Supplementary for “Seasonal characteristics of atmospheric peroxyacetyl nitrate (PAN) in a coastal city of Southeast China: Explanatory factors and photochemical effects”

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Captions:

Fig. S1. Scatter plots of PAN versus O₃ during the observation periods.

Fig. S2. Wind direction frequency and wind speed plots in (a) spring and (b) autumn during the observation periods.

Fig. S3. Bivariate plot of PAN maxing ratios in (a) spring and (b) autumn, and O₃ mixing ratios in (c) spring and (d) autumn, respectively (units: ppbv of PAN and O₃ maxing ratio, m·s⁻¹ of wind speed).

Fig. S4. Response curves (autumn) in the multiple-factor model of PAN mixing ratio to changes in (a) NO, (b) O_x (O_x=O₃+NO₂), (c) TVOCs, (d) PM_{2.5} concentration, (e) ultraviolet radiation (UV), (f) air temperature (T), (g) relative humidity (RH), and (h) wind speed (WS). The y-axis is the smoothing function values. For example, s(NO, df) shows the trend in PAN concentration when NO concentration changes, and the number of df is the degree of freedom. The x-axis is the influencing factor, and the shaded area around the solid red line indicates the 95% confidence interval of PAN concentration. The blue vertical short lines represent the concentration distribution characteristics of the explanatory variables (units: NO (ppbv), O_x (O₃+NO₂) (ppbv), TVOCs (ppbv), PM_{2.5} (ppbv), UV (W·m⁻²), T (°C), RH (%), WS (m·s⁻¹)).

Fig. S5. The OBM-MCM calculated relative incremental reactivity (RIR) for major O₃ precursor groups in (a) spring and (b) autumn during the daytime (06:00-17:00 LT) on different pollution scenarios.

Fig. S6. Diurnal trends of the relative variations of O₃ net production $\Delta P(O_3)$ (ppbv·h⁻¹) during the daytime in the SC1 to those simulated with PAN chemistry disabled in SC2 during the daytime (06:00-

41 17:00) in (a) spring and (b) autumn (unit: ppbv·h⁻¹ for $\Delta P(O_3)$). The data in the picture came from the
42 days that have significant promotion effects of PAN on O₃ in spring and autumn.

43 **Fig. S7.** Response curves (spring) of $\Delta P(O_3)$ to changes in (a) ΔROx , (b) ultraviolet radiation (UV), (f)
44 air temperature (T), (g) relative humidity (RH), and (h) wind speed (WS). The y-axis is the smoothing
45 function values. For example, s(UV, df) shows the trend in $\Delta P(O_3)$ when UV changes, and the number
46 of df is the degree of freedom. The x-axis is the influencing factor, and the shaded area around the solid
47 red line indicates the 95% confidence interval of $\Delta P(O_3)$. The blue vertical short lines represent the
48 concentration distribution characteristics of the explanatory variables (units: ΔROx (molecules·cm⁻³),
49 UV (W·m⁻²)).

50 **Fig. S8.** Response curves (autumn) of $\Delta P(O_3)$ to changes in (a) ΔROx , (b) ultraviolet radiation (UV),
51 (c) air temperature (T), (d) wind speed (WS). The y-axis is the smoothing function values. For example,
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54 confidence interval of $\Delta P(O_3)$. The blue vertical short lines represent the concentration distribution
55 characteristics of the explanatory variables (units: ΔROx (molecules·cm⁻³), UV (W·m⁻²), T (°C), WS
56 (m·s⁻¹)).

57 **Table S1.** Detailed uncertainty and detection limit of instruments used for trace gas observation at the
58 observation site.

59 **Table S2.** Descriptive statistics of measured VOCs concentrations (Units: ppbv).

60 **Table S3.** Variance inflation factor values quantify the degree of multicollinearity for the PAN influencing
61 factors.

62 **Table S4.** The measured species and parameters on the inhibition effect stages and promotion effect stages
63 of PAN on O₃ in spring and autumn.

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121 **Table S1. Detailed uncertainty and detection limit of instruments used for trace gas observation at the**
122 **observation site.**

Parameter	Experimental Technique	Uncertainty	Detection limit
PAN	PANs-1000, Focused Photonics Inc., Hangzhou, CN	±10%	50 pptv
O ₃	Model 49i, Thermo Fischer Scientific, USA	±5%	1 ppbv
NO _x	Model 42i, Thermo Fischer Scientific, USA	±10%	0.5 ppbv
CO	Model 48i, Thermo Fischer Scientific, USA	±5%	40 ppbv
SO ₂	Model 43i, Thermo Fischer Scientific, USA	±10%	0.5 ppbv
VOCs	GC-FID/MS, TH-300B, Wuhan, CN	±10%	20-300 pptv
HONO	MARGA, ADI 2080, Applikon Analytical B.V., the Netherlands	±20%	50 pptv

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124 **Table S2. Descriptive statistics of measured VOCs concentrations (Units: ppbv).**

Chemicals	Spring		Autumn		Chemicals	Spring		Autumn	
	Mean	SD	Mean	SD		Mean	SD	Mean	SD
Alkanes	9.41	5.30	5.47	2.88	Alkyne	1.00	0.55	0.63	0.34
Ethane	2.39	1.02	1.31	0.43	Aromatics	2.71	2.33	1.62	1.15
Propane	2.31	1.29	1.19	0.58	Benzene	0.27	0.14	0.16	0.09
iso-Butane	0.87	0.57	0.52	0.37	Toluene	1.37	1.21	0.85	0.84
n-Butane	1.30	0.94	0.77	0.59	m/p-Xylene	0.53	0.63	0.39	0.32
iso-Pentane	1.15	1.27	0.52	0.44	Ethylbenzene	0.18	0.18	0.09	0.10
n-Pentane	0.44	0.42	0.24	0.21	Styrene	0.09	0.16	0.02	0.04
2,2-Dimethylbutane	0.02	0.02	0.02	0.01	o-Xylene	0.19	0.23	0.04	0.09
2,3-Dimethylbutane	0.05	0.06	0.05	0.05	m-Ethyltoluene	0.02	0.02	0.01	0.01
2-Methylpentane	0.08	0.09	0.05	0.04	1,3,5-Trimethylbenzene	0.01	0.01	0.01	0.01
3-Methylpentane	0.14	0.15	0.06	0.06	p-Ethyltoluene	0.01	0.01	0.01	0.005
n-Hexane	0.20	0.25	0.10	0.20	1,2,4-Trimethylbenzene	0.03	0.05	0.01	0.02
Cyclohexane	0.04	0.04	0.02	0.02	1,2,3-Trimethylbenzene	0.01	0.01	0.01	0.004
2-Methylhexane	0.05	0.06	0.04	0.05	Isoprene (BHC)	0.08	0.14	0.10	0.17
3-Methylhexane	0.08	0.09	0.05	0.08	Halocarbons	2.54	1.27	1.95	0.90
n-Heptane	0.07	0.08	0.05	0.06	Chloromethane	0.51	0.23	0.46	0.18
n-Octane	0.04	0.06	0.09	0.06	Bromomethane	0.06	0.03	0.04	0.02
n-Nonane	0.02	0.01	0.01	0.005	Dichloromethane	1.19	0.81	0.87	0.50
n-Decane	0.01	0.01	0.01	0.01	Trichloromethane	0.07	0.03	0.05	0.02
n-Undecane	0.02	0.02	0.03	0.03	1,2-Dichloroethane	0.51	0.34	0.36	0.22
n-Dodecane	0.12	0.29	0.36	0.84	Trichloroethene	0.02	0.02	0.02	0.01
Alkenes	1.30	0.89	0.85	0.48	1,2-Dichloropropane	0.12	0.13	0.10	0.08
Ethene	0.90	0.65	0.51	0.34	Tetrachloroethene	0.05	0.05	0.04	0.05
Propene	0.20	0.14	0.19	0.11	OVOCs	4.49	1.83	4.17	2.57
1-Butene	0.04	0.03	0.03	0.02	Acrolein	0.06	0.03	0.04	0.02
cis-2-Butene	0.05	0.06	0.03	0.03	Acetone	2.22	0.94	2.21	0.91
trans-2-Butene	0.03	0.06	0.03	0.02	2-Butanone	0.67	0.45	0.50	0.44
1-Pentene	0.02	0.02	0.01	0.01	2-Propanol	0.24	0.31	0.12	0.12
trans-2-Pentene	0.04	0.04	0.04	0.02	2-Methoxy-2-methylpropane	0.24	0.32	0.09	0.09
1,3-Butadiene	0.01	0.02	0.01	0.01	Ethylacetate	1.07	0.83	1.20	1.31

128 **Table S3. Variance inflation factor values quantify the degree of multicollinearity for the PAN influencing**
 129 **factors.**

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Smooth variable	NO (ppbv)	Ox (O ₃ +NO ₂) (ppbv)	TVOCs (ppbv)	PM _{2.5} (ppbv)	UV (W·m ⁻²)	T (°C)	RH (%)	WS (m·s ⁻¹)
Spring	1.437	3.512	1.88	1.545	1.815	1.62	3.5	1.75
Autumn	1.345	2.276	1.732	1.532	1.232	1.806	2.098	1.769

135 **Table S4. The measured species and parameters on the inhibition effect stages and promotion effect stages of PAN**
 136 **on O₃ in spring and autumn.**

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Parameters	Spring				Autumn			
	Inhibition		Promotion		Inhibition		Promotion	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PAN (ppbv)	1.04	0.74	1.89	1.00	0.84	0.53	1.58	0.70
O ₃ (ppbv)	27.32	18.02	50.26	25.77	36.42	16.26	53.51	16.63
NO (ppbv)	6.31	9.76	4.06	7.82	3.42	4.36	2.70	3.50
NO ₂ (ppbv)	13.08	7.38	8.55	6.31	10.23	5.43	9.46	5.74
CO (ppbv)	302.84	69.10	283.35	62.22	252.85	52.89	239.44	46.55
SO ₂ (ppbv)	2.36	1.14	2.66	1.32	3.24	0.68	3.20	0.91
UV (W·m ⁻²)	15.40	13.95	29.76	14.84	17.68	14.07	24.95	13.72
T (°C)	21.57	4.13	26.69	4.22	25.95	3.08	28.39	3.50
RH (%)	70.62	16.31	56.77	17.13	63.77	13.22	54.45	9.94
P (hPa)	1010.08	3.65	1008.24	3.50	1008.92	3.58	1007.61	3.67
Wind speed (m·s ⁻¹)	2.01	1.10	2.83	1.22	3.18	1.44	3.08	1.35
PM _{2.5} (μg·m ⁻³)	9.23	5.45	9.67	4.68	5.40	3.00	5.94	3.15
TVOCs (ppbv)	23.55	10.45	17.51	6.78	15.25	8.11	13.29	5.03