Supplement for

"Photodegradable oxygenated VOCs as large contributors to radicals and ozone production in the atmosphere"

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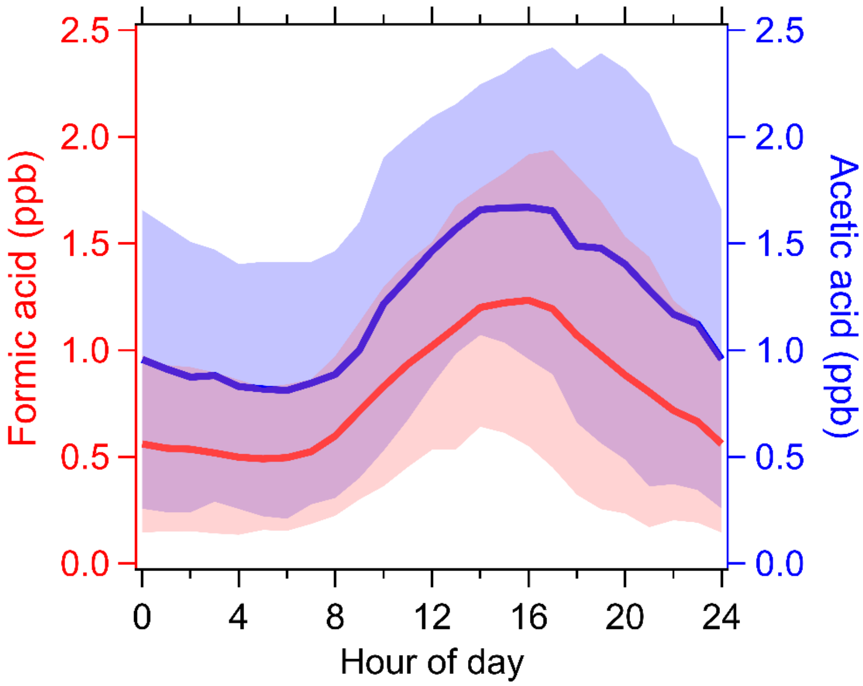

Figure S1. The average diurnal variations of concentrations of formic acid and acetic acid during the campaign.

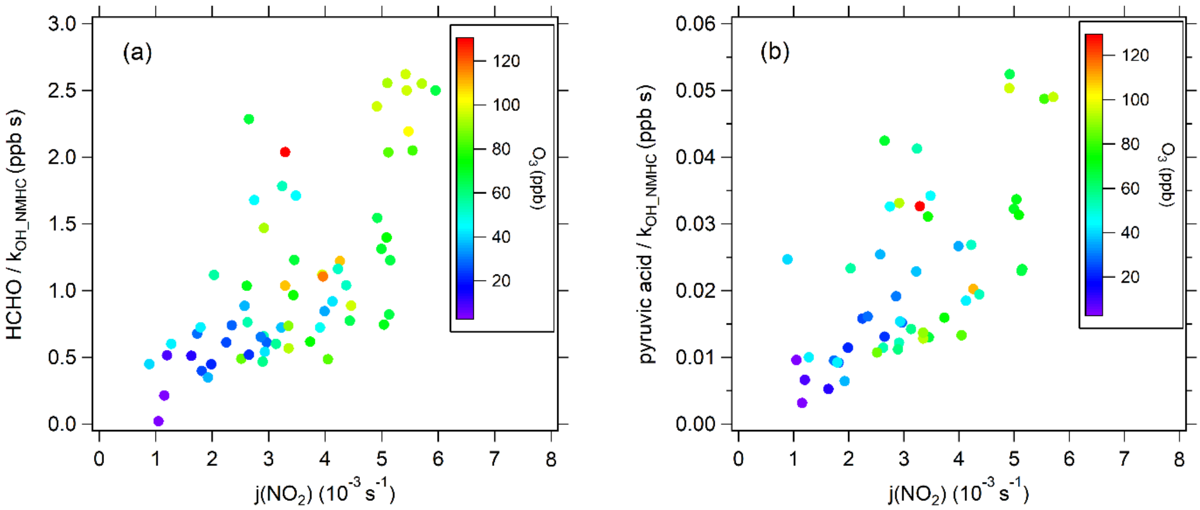

Figure S2. The scatter plot of daily daytime average HCHO/k_{OH_NMHC} (and pyruvic acid/ k_{OH_NMHC}) ratios versus $j(NO_2)$ color-coded using ozone concentrations during the campaign.

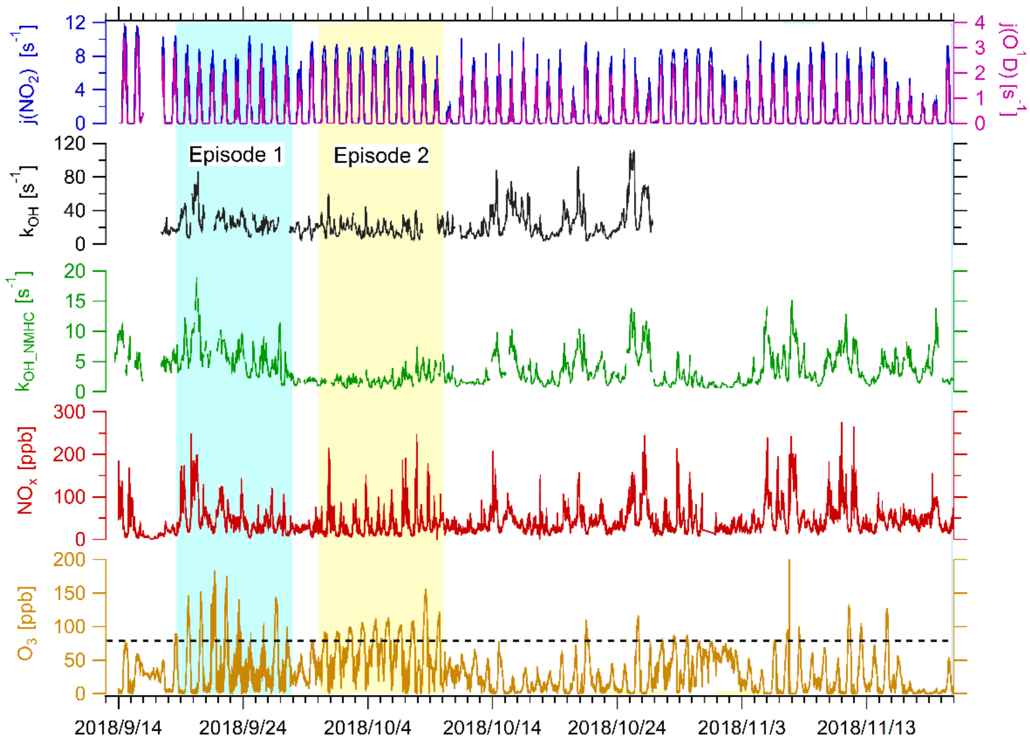

Figure S3. Time series of photolysis frequencies ($j(NO_2)$ and $j(O^1D)$), total reactivity (k_{OH}), OH reactivity of NMHCs (k_{OH_NMHC}), NOx concentration and O_3 concentration during the campaign. The blue shade and yellow shade represent the two ozone pollution periods which are defined as episode 1 and episode 2, respectively.

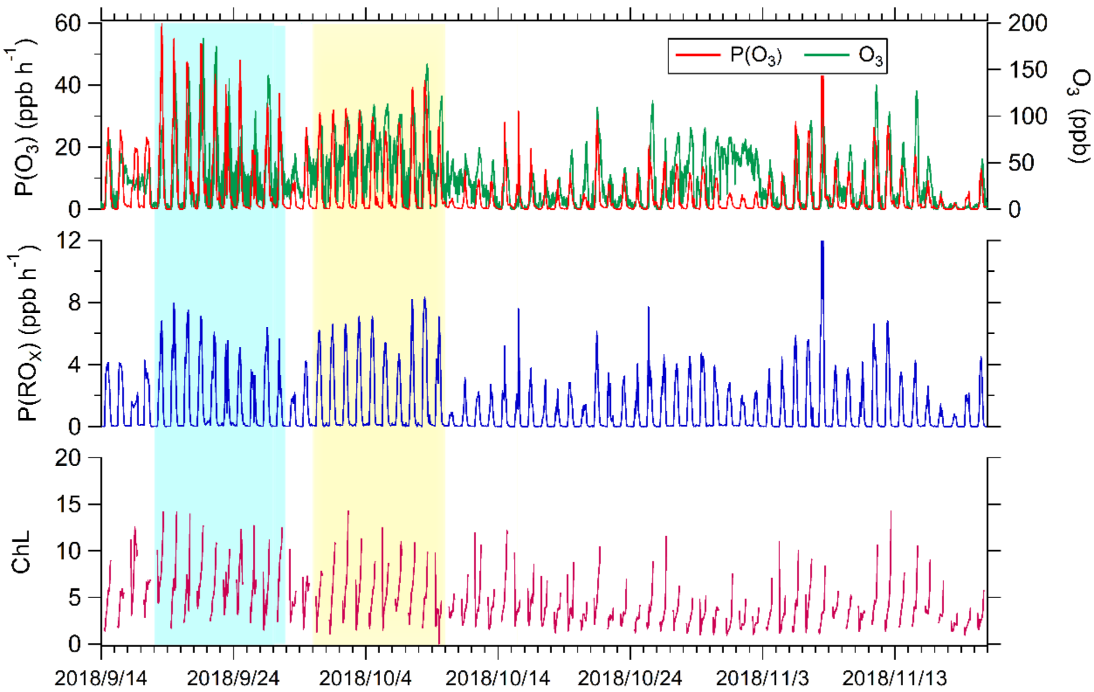

Figure S4. Time series of $P(O_3)$, P(ROx) and ChL during the campaign in Guangzhou. The blue shade and yellow shade represent the two ozone pollution periods which are defined as episode 1 and episode 2 respectively.

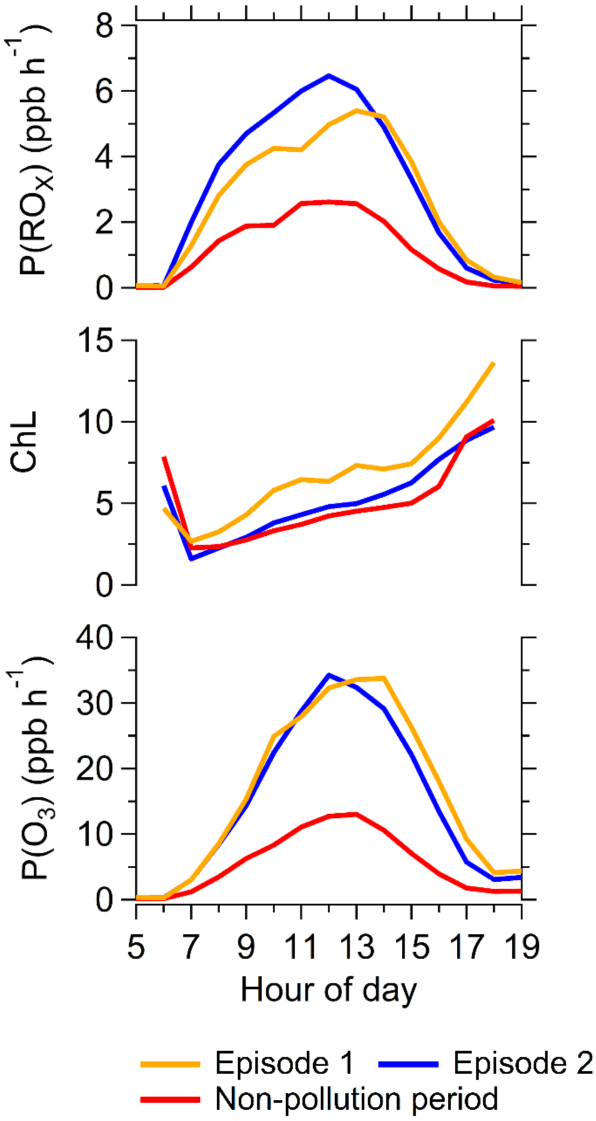

Figure S5. Averaged diurnal variations of P(RO_X), ChL and P(O_3) during episode 1 (yellow line), episode 2 (blue line) and non-pollution period (red line).

Table S1. Molecular formula, photolysis reactions, daytime average concentrations and photolysis frequencies of photodegradable species during the campaign.

Photodegradable species	Molecular formula	Measurement technology	Concentration (ppbv)	Photolysis frequency (s^{-1})
Ozone	O_3	49i O_3 analyzer	48±17	7.0×10^{-6}
Nitrous acid	HONO	LOPAP	0.47±0.20	5.7×10^{-4}
Formaldehyde	HCHO	Hantzsch fluorimetry	5.2±3.8	1.1×10^{-5}
Acetaldehyde	CH_3CHO	GC-MS	2.3±1.2	1.3×10^{-6}
Propanal	C_2H_5CHO	GC-MS	0.35±0.21	6.1×10^{-6}
n-butanal	C_3H_7CHO	GC-MS	0.20±0.14	6.5×10^{-6}
n-pentanal	C4H9CHO	GC-MS	0.21±0.14	6.5×10^{-6}
n-hexanal	C5H11CHO	GC-MS	0.18±0.15	6.7×10^{-6}
Methacrolein	C4H6O	PTR-QiToF-MS, GC-MS	0.22±0.14	1.0×10^{-6}
Acetone	CH_3COCH_3	PTR-QiToF-MS	4.4±2.5	1.4×10^{-7}
Methyl Ethyl Ketone	C_4H_8O	PTR-QiToF-MS	1.8±1.4	1.2×10^{-6}
Methylglyoxal	$C_3H_4O_2$	PTR-QiToF-MS	0.32±0.20	5.5×10^{-5}
Methyl vinyl ketone	C4H6O	PTR-QiToF-MS, GC-MS	0.26±0.15	7.2×10^{-7}
Methyl hydroperoxide	CH_3OOH	PTR-QiToF-MS	0.022±0.015	1.8×10^{-6}
Pyruvic acid	CH_3COCO_2H	PTR-QiToF-MS	0.05±0.04	6.5×10^{-5}
Acrolein	CH_2=CHCHO	PTR-QiToF-MS	0.21±0.10	3.4×10^{-7}
Hydroxyacetone	$CH_3C(O)CH_2OH$	PTR-QiToF-MS	2.0±1.5	1.4×10^{-6}
Hydroxymethyl hydroperoxide	$HOCH_2OOH$	PTR-QiToF-MS	0.06±0.03	1.6×10^{-6}
Benzaldehyde	C7H6O	PTR-QiToF-MS	0.15±0.11	1.0×10^{-6}
Nitrophenol	$C_6H_5NO_3$	PTR-QiToF-MS	0.026±0.018	5.7×10^{-5}
Methyl nitrophenol	$C_7H_7NO_3$	PTR-QiToF-MS	0.023±0.017	5.7×10^{-5}
Carbonyls with more carbons	$C_nH_{2n}O$ (n>5)	PTR-QiToF-MS	0.31±0.24	1.2×10^{-6}~6.5×10^{-6}
	$C_nH_{2n-2}O$ (n>3)	PTR-QiToF-MS	2.04±1.60	1.2×10^{-6}~6.5×10^{-6}
	$C_nH_{2n-2}O_2$ (n>3)	PTR-QiToF-MS	0.42±0.32	1.2×10^{-6}~1.2×10^{-4}
	$C_nH_{2n-4}O_2$ (n>3)	PTR-QiToF-MS	0.20±0.11	1.2×10^{-6}~3.0×10^{-4}
	$C_n H_{2n-4}O_3$ (n>3)	PTR-QiToF-MS	0.13±0.07	1.2×10^{-6}~1.8×10^{-4}
Nitrophenol with more methyl	$C_{6+n}H_{5+2n}NO_3$ (n≥1)	PTR-QiToF-MS	0.021±0.014	5.7×10^{-5}

Benzal with more methyl	$C_{7+n}H_{6+2n}O$ (n≥1)	PTR-QiToF-MS	0.33±0.19	1.0×10^{-6}

Table S2. Observed and box-model simulated daytime average concentrations of photodegradable OVOCs and the underestimation fraction of simulation during the campaign.

Photodegradable species	Molecular formula	Observed Concentration (ppbv)	Simulated Concentration (ppbv)	Underestimation of simulation (%)
Formaldehyde	HCHO	5.2±3.8	4.1±3.0	21
Acetaldehyde	CH_3CHO	2.3±1.2	1.5±0.85	35
Propanal	C_2H_5CHO	0.35±0.21	0.25±0.16	29
n-butanal	C_3H_7CHO	0.20±0.14	0.048±0.035	76
n-pentanal	C4H9CHO	0.21±0.14	0.029±0.021	86
n-hexanal	C5H11CHO	0.18±0.15	0.0034±0.0030	98
Methacrolein	C4H6O	0.22±0.14	0.29±0.22	-32
Acetone	CH_3COCH_3	4.4±2.5	1.3±1.1	70
Methyl Ethyl Ketone	C_4H_8O	1.8±1.4	0.38±0.29	79
Methylglyoxal	$C_3H_4O_2$	0.31±0.20	0.20±0.16	35
Methyl vinyl ketone	C4H6O	0.26±0.15	0.34±0.30	-31
Methyl hydroperoxide	CH_3OOH	0.022±0.015	0.016±0.013	27
Pyruvic acid	CH_3COCO_2H	0.05±0.04	0.026±0.022	48
Acrolein	$CH_2{=}CHCHO$	0.21±0.10	0.005±0.004	97
Hydroxyacetone	$CH_3C(O)CH_2OH$	2.0±1.5	0.66±0.54	67
Hydroxymethyl Hydroperoxide	$HOCH_2OOH$	0.06±0.03	0.02±0.01	67
Benzaldehyde	C7H6O	0.15±0.11	0.11±0.09	27
Nitrophenol	$C_6H_5NO_3$	0.026±0.018	0.022±0.020	15
Methyl nitrophenol	$C_7H_7NO_3$	0.023±0.017	0.021±0.018	8.7
Carbonyls with more carbons	$C_nH_{2n}O$ (n>5)	0.31±0.24	0.11±0.08	65
	$C_nH_{2n-2}O$ (n>3)	2.04±1.60	0.52±0.37	75
	$C_nH_{2n-2}O_2$ (n>3)	0.42±0.32	0.11±0.07	74
	$C_nH_{2n-4}O_2$ (n>3)	0.20±0.11	0.035±0.26	83
	$C_n H_{2n-4}O_3$ (n>3)	0.13±0.07	0.031±0.022	74
Nitrophenol with more methyl	$C_{6+n}H_{5+2n}NO_3$ (n≥1)	0.021±0.014	0.011±0.009	48

Benzal with more methyl	$C_{7+n}H_{6+2n}O$ (n≥1)	0.33±0.19	0.13±0.08	61

Table S3. Daytime (6:00-19:00) average of O_3, $j(NO_2)$, NOx, k_{OH_NMHC}, k_{OH} and k_{OH_NMHC}/ NOx for the two ozone episodes, other periods, and the campaign average.

Parameter	episode 1	episode 2	Other periods	campaign average
MDA1 O_3 (ppbv)	114±35	106±33	62±22	75±26
MDA8 O_3 (ppbv)	84±27	96±31	48±17	60±19
$j(NO_2)$ (s^{-1})	0.0037±0.0028	0.0053±0.0041	0.0031±0.0025	0.0034±0.0026
NOx (ppbv)	41±27	21±14	37±21	32±17
k_{OH_NMHC} (s^{-1})	6.0±2.8	2.0±0.63	3.2±1.4	3.6±1.6
k_{OH} (s^{-1})	26±16	16±8.0	/	/
k_{OH_NMHC}/ NOx (s^{-1} ppb^{-1})	0.15±0.10	0.095±0.065	0.086±0.055	0.11±0.067