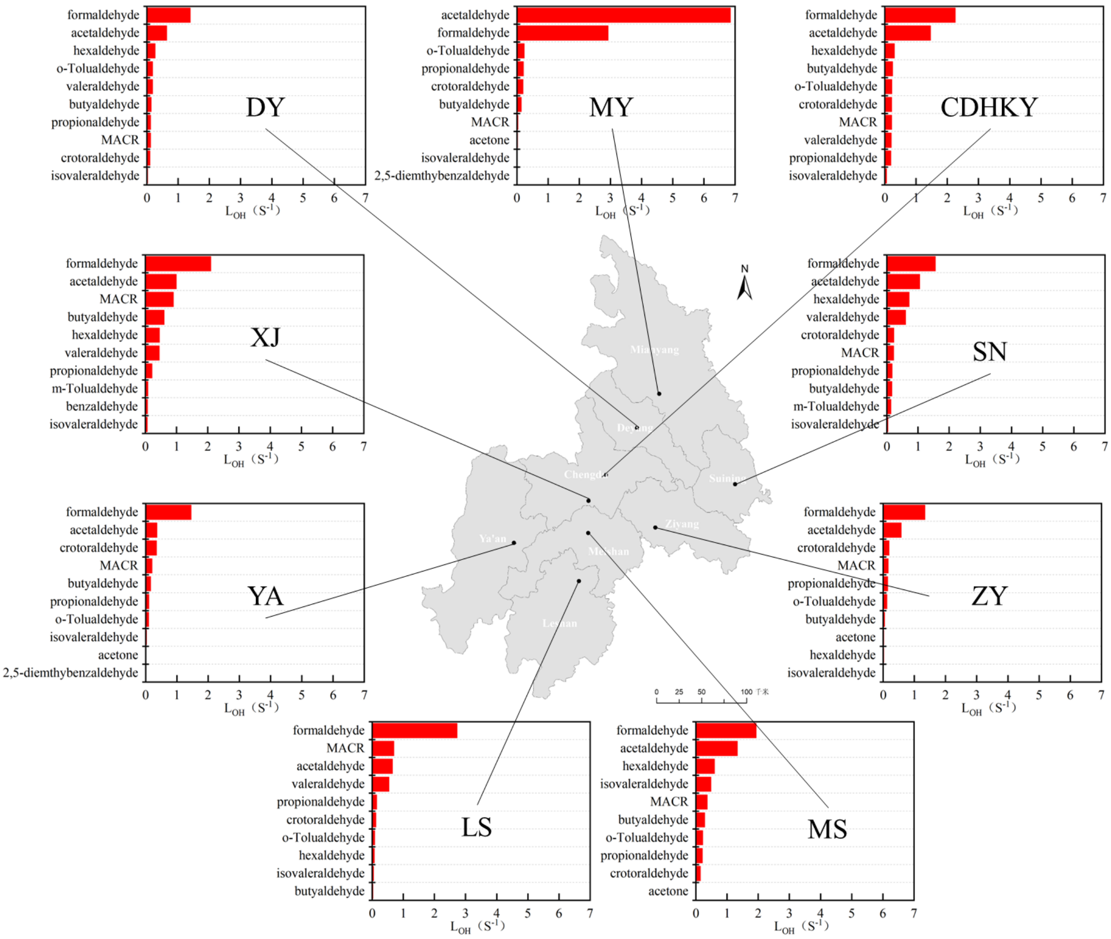

Figure S3. Top Ten Species of Carbonyl Compounds with L_{OH} at Various Sites in the CPUA during the Observation Period.

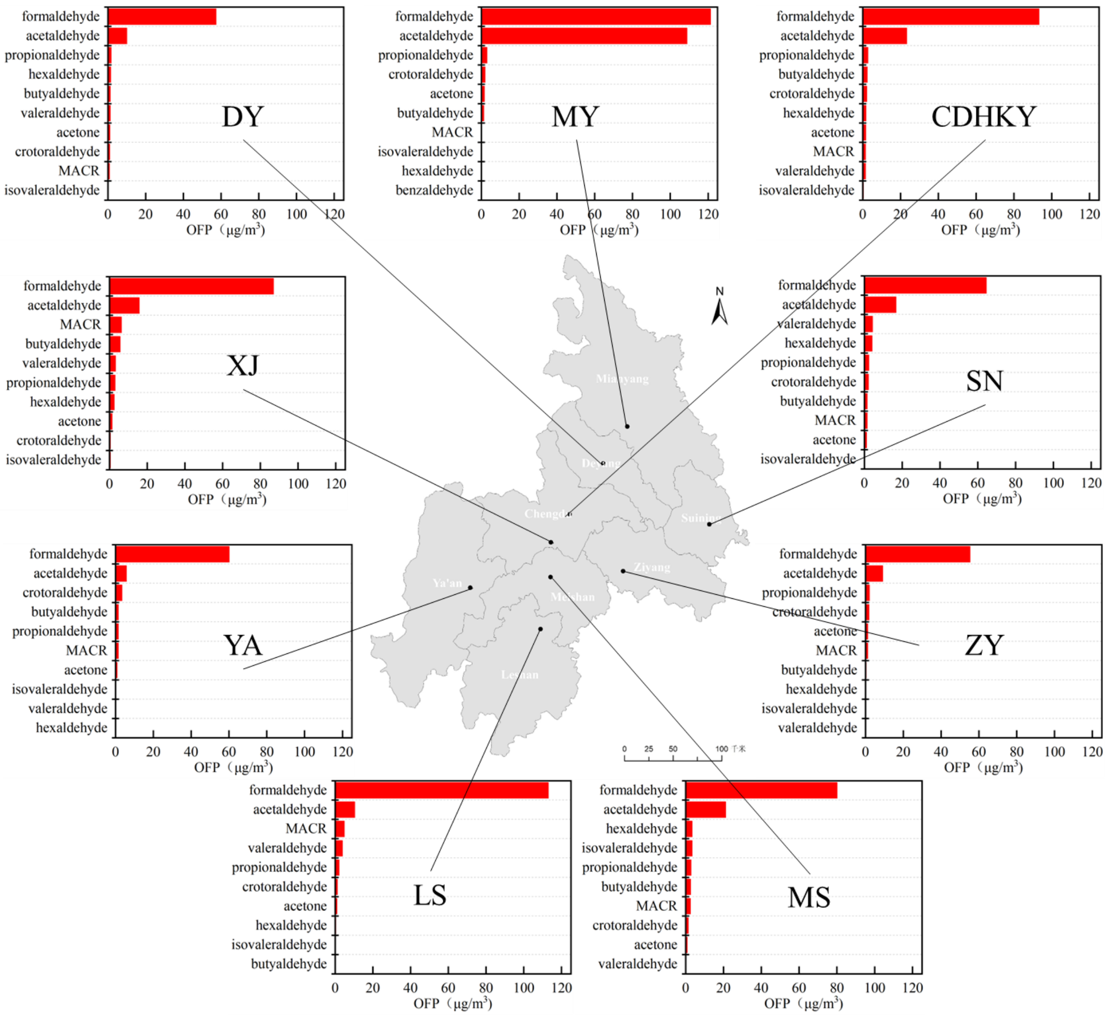

Figure S4. Contribution Values of Various VOC Compounds to OFP at Five Sites in the CPUA during the Observation Period.

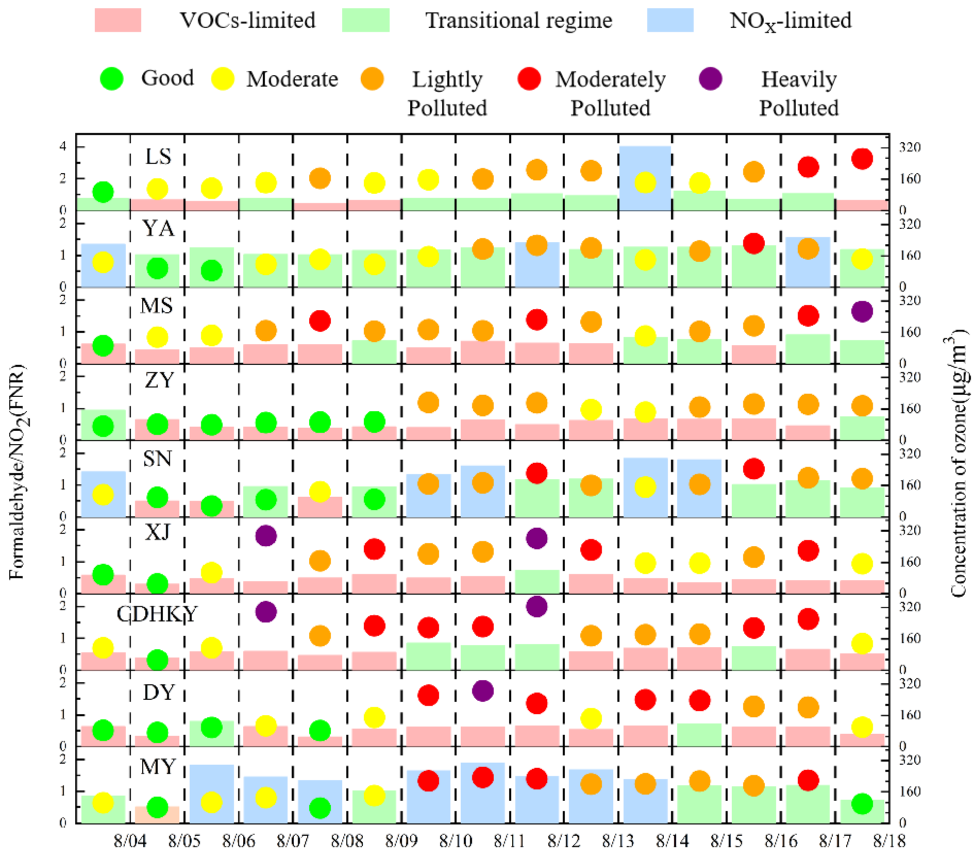

Figure S5. Daily Variation of Ozone Assessment Values, Pollution Status, and Ozone Sensitivity at Sites in the CPUA during the Observation Period.

Table S7. Proportion of formaldehyde, acetaldehyde and acetone by source at each site in the CPUA during the observation period.

Sites	Background and primary emission			Secondary formation		
	Formaldehyde	Acetaldehyde	acetone	Formaldehyde	Acetaldehyde	acetone
MY	56%	-	73%	44%	-	27%
DY	64%	81%	74%	36%	19%	26%
CDHKY	66%	76%	70%	34%	24%	30%
XJ	72%	77%	78%	28%	23%	22%
SN	50%	46%	63%	50%	54%	37%
ZY	56%	81%	65%	44%	19%	35%
MS	58%	62%	75%	42%	38%	25%
YA	50%	54%	45%	50%	46%	55%
LS	80%	83%	76%	20%	17%	24%
Average	61%	70%	69%	39%	30%	31%

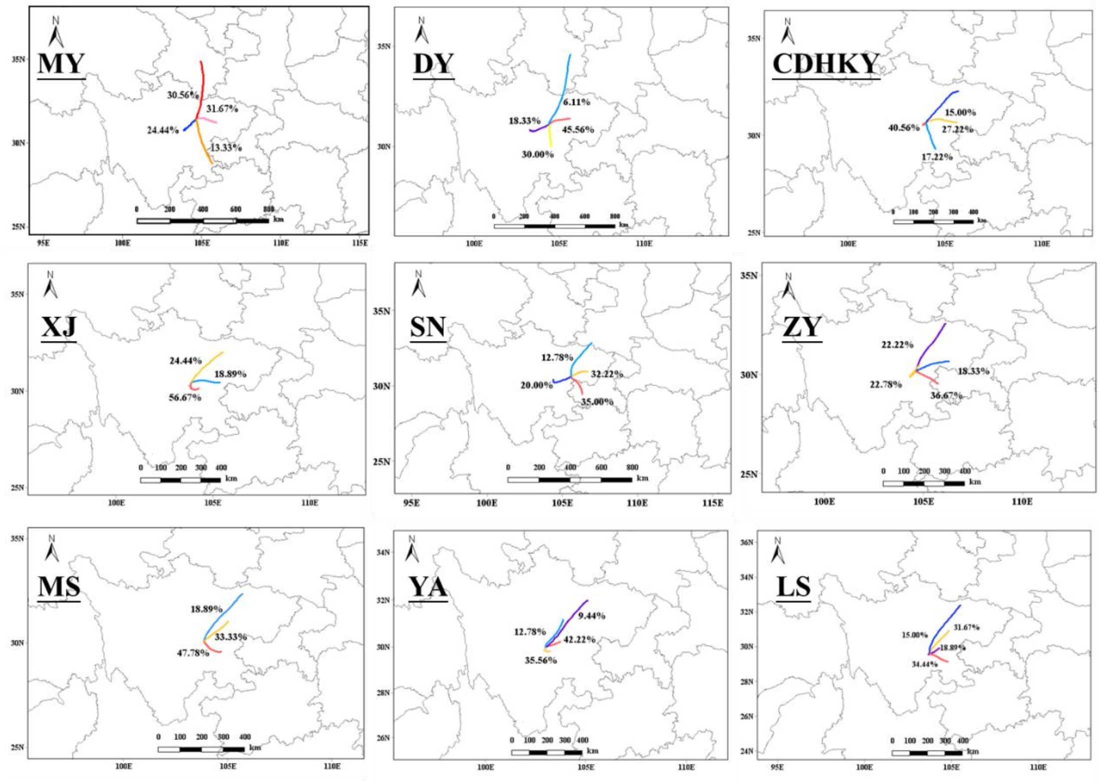

Figure S6. Clustering of backward trajectories of sites in the CPUA during the observation period.