Supplementary Materials

1. Observation-Based Model

Assuming there was an ideal box with the earth's surface as bottom side and boundary layer height as top side, the emitted compounds can be mixed immediately in the box, and the variation of concentration of compound *i* (c_i) with time t (dc_i/dt) can be expressed by the following formulation:

$$\frac{dc_i}{dt} = \frac{q_i}{H} + R_i - \frac{v_{d,i}c_i}{H} + \frac{u}{\Delta x}(c_i^0 - c_i) + \frac{C_i^a - C_i}{H(t)}\frac{dH}{dt} \quad \text{(S1)}$$

where q_i means the emission rate of compound *i* per area; $v_{d,i}$ is the dry deposition rate of compound *i*; R_i means atmospheric chemical reaction rate of compound *i*; H is the boundary layer height; c_i^0 is the background concentration of compound *i* outside the box; *u* is the wind speed; C_i^a means the concentration of compound *i* in the free troposphere. In the OBM, the term $\frac{q_i}{H} + \frac{u}{\Delta x}(c_i^0 - c_i)$ represents the influence of emission and horizonal transport, which is defined as source effect of compound *i*. A total of 81 reactions for 39 lumped species were involved in the OBM developed by Cardelino and Chameides (1995).

2. OH and HO_2 Simulation

Since OH and HO_2 are considered mainly from photochemical production, the influences of chemical reactions (*i.e.*, the term R_i in Equation (S1)) and temporal variations of boundary height (i.e., the term $\frac{C_i^a - C_i}{H(t)}\frac{dH}{dt}$ in Equation (S1)) were considered in the calculation of OH and HO_2 concentrations. Among the 89 reactions involved in the OBM, there are 53 reactions related to OH radical (18 formation reactions and 25 removal reactions) and 54 reactions related to HO_2 radical (47 formation reactions and 7 removal reactions). The OH and HO_2 concentrations were then calculated by integrating differential equations with *t*. The detailed reaction related OH and HO_2 can be found in the Tables S1 and S2.

Table S1. Reactions related to OH radical in the OBM.

	Formation Reactions for OH	
OH1	O1D+H2O→2OH	R11
OH2	O3+HO2→OH	R13
OH3	HONO+hv→OH+NO	R23
OH4	HO2+NO→OH+NO2	R28
OH5	H2O2+hv→2OH	R34
OH6	FORM(S)+O→OH+HO2+CO	R40
OH7	ALD2(S)+O→C2O3+OH	R42
OH8	C2O3+HO2→0.79FORM+0.79XO2+0.79HO2+0.79OH	R50
OH9	O+OLE(S)→0.63ALD2+0.38HO2+0.28XO2+0.3CO+0.2FORM+0.02XO2N+0.22PAR+0.2OH	R56
OH10	O3+OLE(S)→0.5ALD2+0.74FORM+0.33CO+0.44HO2+0.22XO2+0.1OH-PAR	R58
OH11	O+ETH(S)→FORM+0.7XO2+CO+1.7HO2+0.3OH	R60
OH12	O3+OPEN→0.03ALD2+0.62C2O3+0.7FORM+0.03XO2+0.69CO+0.08OH+0.76HO2+0.2MGLY	R72
OH13	O3+ISOP→FORM+0.4ALD2+0.55ETH+0.2MGLY+0.06CO+0.1PAR+0.44HO2+0.1OH	R77
OH14	FORM(P)+O→OH+HO2+CO	R40
OH15	ALD2(P)+O→C2O3+OH	R42
OH16	O+OLE(P)→0.63ALD2+0.38HO2+0.28XO2+0.3CO+0.2FORM+0.02XO2N+0.22PAR+0.2OH	R56
OH17	O3+OLE(P)→0.5ALD2+0.74FORM+0.33CO+0.44HO2+0.22XO2+0.1OH-PAR	R58
OH18	O+ETH(P)→FORM+0.7XO2+CO+1.7HO2+0.3OH	R60
	Removal Reactions for OH	
OH19	O3+OH→HO2	R12

OH20	OH+NO→HONO	R22
OH21	OH+HONO→NO2	R24
OH22	OH+NO2→HNO3	R26
OH23	OH+HNO3→NO3	R27
OH24	OH+PNA→NO2	R31
OH25	OH+H2O2→HO2	R35
OH26	OH+CO→HO2	R36
OH27	FORM(S)+OH→HO2+CO	R37
OH28	ALD2(S)+OH→C2O3	R43
OH29	OH→FORM+XO2+HO2	R51
OH30	PAR(S)+OH→0.87XO2+0.13XO2N+0.11HO2+0.11ALD2+0.76ROR-0.11PAR	R52
OH31	OH+OLE(S)→FORM+ALD2+XO2+HO2-PAR	R57
OH32	OH+ETH(S)→XO2+1.56FORM+HO2+0.22ALD2	R61
OH33	OH+TOL→0.08XO2+0.36CRES+0.44HO2+0.56TO2	R63
OH34	OH+CRES→0.4CRO+0.6XO2+0.6HO2+0.3OPEN	R66
OH35	OH+OPEN→XO2+C2O3+2HO2+2CO+FORM	R70
OH36	OH+XYL→0.7HO2+0.5XO2+0.2CRES+0.8MGLY+1.1PAR+0.3TO2	R69
OH37	OH+MGLY→XO2+C2O3	R73
OH38	OH+ISOP→FORM+XO2+0.67HO2+0.4MGLY+0.2C2O3+ETH+0.2ALD2+0.13XO2N	R76
OH39	FORM(P)+OH→HO2+CO	R37
OH40	ALD2(P)+OH→C2O3	R43
OH41	OH+OLE(P)→FORM+ALD2+XO2+HO2-PAR	R57
OH42	OH+ETH(P)→XO2+1.56FORM+HO2+0.22ALD2	R61
OH43	PAR(P)+OH→0.87XO2+0.13XO2N+0.11HO2+0.11ALD2+0.76ROR-0.11PAR	R52

Table S2. Reactions related to HO_2 radical in the OBM.

	Formation Reactions for HO_2	
HO2_1	O3+OH→HO2	R12
HO2_2	PNA→HO2+NO2	R30
HO2_3	OH+H2O2→HO2	R35
HO2_4	OH+CO→HO2	R36
HO2_5	FORM(S)+OH→HO2+CO	R37
HO2_6	FORM(S)+hv→2HO2+CO	R38
HO2_7	FORM(S)+O→OH+HO2+CO	R40
HO2_8	FORM(S)+NO3→HNO3+HO2+CO	R41
HO2_9	ALD2(S)+hv→FORM+XO2+CO+2HO2	R45
HO2_10	C2O3+NO→FORM+XO2+HO2+NO2	R46
HO2_11	C2O3+C2O3→2FORM+2XO2+2HO2	R49
HO2_12	C2O3+HO2→0.79FORM+0.79XO2+0.79HO2+0.79OH	R50
HO2_13	OH→FORM+XO2+HO2	R51
HO2_14	PAR(S)+OH→0.87XO2+0.13XO2N+0.11HO2+0.11ALD2+0.76ROR-0.11PAR	R52
HO2_15	ROR(S)→1.1ALD2+0.96XO2+0.94HO2+0.04XO2N+0.02ROR-2.1PAR	R53
HO2_16	ROR(S)→HO2	R54
HO2_17	O+OLE(S)→0.63ALD2+0.38HO2+0.28XO2+0.3CO+0.2FORM+0.02XO2N+0.22PAR+0.2OH	R56
HO2_18	OH+OLE(S)→FORM+ALD2+XO2+HO2-PAR	R57
HO2_19	O3+OLE(S)→0.5ALD2+0.74FORM+0.33CO+0.44HO2+0.22XO2+0.1OH-PAR	R58
HO2_20	O+ETH(S)→FORM+0.7XO2+CO+1.7HO2+0.3OH	R60
HO2_21	OH+ETH(S)→XO2+1.56FORM+HO2+0.22ALD2	R61
HO2_22	O3+ETH(S)→FORM+0.42CO+0.12HO2	R62
HO2_23	OH+TOL→0.08XO2+0.36CRES+0.44HO2+0.56TO2	R63
HO2_24	TO2+NO→0.9NO2+0.9OPEN+0.9HO2	R64
HO2_25	TO2→HO2+CRES	R65
HO2_26	OH+CRES→0.4CRO+0.6XO2+0.6HO2+0.3OPEN	R66

HO2_27	OPEN+hv→C2O3+CO+HO2	R71
HO2_28	OH+OPEN→XO2+C2O3+2HO2+2CO+FORM	R70
HO2_29	O3+OPEN→0.03ALD2+0.62C2O3+0.7FORM+0.03XO2+0.69CO+0.08OH+0.76HO2+0.2MGLY	R72
HO2_30	OH+XYL→0.7HO2+0.5XO2+0.2CRES+0.8MGLY+1.1PAR+0.3TO2	R69
HO2_31	MGLY+hv→C2O3+CO+HO2	R74
HO2_32	O+ISOP→0.6HO2+0.8ALD2+0.55OLE+0.5XO2+0.5CO+0.45ETH+0.9PAR	R75
HO2_33	OH+ISOP→FORM+XO2+0.67HO2+0.4MGLY+0.2C2O3+ETH+0.2ALD2+0.13XO2N	R76
HO2_34	O3+ISOP→FORM+0.4ALD2+0.55ETH+0.2MGLY+0.06CO+0.1PAR+0.44HO2+0.1OH	R77
HO2_35	FORM(P)+OH→HO2+CO	R37
HO2_36	FORM(P)+hv→2HO2+CO	R38
HO2_37	FORM(P)+O→OH+HO2+CO	R40
HO2_38	FORM(P)+NO3→HNO3+HO2+CO	R41
HO2_39	ALD2(P)+hv→FORM+XO2+CO+2HO2	R45
HO2_40	O+OLE(P)→0.63ALD2+0.38HO2+0.28XO2+0.3CO+0.2FORM+0.02XO2N+0.22PAR+0.2OH	R56
HO2_41	OH+OLE(P)→FORM+ALD2+XO2+HO2-PAR	R57
HO2_42	O3+OLE(P)→0.5ALD2+0.74FORM+0.33CO+0.44HO2+0.22XO2+0.1OH-PAR	R58
HO2_43	O+ETH(P)→FORM+0.7XO2+CO+1.7HO2+0.3OH	R60
HO2_44	OH+ETH(P)→XO2+1.56FORM+HO2+0.22ALD2	R61
HO2_45	O3+ETH(P)→FORM+0.42CO+0.12HO2	R62
HO2_46	ROR(P)→1.1ALD2+0.96XO2+0.94HO2+0.04XO2N+0.02ROR-2.1PAR	R53
HO2_47	ROR(P)→HO2	R54
HO2_48	PAR(P)+OH→0.87XO2+0.13XO2N+0.11HO2+0.11ALD2+0.76ROR-0.11PAR	R52
	Removal Reactions for HO_2	
HO2_49	O3+HO2→OH	R13
HO2_50	HO2+NO→OH+NO2	R28
HO2_51	HO2+NO2→PNA	R29
HO2_52	HO2+HO2→H2O2	R32
HO2_53	HO2+HO2+H2O→H2O2	R33
HO2_54	C2O3+HO2→0.79FORM+0.79XO2+0.79HO2+0.79OH	R50

3. OBM Parameters Settings

The concentrations of O_3, 56 NMHCs, NO, and meteorological data as input to simulate the total amount of photochemical O_3 formation at two sites. For those species as constraints, their concentrations measured at 07:00 LT of each days were set as initial concentrations on that day. For those 27 simulated species, their initial concentrations were assumed to be zero (Cardelino and Chameides, 1995). For NO_2, we assumed an initial concentration of one to third of NO concentration (He et al., 2019). The C_i^a values for all species were assumed to be zero.

The boundary layer height *H(t)* was simulated by the equation $H(t) = H_0+F_G*\Delta H$, where H_0 means mixing height at time of sunrise (*i.e.*, the minimum mixing height); F_G = fraction of H growth. ΔH = the difference of maximum mixing height at noon with H_0. The daily maximum boundary layer height was assumed to be 1215m in this study and the lowest value was assumed to be 250m.

References:

1 Cardelino, C.A. and Chameides,W.L. An observation-based model for analyzing ozone precursor relationships in the urban atmosphere. *J. Air & Waste Manag. Association* **1995**, *45*, 161–180.

2 He, Z.; Wang, X.; Ling, Z.; Zhao, J.; Guo, H.; Shao, M.; et al. Contributions of different anthropogenic volatile organic compound sources to ozone formation at a receptor site in the Pearl River Delta region and its policy implications. *Atmos. Chem. and Phys.*,**2019**, *19*, 8801–8816.