Dear Dr. Willy Maenhaut,

Thank you again for your careful checking on our manuscript (acp-2018-1256). We are sorry for the spelling mistakes in the manuscript. Please see the point-by-point responses below and changes are marked blue in the revised manuscript.

The following alteration is still needed in the Supplement before the manuscript can be published in ACP:
Page 9, last line: Replace " negtive values" by "negative values".

Response: Changed accordingly in the Supplement.

Most sincerely,

Min Hu and Jianzhen Yu

Supplement for
The formation of nitro-aromatic compounds under high NO_x and anthropogenic VOC conditions in urban Beijing, China

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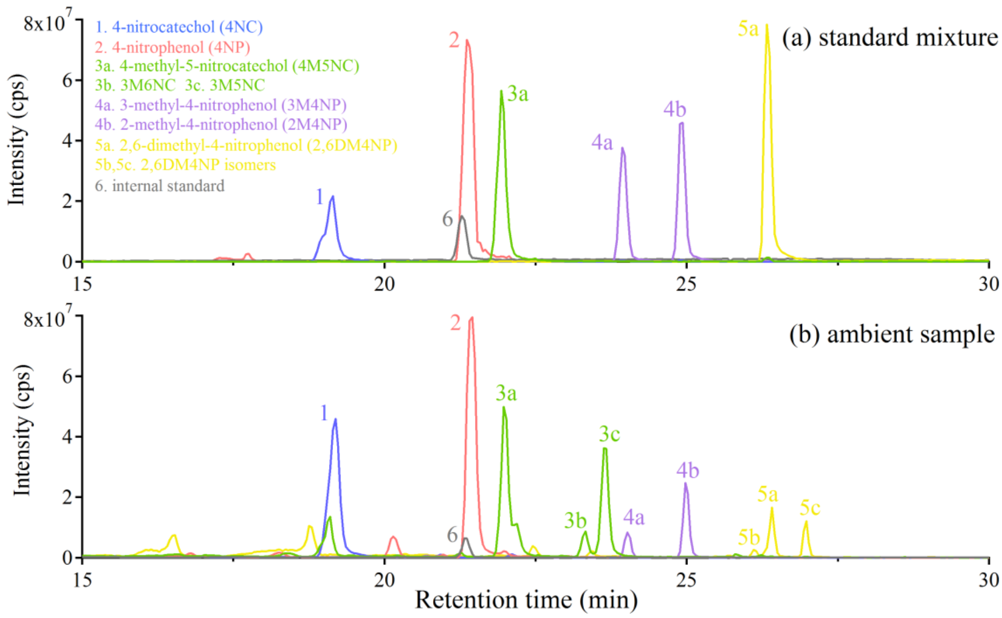

Figure S1 Extracted ion chromatograms for (a) a standard solution containing 4-nitrocatechol (4NC), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 2,6-dimethyl-4-nitrophenol (2,6DM4NP) and internal standard and (b) an ambient sample collected during the campaign.

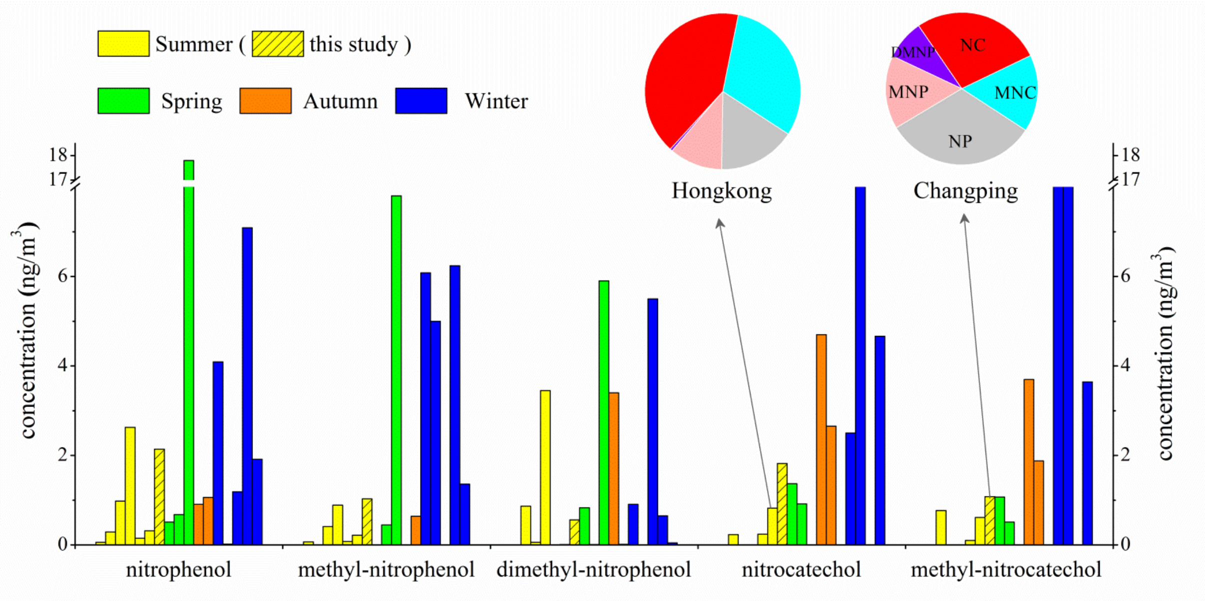

Figure S2 Comparison of individual NAC species across this and previous studies. For each species, the concentrations are respectively reported in summer (yellow) in Melpitz, Germany (Teich et al., 2017), Flanders, Belgium (Kahnt et al., 2013), Xianghe, China (Teich et al., 2017), Wangdu, China (Teich et al., 2017), Ljubljana, Slovenia (Kitanovski et al., 2012), Hong Kong, China (Chow et al., 2016), Beijing, China (this study); in spring (green) in Flanders, Belgium (Kahnt et al., 2013), Hong Kong, China (Chow et al., 2016), Rome, Italy (Cecinato et al., 2005); in autumn (orange) in Flanders, Belgium (Kahnt et al., 2013), Hong Kong, China (Chow et al., 2016); and in winter (blue) in Melpitz, Germany (Teich et al., 2017), Detling, UK (Mohr et al., 2013), Flanders, Belgium (Kahnt et al., 2013), TROPOS, Germany (Teich et al., 2017) and Hong Kong, China (Chow et al., 2016) from left side to right side. The inserted pie charts represent the NAC compositions in summer in Hong Kong (Chow et al., 2016) and Changping, respectively.

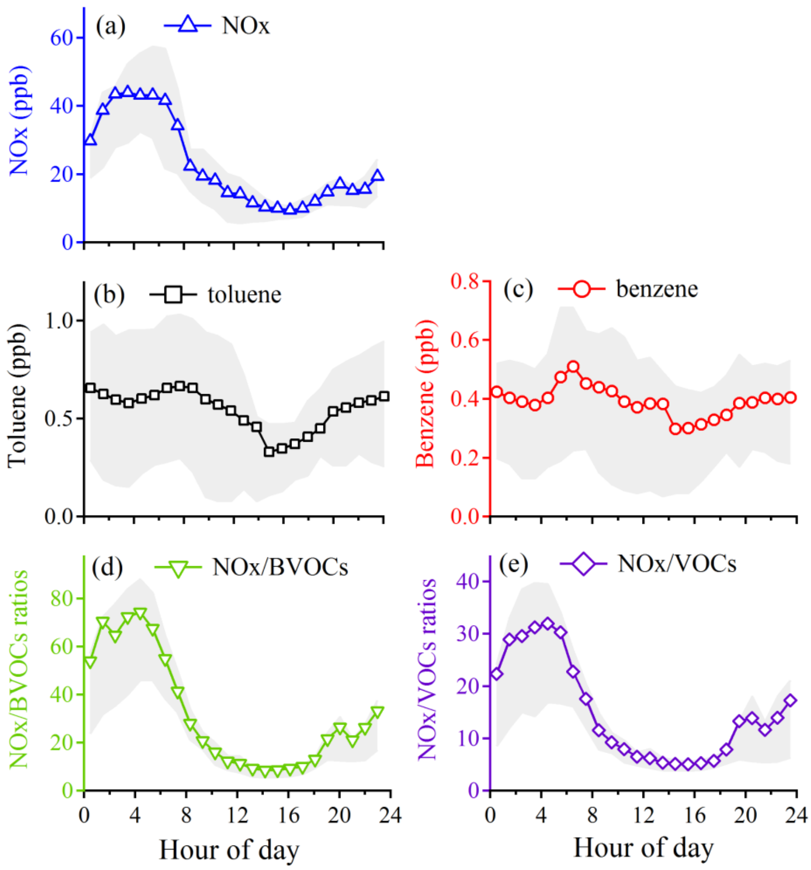

Figure S3 Diurnal variation of (a) NO_x, (b) toluene, (c) benzene, (d) NO_x/BVOCs ratios and (e) NO_x/VOCs ratios.

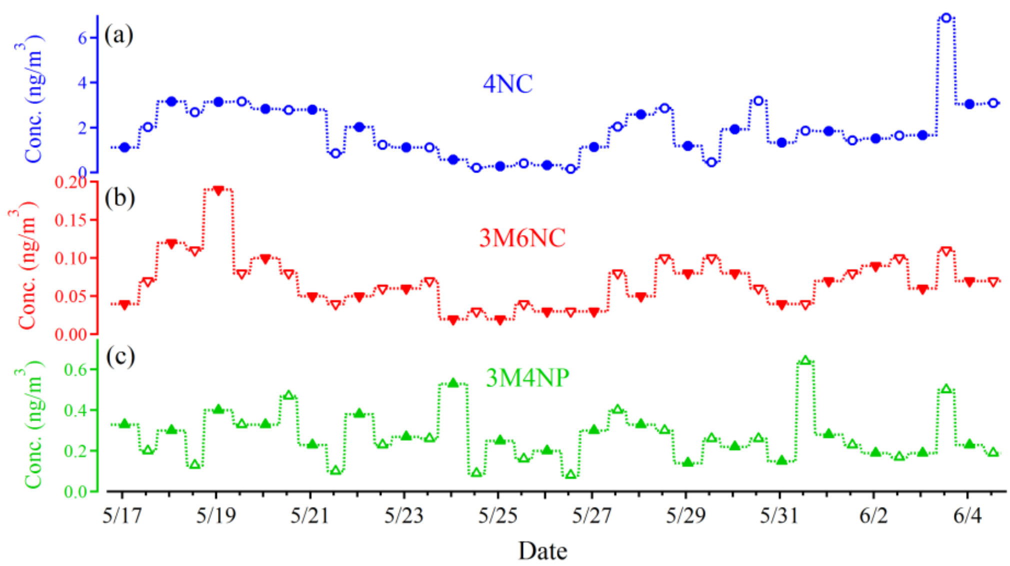

Figure S4 Time series of (a) 4-nitrocatechol (4NC), (b) 4-methyl-6-nitrocatechol (4M6NC), and (c) 3-methyl-4-nitrophenol (3M4NP).

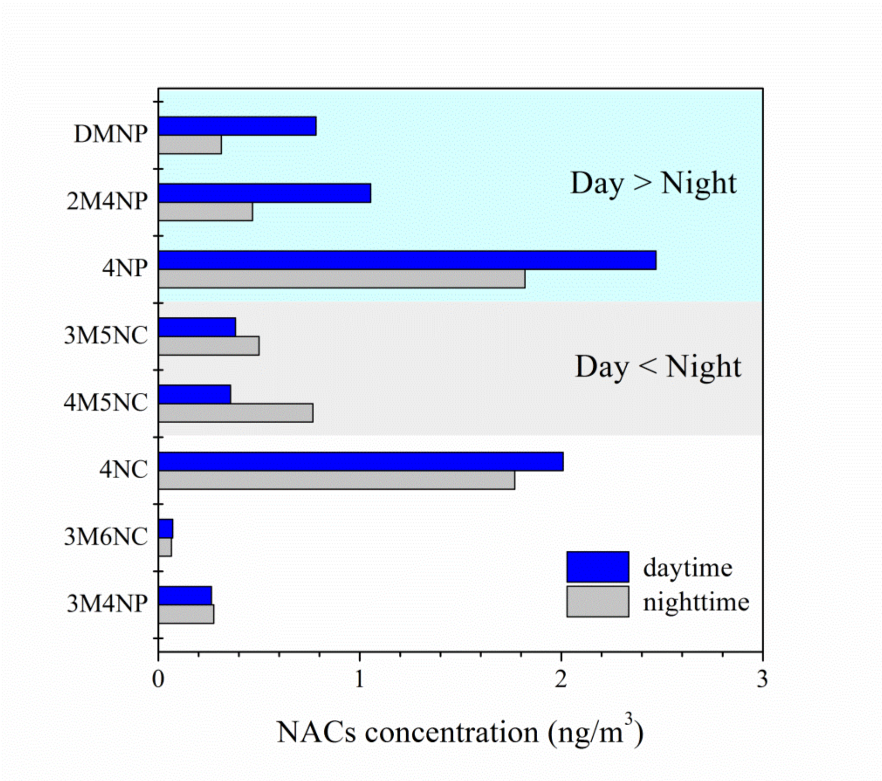

Figure S5 Day-night variations of NACs.

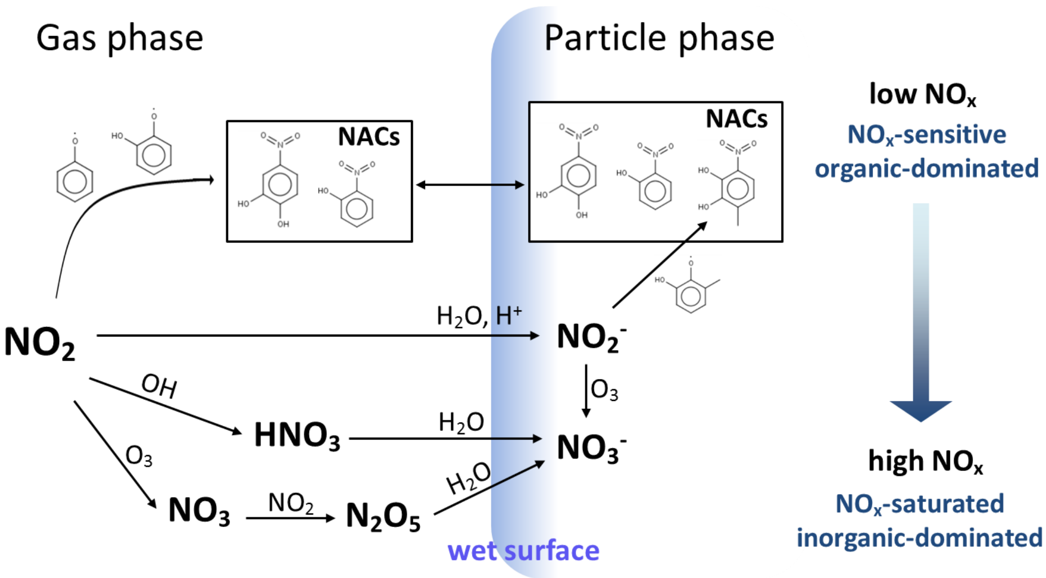

Figure S6 Schematic diagram and simplified mechanisms of the competing formation of inorganic nitrates and NACs

Table S1 Saturation pressure (P_v), NAC fraction in particles (F_p) and NAC concentrations in gas-phase

compounds	P_v [a] (Pa)	F_p (%)		conc. in gas phase (ng/m^3)	
		range	average	range	average
4NP	3.0E-02	0.25-1.3	0.83	143-566	268
2M4NP	4.2E-03	1.2-7.6	5.1	5.2-42	15
3M4NP	4.2E-03	1.2-7.6	5.1	1.9-20	5.8
DMNP	5.3E-04	99-100	100	0.000-0.007	0.002
4NC	3.4E-05	67-91	85	0.06-0.79	0.27
3M6NC	3.1E-06	95-99	98	0.000-0.003	0.001
3M5NC	3.1E-06	95-99	99	0.002-0.017	0.007
4M5NC	3.1E-06	95-99	98	0.001-0.028	0.009

Note: a. P_v values were estimated by UManSysProp using approaches outlined in section 2.4.

Table S2 Concentration of nitroaromatic compounds in this and previous studies

sites	sampling period	concentrations (ng/m^3)									references
		4NP (NP)	3M4NP	2M4NP	2,6D4NP (DMNP)	4NC (NC)	4M5NC	3M6NC	3M5NC	Total	
TROPOS, Germany	Jan-Feb, 2014	7.09	2.6	3.64	0.65					13.98	(Teich et al., 2017)
Melpitz, Germany	Jan-Feb, 2014	4.09	2.44	3.64	0.91					11.08	(Teich et al., 2017)
Maniz, Germany	May, 2006-June, 2007	2.48				6.4				8.88	(Zhang et al., 2010)
Melpitz, Germany	Jul, 2014	0.06	0.03	0.04	n.d.					0.13	(Teich et al., 2017)
Seiffen, Saxony, Germany	Oct, 2007-Mar, 2008						2	2.9	0.37	5.27	(Iinuma et al., 2010)
Detling, UK	Jan-Feb, 2012	0.02	5			2.5	8.2				(Mohr et al., 2013)
Ljubljana, Slovenia	Dec, 2010-Jan, 2011	1.8	0.61	0.75		75	29	6.2	34	147.36	(Kitanovski et al., 2012)
Ljubljana, Slovenia	Aug, 2010	0.15	<0.03	0.05		0.24	0.06	<0.03	0.01	0.57	(Kitanovski et al., 2012)
Rome, Italy	Feb- Apr, 2003	17.8	7.8		5.9					31.50	(Cecinato et al., 2005)
Hamme, Flanders, Belgium	Spring , 2010	0.51			0.83	1.37	1.07			3.78	(Kahnt et al., 2013)
	Summer, 2010	0.29			0.87	0.23	0.77			2.16	
	Autumn, 2010	0.91			3.4	4.7	3.7			12.71	
	Winter, 2010	1.19			5.5	11.6	13.9			32.19	
Los Angeles	May-June, 2010		1.24		0.92	1.67	0.36			4.19	(Zhang et al., 2013)
Hong Kong	Winter, 2009-2012	1.92	0.17	1.20	0.05	4.67	1.28	0.27	2.10	11.63	(Chow et al., 2016)
	Spring, 2009-2012	0.68	0.06	0.39	0.01	0.92	0.17	0.10	0.24	2.57	
	Summer, 2009-2012	0.32	0.02	0.20	0.01	0.82	0.17	0.07	0.37	1.99	
	Antumn, 2009-2012	1.06	0.06	0.58	0.01	2.66	0.58	0.15	1.15	6.26	
Xianghe, China	Jul-Aug, 2013	0.98	0.09	0.32	0.06					1.45	(Teich et al., 2017)
Wangdu, China	Jun, 2014	2.63	0.21	0.68	3.45					6.97	(Teich et al., 2017)
		5.9 [a]								5.90	(Wang et al., 2018)
Jinan, China	Nov. 2013- Jan, 2014	48.4 [a]								48.40	(Wang et al., 2018)
Jinan, China	Sep, 2014	9.8 [a]								9.80	(Wang et al., 2018)
Yucheng, China	June, 2014	5.7 [a]								5.70	(Wang et al., 2018)
Mt. Tai, China	July-Aug, 2014	2.5 [a]								2.50	(Wang et al., 2018)
Beijing, China	May-Jun, 2016	2.15	0.27	0.76	0.55	1.89	0.56	0.07	0.44	6.62	This study

Note: a: The identified NACs included 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-5-nitrocatechol (3M5NC), 3-methyl-6- nitrocatechol (3M6NC), 3-nitro-salicylic acid (3NSA), and 5-nitro-salicylic acid (5NSA).

Table S3 Pearson correlations between individual NAC species as well as their correlations with aerosol components, aerosol surface area, VOC precursors, oxidants, RH and temperature (n=38)

	total NACs	4NP	DMNP	2M4NP	3M4NP	4NC	3M6NC	3M5NC	4M5NC
total NACs	1.00								
4NP	0.88**	1.00							
DMNP	0.68**	**0.72****	1.00						
2M4NP	**0.85****	**0.80****	**0.88****	1.00					
3M4NP	0.63**	0.56**	**0.70****	0.59**	1.00				
4NC	**0.92****	0.69**	0.42**	**0.71****	0.41**	1.00			
3M6NC	0.58**	0.53**	0.13	0.34*	0.14	0.58**	1.00		
3M5NC	**0.76****	0.54**	0.23	0.37*	0.45**	**0.80****	0.59**	1.00	
4M5NC	0.52**	0.24	(0.08)	0.05	0.34**	0.60**	0.49**	**0.84****	1.00
OM	0.62**	0.62**	0.11	0.38*	0.17	0.65**	0.49**	0.57**	0.46**
EC	0.39**	0.29	(0.21)	(0.01)	0.21	0.46**	0.39**	**0.64****	**0.74****
K^+	**0.49****	0.39**	0.12	0.24	0.25	**0.50****	**0.43****	**0.64****	**0.53****
SO_4^{2-}	**0.45****	0.36*	0.02	0.18	0.04	**0.52****	**0.51****	**0.59****	**0.47****
benzene	**0.64****	**0.57****	0.23	0.39**	0.23	**0.68****	0.34*	**0.67****	**0.48****
toluene	**0.70****	**0.58****	0.18	0.39**	0.23	**0.76****	**0.46****	**0.74****	**0.63****
acetonitrile	**0.61****	**0.56****	0.20	0.38**	0.15	**0.63****	0.41**	**0.59****	**0.46****
NO_2	0.33*	0.16	(0.17)	(0.02)	0.21	**0.42****	0.26	**0.55****	**0.75****
O_3	0.34*	**0.43****	0.37*	**0.49****	(0.19)	0.32*	0.17	0.11*	(0.31)*
aerosol surface area	**0.60****	**0.49****	0.11	0.33*	0.05	**0.69****	**0.50****	**0.70****	**0.53****
RH	0.13	(0.06)	(0.21)	(0.15)	0.27	0.20	0.16	**0.39****	**0.59****
Temperature	0.21	0.38**	0.30*	**0.40****	(0.32)*	0.17	0.16	(0.12)	(0.45)**

**significant correlation at the 0.01 level

* significant correlation at the 0.05 level

Data in bold indicates relatively higher correlation coefficients in each row.

Red data in parentheses represent negative values.

Table S4 Pearson correlations between individual NAC species as well as their correlations with aerosol components, aerosol surface area, VOC precursors, oxidants, RH and temperature during daytime and nighttime, respectively (n=19)

Daytime									
	total NACs	4NP	DMNP	2M4NP	3M4NP	4NC	3M6NC	3M5NC	4M5NC
total NACs	1.00								
4NP	0.90	1.00							
DMNP	0.79	0.84	1.00						
2M4NP	0.96	0.84	0.86	1.00					
3M4NP	0.80	0.87	0.94	0.82	1.00				
4NC	0.92	0.68	0.51	0.84	0.54	1.00			
3M6NC	0.58	0.48	0.26	0.50	0.25	0.60	1.00		
3M5NC	0.83	0.72	0.49	0.67	0.54	0.85	0.63	1.00	
4M5NC	0.85	0.64	0.41	0.75	0.49	0.92	0.68	0.85	1.00
OM	0.69	0.63	0.32	0.57	0.35	0.69	0.55	0.73	0.80
K^+	0.47	0.46	0.21	0.34	0.35	0.44	0.41	0.61	0.62
SO_4^{2-}	0.40	0.32	0.07	0.23	0.09	0.49	0.25	0.64	0.51
benzene	0.75	0.68	0.50	0.62	0.51	0.72	0.46	0.89	0.75
toluene	0.81	0.71	0.51	0.71	0.52	0.80	0.55	0.89	0.82
acetonitrile	0.74	0.56	0.32	0.48	0.31	0.58	0.43	0.77	0.64
NO_2	0.77	0.63	0.48	0.74	0.47	0.75	0.57	0.73	0.85
O_3	0.38	0.35	0.03	0.21	(0.01)	0.47	0.39	0.62	0.43
aerosol surface area	0.57	0.46	0.19	0.42	0.20	0.65	0.50	0.79	0.73
RH	0.30	0.15	0.10	0.24	0.11	0.36	0.21	0.47	0.55
$J(O^1D)$	(0.72)	(0.56)	(0.63)	(0.76)	(0.67)	(0.68)	(0.14)	(0.49)	(0.60)
Temperature	0.10	0.17	(0.11)	0.01	(0.16)	0.17	0.25	0.10	0.01

Nighttime									
	total NACs	4NP	DMNP	2M4NP	3M4NP	4NC	3M6NC	3M5NC	4M5NC
total NACs	1.00								
4NP	0.83	1.00							
DMNP	0.23	(0.12)	1.00						
2M4NP	0.75	0.65	0.58	1.00					
3M4NP	0.27	0.01	0.60	0.46	1.00				
4NC	0.97	0.79	0.12	0.65	0.11	1.00			
3M6NC	0.70	0.70	(0.15)	0.40	0.07	0.68	1.00		
3M5NC	0.91	0.59	0.24	0.53	0.34	0.88	0.63	1.00	
4M5NC	0.92	0.59	0.34	0.58	0.37	0.88	0.62	0.98	1.00
OM	0.64	0.79	(0.31)	0.50	(0.09)	0.67	0.48	0.43	0.41
K^+	0.66	0.46	0.12	0.57	0.18	0.67	0.44	0.68	0.61
SO_4^{2-}	0.66	0.58	0.05	0.60	(0.02)	0.68	0.65	0.56	0.53
benzene	0.64	0.65	(0.04)	0.57	(0.20)	0.72	0.29	0.46	0.42
toluene	0.79	0.76	(0.01)	0.65	(0.16)	0.86	0.45	0.60	0.58
acetonitrile	0.72	0.71	0.01	0.63	(0.18)	0.77	0.44	0.56	0.54
NO_2	0.60	0.56	(0.00)	0.44	(0.05)	0.61	0.37	0.52	0.55
O_3	0.03	0.11	(0.19)	0.11	(0.65)	0.14	(0.04)	(0.05)	(0.11)
aerosol surface area	0.76	0.68	0.02	0.63	(0.17)	0.82	0.52	0.62	0.59
RH	0.46	0.37	0.59	0.77	0.62	0.33	0.34	0.31	0.34
Temperature	0.02	0.23	(0.61)	(0.17)	(0.84)	0.17	0.09	(0.06)	(0.12)

Red data in parentheses represent negative values.

References

Cecinato, A., Di Palo, V., Pomata, D., Tomasi Sciano, M. C., and Possanzini, M.: Measurement of phase-distributed nitrophenols in Rome ambient air, Chemosphere, 59, 679-683, 10.1016/j.chemosphere.2004.10.045, 2005.

Chow, K. S., Huang, X. H. H., and Yu, J. Z.: Quantification of nitroaromatic compounds in atmospheric fine particulate matter in Hong Kong over 3 years: field measurement evidence for secondary formation derived from biomass burning emissions, Environ. Chem., 13, 665-673, 10.1071/en15174, 2016.

Iinuma, Y., Boge, O., Grafe, R., and Herrmann, H.: Methyl-nitrocatechols: atmospheric tracer compounds for biomass burning secondary organic aerosols, Environ. Sci. Technol., 44, 8453-8459, 10.1021/es102938a, 2010.

Kahnt, A., Behrouzi, S., Vermeylen, R., Safi Shalamzari, M., Vercauteren, J., Roekens, E., Claeys, M., and Maenhaut, W.: One-year study of nitro-organic compounds and their relation to wood burning in PM_{10} aerosol from a rural site in Belgium, Atmos. Environ., 81, 561-568, 10.1016/j.atmosenv.2013.09.041, 2013.

Kitanovski, Z., Grgic, I., Vermeylen, R., Claeys, M., and Maenhaut, W.: Liquid chromatography tandem mass spectrometry method for characterization of monoaromatic nitro-compounds in atmospheric particulate matter, J. Chromatogr., A, 1268, 35-43, 10.1016/j.chroma.2012.10.021, 2012.

Mohr, C., Lopez-Hilfiker, F. D., Zotter, P., Prevot, A. S., Xu, L., Ng, N. L., Herndon, S. C., Williams, L. R., Franklin, J. P., Zahniser, M. S., Worsnop, D. R., Knighton, W. B., Aiken, A. C., Gorkowski, K. J., Dubey, M. K., Allan, J. D., and Thornton, J. A.: Contribution of nitrated phenols to wood burning brown carbon light absorption in Detling, United Kingdom during winter time, Environ. Sci. Technol., 47, 6316-6324, 10.1021/es400683v, 2013.

Teich, M., van Pinxteren, D., Wang, M., Kecorius, S., Wang, Z., Müller, T., Močnik, G., and Herrmann, H.: Contributions of nitrated aromatic compounds to the light absorption of water-soluble and particulate brown carbon in different atmospheric environments in Germany and China, Atmos. Chem. Phys., 17, 1653-1672, 10.5194/acp-17-1653-2017, 2017.

Wang, L., Wang, X., Gu, R., Wang, H., Yao, L., Wen, L., Zhu, F., Wang, W., Xue, L., Yang, L., Lu, K., Chen, J., Wang, T., Zhang, Y., and Wang, W.: Observations of fine particulate nitrated phenols in four sites in northern China: concentrations, source apportionment, and secondary formation, Atmos. Chem. Phys., 18, 4349-4359, 10.5194/acp-18-4349-2018, 2018.

Zhang, X., Lin, Y. H., Surratt, J. D., and Weber, R. J.: Sources, composition and absorption Angstrom exponent of light-absorbing organic components in aerosol extracts from the Los Angeles Basin, Environ. Sci. Technol., 47, 3685-3693, 10.1021/es305047b, 2013.

Zhang, Y. Y., Müller, L., Winterhalter, R., Moortgat, G. K., Hoffmann, T., and Pöschl, U.: Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter, Atmos. Chem. Phys., 10, 7859-7873, 10.5194/acp-10-7859-2010, 2010.