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Ambient nitro-aromatic compounds – biomass burning versus secondary formation in rural China

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Supplement for

Ambient Nitro-Aromatic Compounds - Biomass Burning versus Secondary Formation in a Rural City in China

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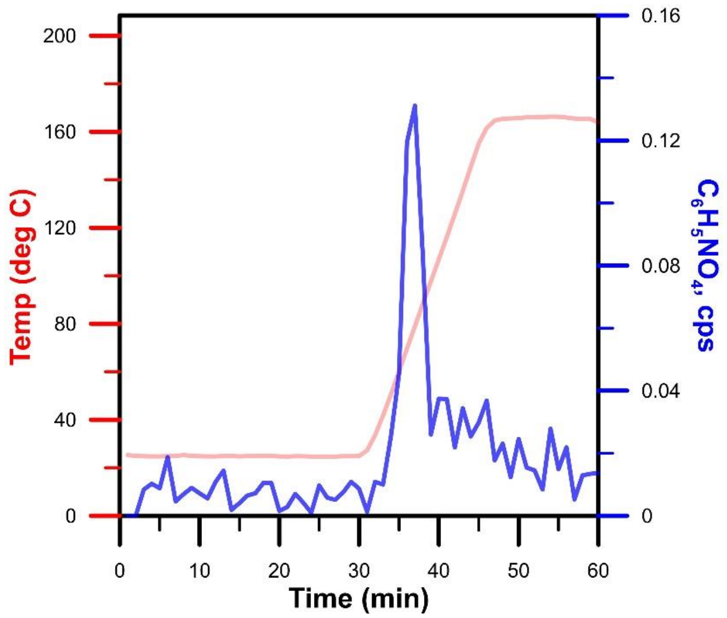
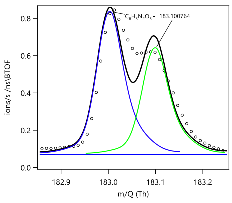
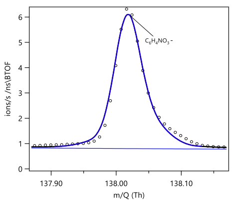


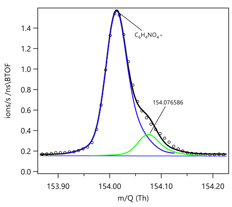
Figure S1. *Typical desorption profile FIGAERO settings used in this study*



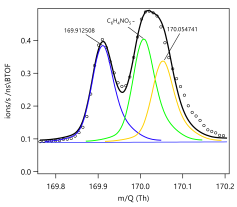
NAC 1 $C_6H_4N_2O_5$ (*183.004*)



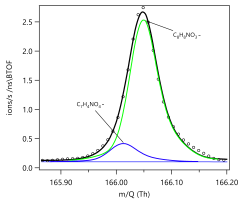
NAC 2 $C_6H_5NO_3$ (*138.019*)



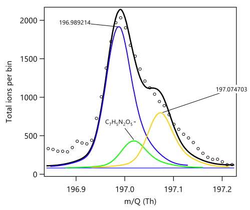
NAC 3 $C_6H_5NO_4$ (*154.014*)



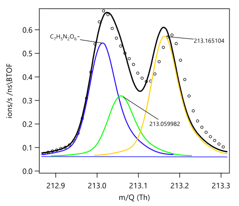
NAC 4 $C_6H_5NO_5$ (*170.009*)



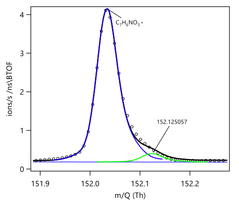
NAC 5 $C_7H_5NO_4$ (*166.014*)



NAC 6 $C_7H_6N_2O_5$(*197.020*)

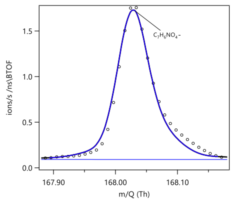


NAC 7 $C_7H_6N_2O_6$ (*213.015*)

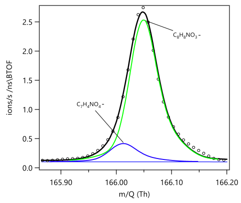


NAC 8 $C_7H_7NO_3$ (*152.035*)

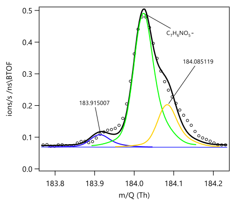
Figure S2. *High Resolution peak fitting of individual nitro-aromatic compounds (NACs) (part 1)*



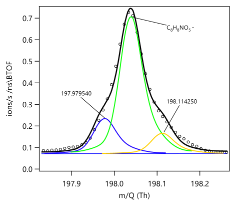
NAC 9 $C_7H_7NO_4$ (*168.030*)



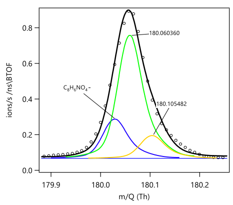
NAC 13 $C_8H_9NO_3$ (166.050)



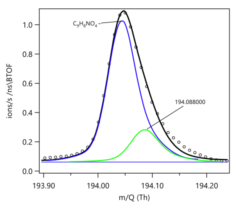
NAC 10 $C_7H_7NO_5$ (*184.024*)



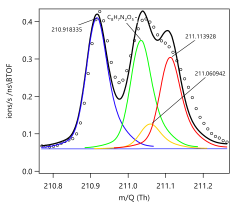
NAC 14 $C_8H_9NO_5$ (*198.040*)



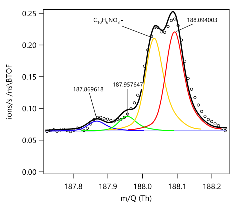
NAC 11 $C_8H_7NO_4$ (*180.030*)



NAC 15 $C_9H_9NO_4$ (*194.045*)



NAC 12 $C_8H_8N_2O_5$ (*211.035*)



NAC 16 $C_{10}H_7NO_3$ (*188.035*)

Figure S2*. High Resolution peak fitting of individual nitro-aromatic compounds (NACs) (part 1)*

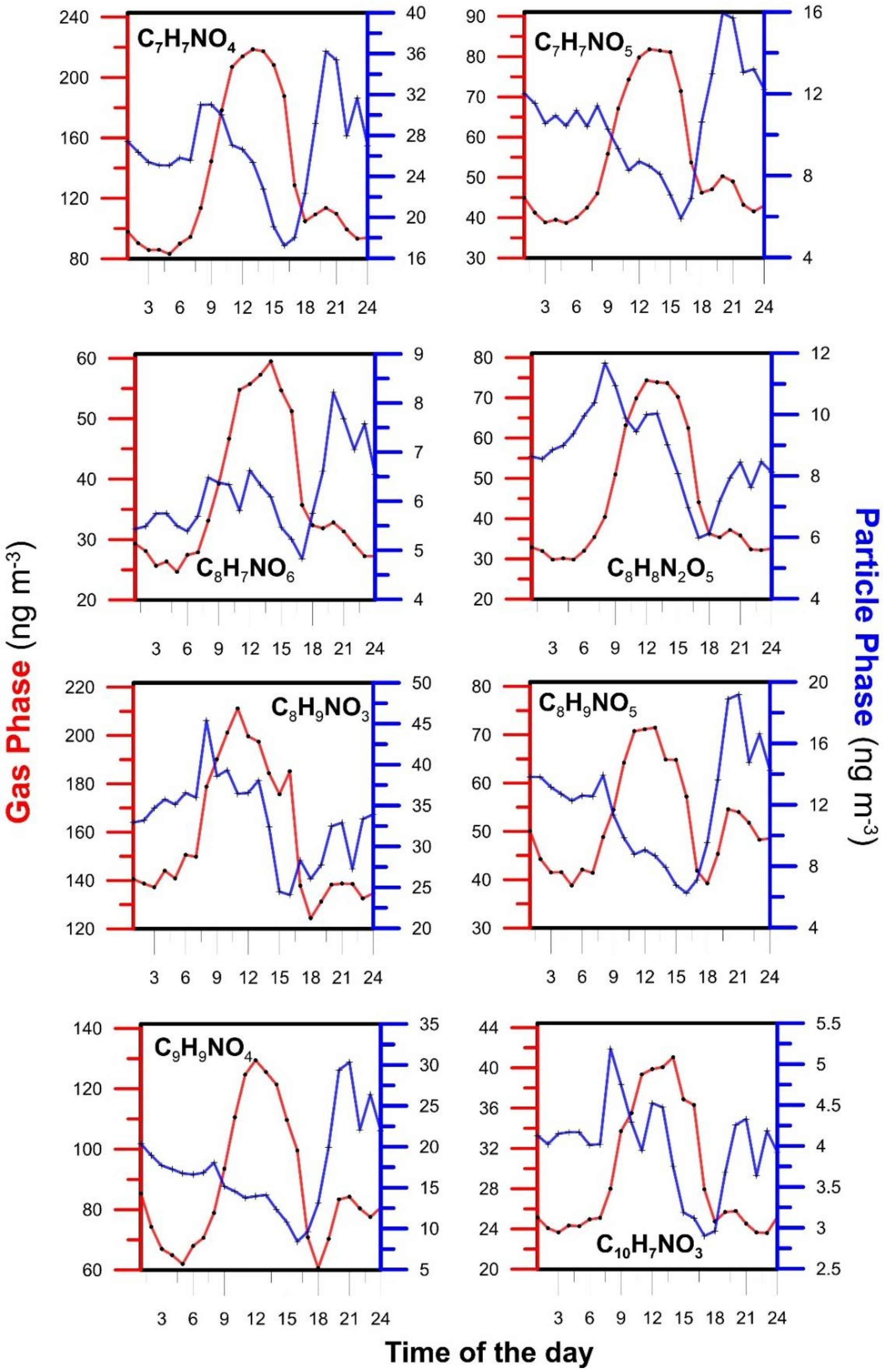


Figure S3. *Diurnal profile of nitro-aromatic compounds measured in gas and particle phase (part 1)*

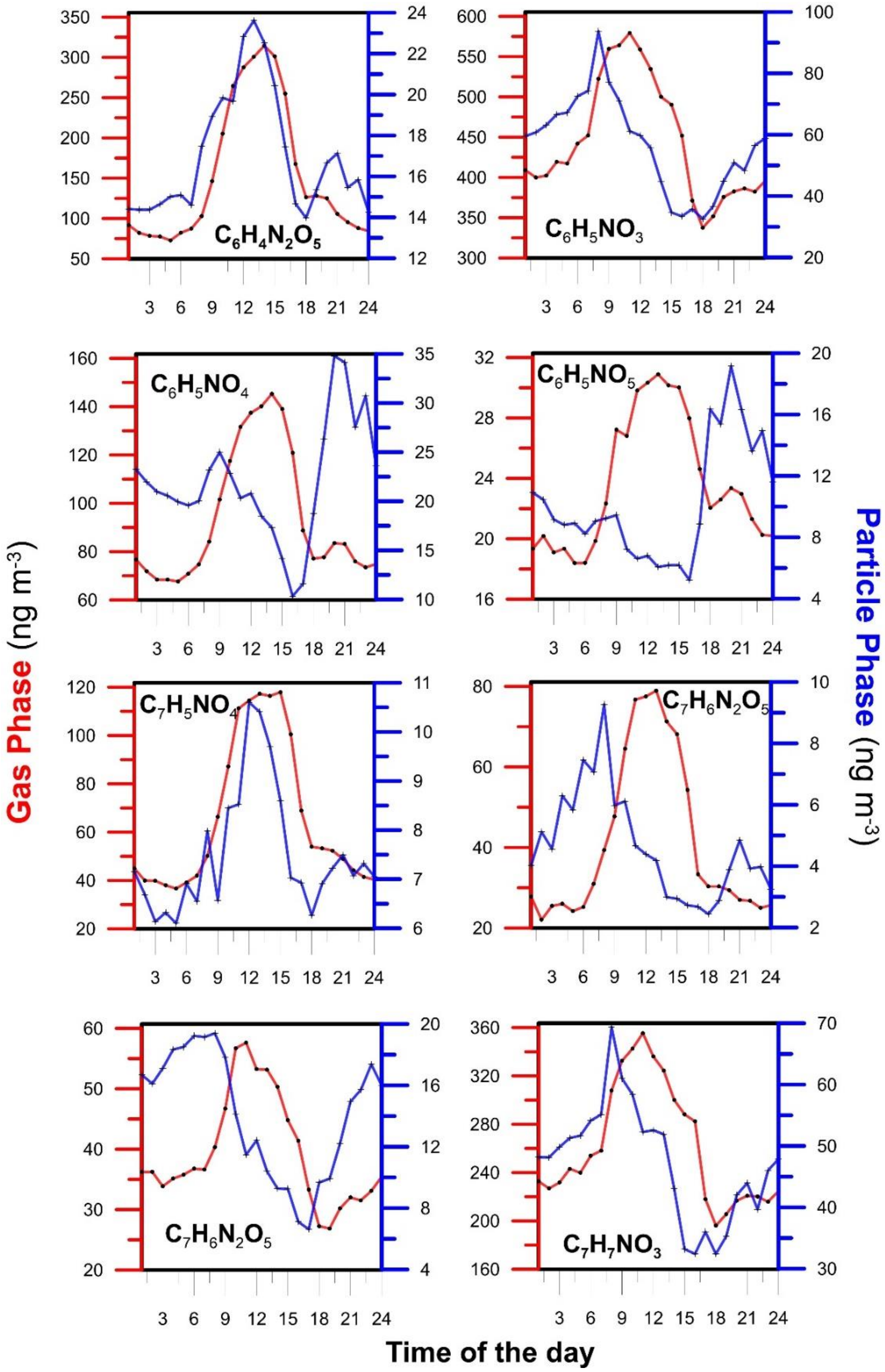


Figure S3. *Diurnal profile of nitro-aromatic compounds measured in gas and particle phase (part 2)*

***Table S1**. Physical information of nitro-aromatic compounds (NACs) measured in this study*

NACs	**Sensitivity Factor$^{\$}$**	**Class***	**Exact Mass [M-H]**	**Campaign Ave_Conc**	**Daytime Conc**	**Night-time Conc**	**Regime Concentration** 1	2	3	4	**Fp**
$C_6H_4N_2O_5$	0.009	DNP	183.004	151.99/17.00	241.29/20.45	99.90/15.05	108.47/28.39	135.70/12.26	184.45/20.16	203.86/11.46	13.03
$C_6H_5NO_3$	0.019	NP	138.019	444.42/56.70	529.98/59.60	394.51/55.18	623.76/161.89	275.43/14.66	622.00/78.54	423.64/24.09	9.11
$C_6H_5NO_4$	0.272	NC	154.014	93.46/21.99	124.03/19.36	75.63/23.58	116.82/63.27	74.23/10.75	107.77/22.15	105.30/8.94	17.90
$C_6H_5NO_5$	-	NC	170.009	23.62/10.24	28.41/7.03	20.83/12.13	27.96/25.98	19.75/10.35	27.32/4.23	23.66/1.46	28.09
$C_7H_5NO_4$	-	NB	166.014	64.92/7.49	97.81/8.72	45.73/6.80	54.84/11.69	54.38/5.05	79.15/9.86	90.43/5.20	13.39
$C_7H_6N_2O_5$	-	DNP	197.020	40.98/4.64	64.31/4.85	27.33/4.54	31.09/10.64	32.44/2.67	56.36/5.24	51.38/2.59	14.25
$C_7H_6N_2O_6$	-	DNP	213.015	39.27/14.14	49.49/12.45	33.31/15.16	47.35/30.09	32.44/14.97	47.08/7.74	34.69/2.09	24.24
$C_7H_7NO_3$	-	NP	152.035	260.91/47.36	319.55/50.95	226.71/45.41	416.36/141.28	111.15/9.27	423.91/67.61	230.60/18.76	12.00
$C_7H_7NO_4$	-	NC	168.030	131.57/26.67	187.64/25.82	98.87/27.23	178.51/74.00	90.45/10.10	164.80/32.36	153.06/13.25	16.59
$C_7H_7NO_5$	-	NC	184.024	53.95/10.66	70.92/8.66	44.05/11.85	57.83/25.36	42.52/7.33	64.42/9.64	72.85/5.94	17.62
$C_8H_7NO_4$	-	NB	180.030	36.92/6.17	50.18/6.12	29.19/6.22	35.94/13.41	28.77/4.09	46.97/6.53	48.04/3.19	15.16
$C_8H_8N_2O_5$	-	DNP	211.035	45.11/8.77	64.33/9.62	33.90/8.30	47.45/20.17	36.42/6.93	55.20/7.23	52.60/3.28	17.03
$C_8H_9NO_3$	-	NP	166.050	158.13/33.43	191.86/35.36	138.45/32.41	275.86/105.37	56.13/5.96	264.20/45.85	132.63/12.75	13.91
$C_8H_9NO_5$	-	NC	198.040	52.05/12.01	63.14/9.23	45.58/13.65	80.44/37.39	29.94/5.54	69.00/11.10	62.29/5.01	17.60
$C_9H_9NO_4$	-	NB	194.045	87.01/17.48	110.42/13.56	73.35/19.80	131.44/58.59	45.51/6.06	118.43/16.73	124.23/9.10	14.90
$C_{10}H_7NO_3$	-	NP	188.035	29.24/3.99	36.75/4.17	24.85/3.90	31.69/9.01	21.98/1.70	38.19/5.29	33.28/3.13	11.89

$^{\$}$ A post-campaign calibration of nitrophenol, nitrocatechol, and dinitrophenol was utilized to characterize the sensitivity factor of NACs. The FIGAERO filter for the collection of particle phase was doped (20-30 µL) with freshly prepared standards in methanol solvent. The calibration was performed using the same thermal desorption profile to characterize ambient aerosols. The filters were then desorbed in the same way as for the field sampling. Sensitivities calculated for nitrophenol and dinitrophenol were enormously low, which will result in unusual high mixing ratios of NACs. Instead, the concentration of all the NACs were calculated based on the sensitivity factor of nitrocatechol.

**Classification: (NP) Nitrophenol; (NC) Nitrocatechol, (DNP) Dinitrophenol, (NB) Nitrobenzoic acid analog*

*** All concentrations presented here are in ng m^{-3}. The first and second values indicate concentration in gas and particle phase, respectively.*

Table S2. *Correlation coefficient (r) of mixing ratios of NACs in gas and particle phase. Values in red highlight the nitrophenols with strong association between the gas and particle phase.*

NAC	**All**	**Regime**			
		1	2	3	4
$C_6H_4N_2O_5$	0.351	0.321	0.417	0.643	0.589
$C_6H_5NO_3$	0.828	**0.949**	0.537	0.835	0.793
$C_6H_5NO_4$	0.355	0.233	0.448	0.199	0.001
$C_6H_5NO_5$	0.147	0.071	0.261	-0.023	0.104
$C_7H_5NO_4$	0.285	0.543	0.115	0.51	0.476
$C_7H_6N_2O_5$	0.173	0.375	0.199	0.272	0.124
$C_7H_6N_2O_6$	0.38	0.534	0.606	0.516	0.549
$C_7H_7NO_3$	0.835	**0.937**	0.672	0.867	0.858
$C_7H_7NO_4$	0.505	0.511	0.502	0.524	0.593
$C_7H_7NO_5$	0.156	0.118	0.243	0.044	0.357
$C_8H_7NO_4$	0.262	0.146	0.363	0.397	0.587
$C_8H_8N_2O_5$	0.296	0.256	0.363	0.52	0.758
$C_8H_9NO_3$	0.838	**0.917**	0.642	0.887	0.873
$C_8H_9NO_5$	0.602	**0.854**	0.392	0.404	0.806
$C_9H_9NO_4$	0.474	**0.756**	0.51	0.352	0.799
$C_{10}H_7NO_3$	0.57	0.406	0.521	0.657	0.374

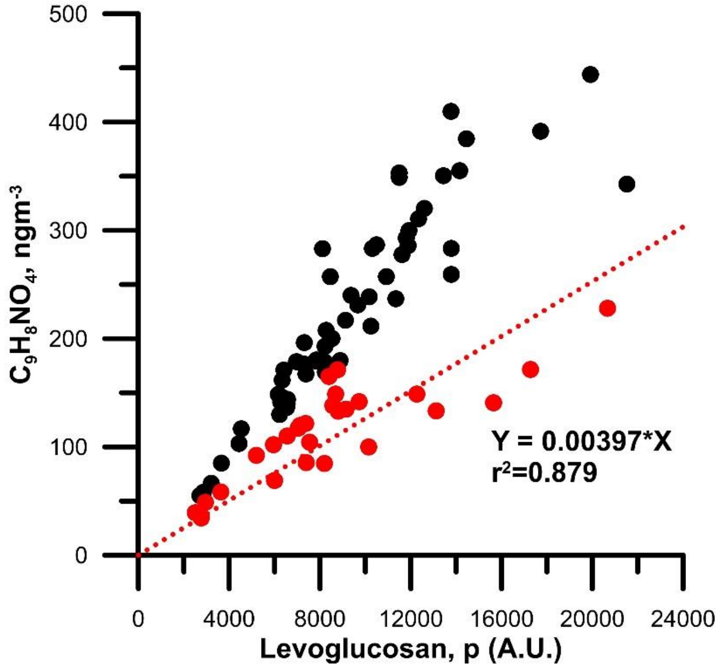


Figure S4. *Correlation analysis of $C_9H_8NO_4$ and levoglucosan for the analysis of the contribution of biomass burning using EC tracer method. Red points are the data used to determine $[NAC/lev]_{BB}$ (A.U. =arbitrary units)*

Table S3*. Measured concentration of major gaseous atmospheric components in Dezhou, China constrained in the model (mean ± standard deviation)*

Species	Mixing Ratio, ppbv
CO	1213±683
NO	21±25
O_3	17±11
NO_2	26±9
Catechol	0.0061±0.0025
HONO	2.948±2.17
HCHO	4.832±2.834
HNO_3	1.123±0.98
Propylene	2.244±1.718
Isoprene	0.047±0.129
Ethane	11.37±8.557
Ethylene	7.731±5.212
m/p-Xylene	0.699±0.852
o-Xylene	0.242±0.349
Toluene	1.676±2.122
Styrene	0.152±0.277
Trimethylbenzene 1,3,5-	0.032±0.117
Trimethylbenzene1,2,4-	0.091±0.173
Trimethylbenzene1,2,3-	0.033±0.121
Propane	7.418±7.137
Acetylene	6.133±5.849
Dichloromethane	4.993±20.014
Isobutane	1.687±1.388
n-Butane	3.742±3.727
Acetaldehyde	3.203±1.702
Acetone	2.408±1.153

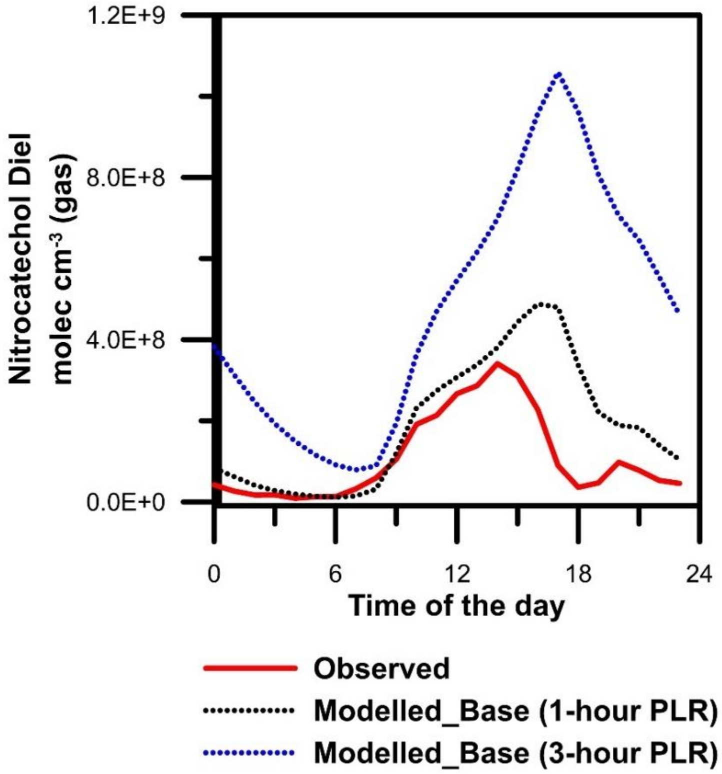


Figure S5. *Sensitivity test physical loss rate (PLR) of nitrocatechol*

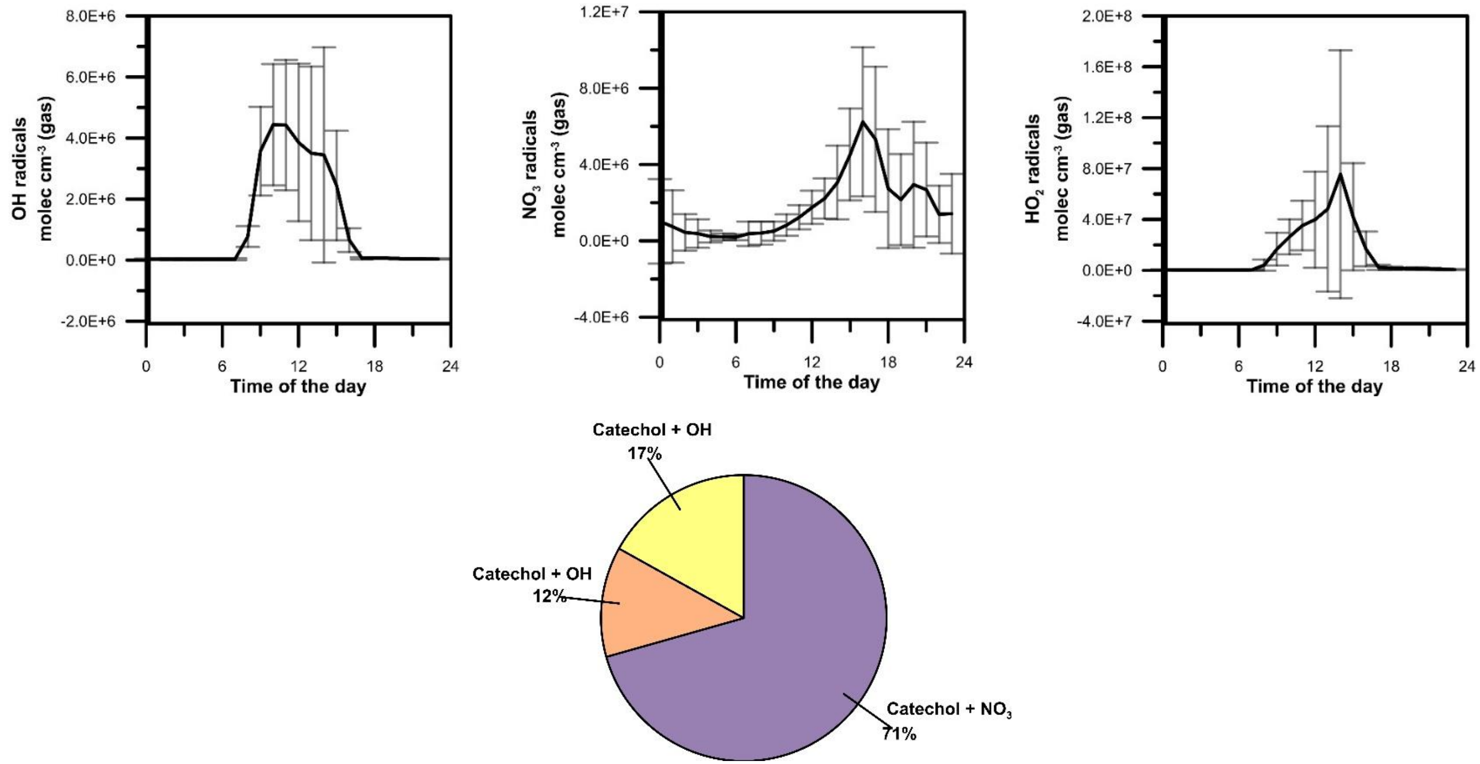


Figure S6. *(Top) Diurnal profile of OH, NO_3, and HO_2 radicals calculated in Dezhou. Variabilities are given in standard deviation (Bottom) . Overall production of CATEC1O from the reaction with OH, NO_3 and NO. Minor contributors (<1%) are not included.*

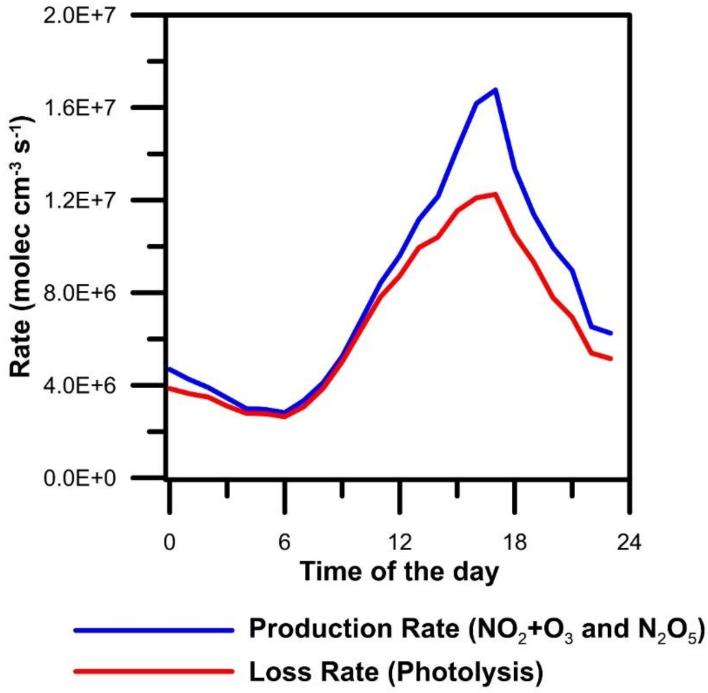
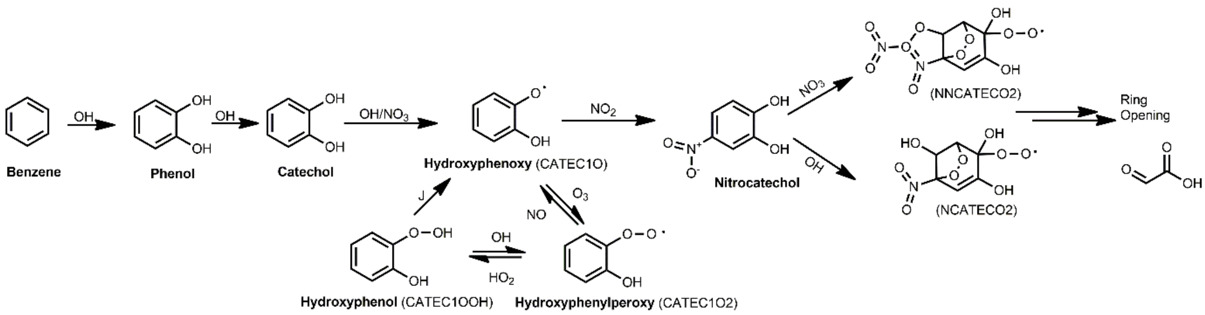


Figure S7. *Major production and loss pathways of NO_3 radicals*

Contribution of Traffic Sources to the formation of NACs

Traffic emission was deemed as not a significant source of the measured NACs based on the weak association of nitro-aromatic compounds to automobile exhaust tracers. To further verify such claim, another set of model simulation was developed to account for the contribution of traffic emission by constraining benzene as the primary precursor. The time series of benzene during this study coincided with the influx of traffic in the rural city, thus making such anthropogenic VOC as a suitable representative of traffic emissions. In MCM, OH oxidation of benzene forms phenol and further reaction of phenol with OH radicals yield catechol. The calculated nitrocatechol concentration in the new model simulation only accounted for less than 1.5% of the observed nitrocatechol. This validates the negligible involvement of traffic emission in the secondary production of NACs in the rural city of China.



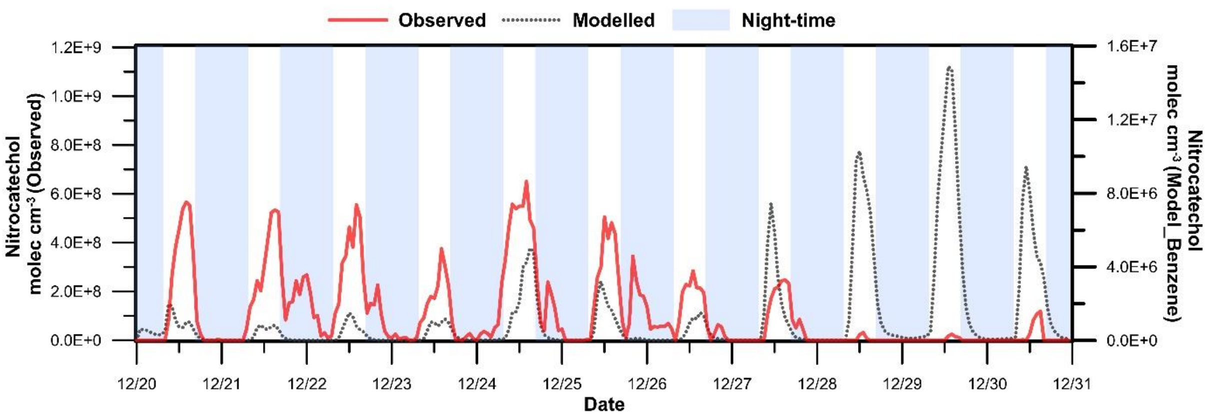


***Figure S8**. Comparison of time series profile of calculated nitrocatechol when benzene (traffic) as primary precursor. Note that the observed and calculated concentrations are given in two different axes.*