

# 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

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**Environmental context.** Nitroaromatic compounds constitute an important portion of brown carbon and thereby contribute to the light-absorbing properties of atmospheric aerosols. We report their abundance in Hong Kong over 3 years and show that they were mainly associated with aged biomass burning particles. Knowledge of the abundance and sources of nitroaromatic compounds could assist in evaluating their contribution to brown carbon and in apportioning secondary organic aerosols from biomass burning sources.

**Abstract.** Biomass burning is a major source of atmospheric aerosols on both global and regional scales. Among the large number of unidentified organic compounds related to biomass burning, nitroaromatic compounds (NACs) have drawn attention because of their UV light-absorbing ability. In this study, an analytical method based on liquid chromatography–mass spectrometry was used to quantify a group of NACs (nitrophenol, methylnitrophenols, dimethyl-nitrophenol, nitrocatechol and methylnitrocatechols) in aerosol samples. The nitrocatechol–metal complex interference, sample matrix effects, sample stability, precision and reproducibility were investigated. The method detection limits ranged from 0.10 to 0.23 ng mL<sup>−1</sup> and the recoveries for the target NACs were in the range of 96–102 %. The method was applied to a total of 184 ambient PM<sub>2.5</sub> samples (particulate matter of 2.5 µm or less in aerodynamic diameter) collected at an urban site in Hong Kong over 3 years (2010–2012). The NACs quantified showed a distinct seasonal variation with higher concentrations in autumn and winter (3.6–21.0 ng m<sup>−3</sup>), coinciding with more biomass burning activities coming from the regions west and north-east to Hong Kong, and lower levels during spring and summer (0.3–3.8 ng m<sup>−3</sup>). The good correlations between NACs and levoglucosan ( $R = 0.82$ ), a known biomass burning tracer compound, support the common origin from biomass burning. Moderate to good correlations between NACs and nitrate suggest that they might be products of secondary formation processes involving the same precursor gases (e.g. NO<sub>x</sub>). Additional lines of circumstantial evidence were also found and presented in the paper to support secondary formation derived from biomass burning as the main contributing source of NACs.

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## Introduction

The composition of PM<sub>2.5</sub> (particulate matter of 2.5 µm or less in aerodynamic diameter) organic carbon (OC) is still a mystery in many studies and partly stems from the unknown composition of brown carbon (BrC). Previous studies have shown that BrC, brown in colour, is a significant contributor of short wavelength absorption near UV.<sup>[1]</sup> Owing to its optical properties, BrC could influence the radiative balance of the Earth<sup>[2]</sup> and affect the photochemistry in the atmosphere.<sup>[3]</sup> Studies on BrC speciation have identified several groups of organic species, e.g. imidazole-based products which were formed through aqueous chemistry of  $\alpha$ -dicarbonyls,<sup>[4,5]</sup> *N*-heterocyclic compounds,<sup>[6,7]</sup> quinones<sup>[8]</sup> and oligomers such as vanillin dimers<sup>[9]</sup> and acetaldehyde dimers.<sup>[10]</sup> In addition to the different groups of

organic species mentioned above, the nitroaromatic compounds (NACs), i.e. organic molecules that contain at least one nitro group (–NO<sub>2</sub>) attached to an aromatic ring, are also found to be an important constituent group of BrC.<sup>[11–13]</sup> The NAC group includes nitrophenols and derivatives (NPs), nitrocatechols and derivatives (NCs), nitrosalicylic acids (NSAs) and nitroguaiacol (NG). With the –NO<sub>2</sub> and –OH functional groups on the benzene ring as the common moieties, the NACs exhibit enhanced toxicity towards human beings.<sup>[14]</sup>

The atmospheric NACs are known to have primary emission sources and have also been shown to be formed as oxidation products of phenol and derivatives in laboratory and smog chamber experiments. A few primary sources reported include automobile emissions,<sup>[15,16]</sup> coal combustion,<sup>[17]</sup> industrial

manufacturing and processing and usage of pesticides.<sup>[18]</sup> NACs were detected as oxidation products in several chamber studies on secondary organic aerosol (SOA) formation from precursors including *m*-cresol, guaiacol, phenols, nitrobenzene and aromatic hydrocarbons (e.g. benzene and toluene).<sup>[19–26]</sup> However, little is known about their relative importance of primary v. secondary sources in ambient environments because of very limited measurements made so far. Available measurements of NACs were mostly conducted in Europe and North America.<sup>[13,27–32]</sup> In general, the concentrations of NACs ranged from less than one to several hundred nanograms per cubic metre in both PM<sub>2.5</sub> and PM<sub>10</sub> (particulate matter of 10 µm or less in aerodynamic diameter). To the best of our knowledge, no quantitative measurements of NACs have been made in Asia.

Different analytical methods have been adopted in the determination of NACs in the atmospheric environment. Cecinato et al.<sup>[27]</sup> used a denuder-filter system and determined nitrophenols in both gas and particle phases. The extracts from the denuder and the filter samples were trimethylsilylated and analysed using gas chromatography–mass spectrometry (GC-MS). Mohr et al.<sup>[31]</sup> measured five nitrophenols with a micro-orifice volatilisation impactor (MOVI) high-resolution chemical ionisation mass spectrometer for 2 months in the United Kingdom. NACs are more commonly detected and quantified by a high-performance liquid chromatography (HPLC) system coupled with a mass spectrometer equipped with an electrospray ionisation (ESI) source.<sup>[28,33,34]</sup> The chemical properties of the NACs favour the use of negative ESI mode because they all contain one or two phenol groups which are acidic and readily ionised, with the facilitation of the electron-withdrawing –NO<sub>2</sub> group, to produce [M – H]<sup>–</sup> ions through deprotonation.

In this study, an analytical approach using liquid chromatography–mass spectrometry (LC-MS) with ESI based on a modified version of the method developed by Kitanovski et al.<sup>[34]</sup> was established and used to quantify a group of NACs. The method was subsequently applied to determine ambient concentrations of NACs in PM<sub>2.5</sub> filter samples collected over a course of 3 years (2010–2012) at an urban site in Hong Kong. The source characteristics of NACs were investigated through examining their seasonal variations, correlations with major PM<sub>2.5</sub> components and air mass origins by backward-trajectory analysis.

## Methods

### Chemicals and solvents

All analytical standards used in this study had purities higher than 95%. They included: 4-nitrocatechol (4NC), 4-nitrophenol (4NP), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP) and 2,6-dimethyl-4-nitrophenol (2,6D4NP) from Sigma–Aldrich (St. Louis, MO, USA); 4-nitroguaiacol (4NG) from Acros organics (NJ, US) and 4-methyl-5-nitrocatechol (4M5NC) from Santa Cruz Biotech (Dallas, TX, USA). 4-Nitrophenol-2,3,5,6-*d*<sub>4</sub> was used as an internal standard (IS) and was obtained from Sigma–Aldrich. Other chemicals and solvents included methanol (LiChrosolv LC grade, ≥99.9%, Merck Millipore, Darmstadt, Germany), acetonitrile (ACN, HPLC grade, ≥99.9%; Anaqua Chemicals Supply Inc., Houston, TX, USA), acetic acid (>99.7%, Sigma–Aldrich), ethylenediaminetetraacetic acid (EDTA) disodium salt (Ultra Pure, Cribcobrl, Life Technologies, Carlsbad, CA, USA) and double de-ionised (DDI) water (>18 MΩ cm, supplied by Barnstead Nanopure Infinity, Thermo Scientific, Waltham, MA, USA).

### Aerosol sample collection

Ambient aerosol samples analysed in this study were collected at Tsuen Wan Air Quality Monitoring Station (TW AQMS, 22.37°N, 114.11°E), an urban background site in a mixed residential, commercial and industrial neighbourhood in Hong Kong. Twenty-four-hour filter-based PM<sub>2.5</sub> sampling was conducted on a 1-in-6 day schedule by a high-volume air sampler (Andersen Instrument, Smyrna, GA, USA) operating at a flow rate of 1.13 m<sup>3</sup> min<sup>–1</sup> and an Andersen Reference Ambient Air Sampler (RAAS, Andersen Instrument) from January 2010 to December 2012. Quartz fibre filters of 8" × 10" (20 × 25 cm) were used in the high-volume sampler, whereas 47-mm Teflon, Nylon and quartz fibre filters were used for individual channels in RAAS sampling. A Na<sub>2</sub>CO<sub>3</sub>-coated denuder was placed before the Nylon filter in order to remove the acidic gases in the ambient air. Field blanks were collected at the end of every sampling month. All the quartz fibre filters were pre-fired at 550 °C for a minimum of 8 h before sampling. Nylon filters were pre-cleaned in the laboratory. All the sampled filters were stored in a freezer at –18 °C until analysis.

### Sample preparation and analytical methods

#### LC-MS analysis of NACs

A 10-cm<sup>2</sup> portion of the high-volume filter sample was extracted three times, each time with 2 mL of methanol containing 30 µL of saturated EDTA solution in methanol–acetic acid in an ultrasonic bath for 10 min. The methanol extract was then filtered through a polytetrafluoroethylene (PTFE) syringe filter (Bulk Acrodisc CR 13 mm, pore size: 0.25 µm; Pall Life Sciences, New Port Richey, FL, USA) and evaporated to dryness under a gentle stream of nitrogen (UHP grade, Air Products, Shenzhen, China). The dried residue was re-dissolved in 100 µL of methanol with 100 ppb IS.

The NACs were determined using a Dionex Ultimate 3000 HPLC system (Dionex, Sunnyvale, CA, USA) coupled to an ion-trap mass spectrometer (amaZon SL; Bruker Daltonics Inc., Billerica, MA, USA) equipped with an ESI source. High-purity liquid nitrogen was used as curtain, nebuliser, auxiliary and collision gas (LN, Linde HKO Ltd., Hong Kong). The ESI source was operated in the negative mode with an ionisation voltage of 4 kV at 300 °C and the selected *m/z* range was 70 to 600. The data processing was performed with the software package *QuantAnalysis 2.0*.

The separation of the NACs was performed on an Acquity UPLC HSS T3 column (2.1 mm × 100 mm, 1.8-µm particle size; Waters, Milford, MA, USA) with a guard column (HSS T3, 1.8 µm) at a flow rate of 0.3 mL min<sup>–1</sup>. The mobile phase contained (A) 0.1% acetic acid in water (v/v) and (B) acetonitrile. Gradient elution of the analytes was set as follows: eluent B was kept at 1% for 4 min, increased to 30% within 2 min, kept at 30% for 7 min, increased to 90% over 13 min and kept at 90% for 6 min. Finally the mobile phase was reset to initial conditions within 3 min and the column was equilibrated for 5 min before the next run. The column temperature was kept at 25 °C and the injection volume was 5 µL. Most of the NACs were eluted during isocratic conditions of ACN/H<sub>2</sub>O (30/70, v/v, pH ~3.3). All the peaks attained normal Gaussian shapes.

The target NACs were identified by comparison of retention time and mass spectra with authentic standards. For the three methyl nitrocatechols (MNCs), use was made of 4M5NC as a reference standard for the other two MNCs, as it was the only available standard, and a response factor of unity was assumed

**Table 1. Molar masses, quantifying ions, retention times, detection limits and precisions of the target nitroaromatic compounds**

Method detection limit (MDL) defined as a 3-fold standard deviation of 1 ng mL<sup>-1</sup> standard solution signals. Limit of quantification (LOQ) defined as a 10-fold standard deviation of 1 ng mL<sup>-1</sup> standard solution signals. Intra-day precision defined as the coefficient of variation of standard solution injections within the same day. Inter-day precision defined as the coefficient of variation of standard solution injections over a period of 2 weeks

Compound	MW (g mol <sup>-1</sup> )	Quan. ion	Retention time (min)	MDL (ng mL <sup>-1</sup> )	LOQ (ng mL <sup>-1</sup> )	Intra-day precision (ng mL <sup>-1</sup> )			Inter-day precision (ng mL <sup>-1</sup> )		
						50	100	500	50	100	500
4-Nitrocatechol (4NC)	155	154	9.1	0.68	2.05	7.1	6.7	6.9	11.4	10.9	10.9
4-Methyl-5-nitrocatechol (4M5NC)	169	168	9.9	0.55	1.66	5.2	4.3	6.2	9.4	7.7	9.2
4-Nitrophenol (4NP)	139	138	10.2	0.29	0.89	2.1	1.6	1.3	3.0	2.6	3.4
3-Methyl-4-nitrophenol (3M4NP)	153	152	11.7	0.23	0.70	1.0	1.6	1.4	6.0	2.6	2.8
2-Methyl-4-nitrophenol (2M4NP)	153	152	12.6	0.30	0.92	3.2	2.1	1.6	7.4	4.2	3.2
2,6-Dimethyl-4-nitrophenol (26D4NP)	184	183	15.4	0.45	1.38	2.2	1.9	0.9	6.5	3.1	3.6

among the three compounds. The molar masses, quantifying ions ( $m/z = [M - 1]^-$ ), retention times, analytical method detection limits (MDL), limits of quantification (LOQ) and the injection precisions of the individual NACs are listed in Table 1.

#### Analysis of PM<sub>2.5</sub> mass, major PM components and anhydrosugars

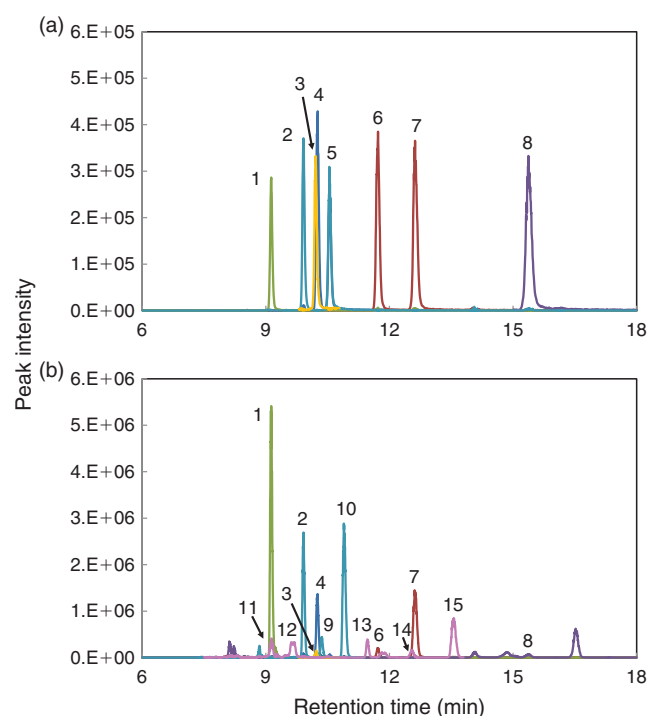
Gravimetric analysis was used to determine the PM<sub>2.5</sub> mass concentrations. The Teflon filters were weighed before and after sampling after they were conditioned in a controlled environment with temperature within 20–23 °C and relative humidity 30–40 % for at least 24 h. Upon the completion of the gravimetric analysis, the Teflon filters were analysed for elements using energy dispersive X-ray fluorescence (ED-XRF, Epsilon 5, PANalytical, the Netherlands). Elements from aluminium to uranium were measured whereas sodium and magnesium were semiquantified. Water soluble ions (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were determined on Nylon filters by ion chromatography. OC and elemental carbon (EC) were analysed using a thermal-optical transmittance (TOT) method on an aerosol carbon analyser (Sunset Laboratory, OR, USA) following the ACE-Asia protocol.<sup>[41]</sup> Anhydrosugars (levoglucosan, mannosan and galactosan) were measured using high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD). More details regarding the analytical measurements can be found elsewhere.<sup>[35,36]</sup>

## Results and discussion

### Method optimisation

The chromatographic separation of all target compounds was achieved using the mobile phase gradient described above (*LC-MS analysis of NACs*). Chromatograms of authentic standards (at 100 µg mL<sup>-1</sup>) and a typical ambient sample are shown in Fig. 1.

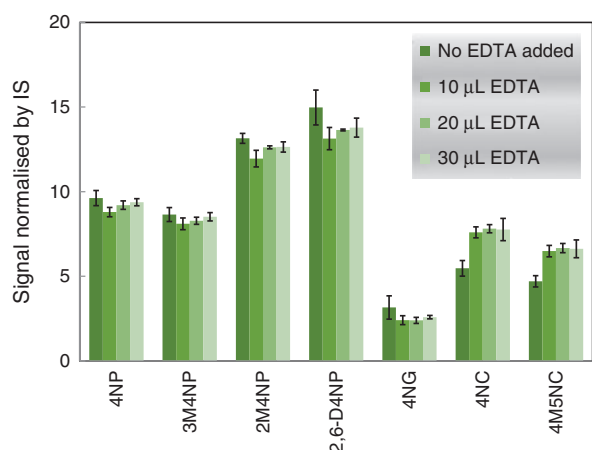
It has been reported in a previous study<sup>[34]</sup> that NCs, because of the presence of two adjacent –OH groups, could form a complex with transition metals. In order to improve the extraction efficiencies of these compounds, the metal-chelating agent EDTA was added during the solvent extraction steps. The comparison results in Fig. 2 indicate that the signals for the two nitrocatechols (4NC and 4M5NC) increased by 41 and 40 % when EDTA was added whereas the addition of EDTA had little effect on the signals of the nitrophenols (slightly lower, not



**Fig. 1.** Extracted ion chromatograms (EICs) for (a) standard solution containing (1) 4-nitrocatechol (4NC), (2) 4-methyl-5-nitrocatechol (4M5NC), (3) internal standard (IS), (4) 4-nitrophenol (4NP), (5) 4-nitroguaiacol (4NG) (6) 3-methyl-4-nitrophenol (3M4NP), (7) 2-methyl-4-nitrophenol (2M4NP) and (8) 2,6-dimethyl-4-nitrophenol (26D4NP) and (b) ambient sample collected at Tsuen Wan Air Quality Monitoring Station (TW AQMS) on 11 February 2012 containing (1)–(8) except (5), (9) 3-methyl-6-nitrocatechol (3M6NC) and (10) 3-methyl-5-nitrocatechol (3M5NC), and (11)–(15) compounds having  $[M - H]^-$  at  $m/z$  182 (proposed to be dimethyl-nitrocatechols or nitrosalicylic acids).

exceeding 10%). Three levels of EDTA (10, 20, and 30 µL of saturated EDTA–methanol solution) were tested and no significant differences in signals were observed with the different amounts of EDTA present in the extraction solvent.

The sample matrix effect was evaluated by comparing the linear regression slopes of the calibration curves to those of the standard solutions prepared in a standard addition manner. Two high-volume filter samples collected at different sampling sites in different seasons were used in this experiment, representing



**Fig. 2.** Nitroaromatic compound detections with or without ethylenediaminetetraacetic acid (EDTA) added during the solvent extraction steps.

different composite aerosol matrices. Briefly, these two filter samples were spiked with five concentration levels of standard mix solutions and extracted according to the sample preparation procedure. These samples were then analysed by LC-MS and the results are plotted in the same figure with those of the standard solutions prepared on the same day (Fig. S1, Supplementary material). The slopes of the spiked filter data do not differ from those of the liquid standard solution by more than 34% (see Table S1, Supplementary material, for the individual slope values) except for 4NG, for which the matrix could lead to higher deviation (53% in the winter sample matrix and 67% in the summer sample matrix). Because aerosol matrix effects did not exert a significant influence on the quantifications of other NACs, and 4NG was not detected in the samples analysed in this study, no further efforts were taken to optimise the method for 4NG. In routine aerosol sample analysis, one set of standard solutions were freshly prepared on each day of ambient sample analysis so as to monitor the conditions of the instrument and were used for quantifications of NACs in the samples analysed on that day.

Recoveries of individual NACs were subsequently determined by spiking a known amount of standard-mix solutions before and after ambient filter sample extraction. The details of this pre and post-extraction-spike method have been described elsewhere.<sup>[34]</sup> This method involves extraction of real-world samples whereas the matrix effect could be minimised during the calculation step. Two high-volume PM<sub>2.5</sub> samples (one in summer and one in winter) were used in this test and despite the different aerosol matrices, satisfactory recoveries (better than 80%) for all the target compounds were achieved (Table 2).

#### NAC concentration levels and seasonal variations

A total of eight NACs were consistently detected in ambient PM<sub>2.5</sub> samples, including 4NP, two methyl-nitrophenols (3M4NP; 2M4NP), 2,6D4NP, 4NC, and three methyl-nitrocatechols (4M5NC; 3-methyl-6-nitrocatechol, 3M6NC; and 3-methyl-5-nitrocatechol, 3M5NC). Two other dimethyl-nitrophenols (*m/z* 166), a group of dimethyl-nitrocatechols (DMNCs) (*m/z* 182) and nitrosalicylic acids (*m/z* 182) were also observed. Altogether there could be four possible structures for DMNCs and nitrosalicylic acids and in most of the samples five peaks were obtained. Strong correlations found between these

**Table 2.** Recoveries of individual nitroaromatic compounds in this study

4-Nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 4-nitroguaiacol (4NG), 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 2,6-dimethyl-4-nitrophenol (2,6D4NP)

Compound	Recovery (%) on NS140726 ( <i>n</i> = 3)	Recovery (%) on TW120101 ( <i>n</i> = 3)
4NC	96.8 ± 10.2	102.4 ± 8.8
4M5NC	97.9 ± 7.8	98.5 ± 8.8
4NG	81.4 ± 22.5	86.5 ± 12.2
4NP	94.9 ± 9.7	106.4 ± 9.0
3M4NP	98.2 ± 10.8	104.9 ± 11.1
2M4NP	94.4 ± 9.8	101.9 ± 13.3
2,6D4NP	90.9 ± 15.3	99.3 ± 13.9

compounds with *m/z* 182 and nitrocatechols (Table S2, Supplementary material) suggest that they might belong to the NAC family. However, because of the lack of authentic standards or reliable surrogates, these compounds were not quantified in this study. Therefore, only the concentrations of the eight NACs were reported and discussed in the following sections. The concentration ranges, average values and standard deviations of the NACs determined in this study were summarised and compared with measurements in previous studies in Table 3.

In general, the NAC concentrations in urban Hong Kong were lower than those found in rural areas in other parts of the world. This is expected because locally there were barely any biomass burning activities and the detected NACs were transported from elsewhere in the adjacent regions. Among the eight NACs, 4NC and MNCs were recorded at higher concentration levels than 4NP and MNPs. This relative abundance among NACs is consistent with observations in the literature.

Seasonal variations of target NACs and other PM<sub>2.5</sub> components were studied. Their seasonal average values are given in Table 4. As Hong Kong has a tropical monsoon climate, meteorological conditions have distinct seasonality. The featured observation in upper layer wind with dramatic changes in wind directions and mixing layer height has been employed to identify the four seasons in Hong Kong: spring from 16 March to 15 May, summer from 16 May to 15 September, autumn from 16 September to 15 November and winter from 16 November to the next 15 March.<sup>[37]</sup> In summertime, the prevailing winds in Hong Kong are southerlies and the region is affected by warm and relatively clean maritime air streams. During winter months, cool north-east monsoons dominate and bring in more polluted air from the continent. In the two transitional seasons, whereas spring is warmer and more humid than autumn, the winds are a combination of southerlies and northerlies.

Throughout the study period, the total NACs were observed at the highest concentration level in winter ( $12.2 \pm 13.5 \text{ ng m}^{-3}$ ) and the lowest in summer ( $2.2 \pm 4.9 \text{ ng m}^{-3}$ ). The NAC levels in different seasons across 3 years (Fig. 3 and Table 4) reveals that different subgroups (NCs and NPs) exhibited similar seasonal variation patterns, with lower concentration levels in spring and summer and higher levels in autumn and winter. These patterns can be well explained by the much stronger biomass burning activities during autumn and winter months in the surrounding areas and the prevailing northerly winds which bring the pollutants into Hong Kong from the continent. It is also noted that the concentrations could



**Table 3. Mass concentrations of individual nitroaromatic compounds in comparison with previous studies**

4-Nitrocatechol (4NC), methyl-nitrocatechols (MNCs), 4-nitrophenol (4NP), methyl-nitrophenols (MNPs), Tsuen Wan Air Quality Monitoring Station (TW AQMS)

Compound	Concentration (ng m <sup>-3</sup> )		Particulate matter type	Location, time	Reference
	Range	Average ± s.d.			
4NC	0.004–24.9	2.31 ± 1.23	PM <sub>2.5</sub>	TW AQMS, urban Hong Kong, 2010–2012	This study
		8.5	PM <sub>2.5</sub>	Urban Budapest, Hungary, 7–14 July 2007	[29]
		0.5	PM <sub>2.5</sub>	Urban Budapest, Hungary, 3–10 June 2008	[29]
		0.3	PM <sub>2.5</sub>	Rural K-pusztá, Hungary, 5–7 June 2008	[29]
		97	PM <sub>2.5</sub>	Rondônia, Brazil, biomass burning expt. (daytime)	[29]
		520	PM <sub>2.5</sub>	Rondônia, Brazil, biomass burning expt. (night time)	[29]
	n.d.–26.30	1.67	PM <sub>2.5</sub>	Pasadena, California, mid-May–mid-June 2010	[13]
		6.4	PM <sub>3</sub>	Mainz, Germany, June 2006–July 2007	[32]
		2.5	PM <sub>3</sub>	Detling, UK, January–February 2012	[31]
	0.49–9.0	1.91	PM <sub>10</sub>	Rural Belgium, February 2010–February 2011	[30]
	0.16–152	56.31	PM <sub>10</sub>	Urban Slovenia, December 2010–January 2011	[34]
MNCs	0.004–25.8	1.73 ± 3.44	PM <sub>2.5</sub>	TW AQMS, urban Hong Kong, 2010–2012	This study
		8.2	PM <sub>3</sub>	Detling, UK, January–February 2012	[31]
	0.02–29	5.2	PM <sub>10</sub>	Rural Germany, October 2007–March 2008	[28]
	0.86–9.3	2.2	PM <sub>10</sub>	Rural Belgium, February 2010–February 2011	[30]
	0.18–134.7	51.9	PM <sub>10</sub>	Urban Slovenia, December 2010–January 2011	[34]
4NP	n.d.–8.66	0.96 ± 1.24	PM <sub>2.5</sub>	TW AQMS, urban Hong Kong, 2010–2012	This study
		0.02	PM <sub>3</sub>	Detling, UK, January–February 2012	[31]
	0.32–1.03	0.65	PM <sub>10</sub>	Rural Belgium, February 2010–February 2011	[30]
	0.12–3.7	1.39	PM <sub>10</sub>	Urban Slovenia, December 2010–January 2011	[34]
MNPs	0.001–7.56	0.68 ± 0.96	PM <sub>2.5</sub>	TW AQMS, urban Hong Kong, 2010–2012	This study
		5.0	PM <sub>3</sub>	Detling, UK, January–February 2012	[31]
	n.d.–2.7	1.04	PM <sub>10</sub>	Urban Slovenia, December 2010–January 2011	[34]

**Table 4. Concentrations of different components in particulate matter of 2.5 µm or less in aerodynamic diameter (PM<sub>2.5</sub>) samples from 2010 to 2012 at the Tsuen Wan site**

4-Nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC), 3-methyl-5-nitrocatechol (3M5NC), 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 2,6-dimethyl-4-nitrophenol (26D4NP), organic carbon (OC), elemental carbon (EC)

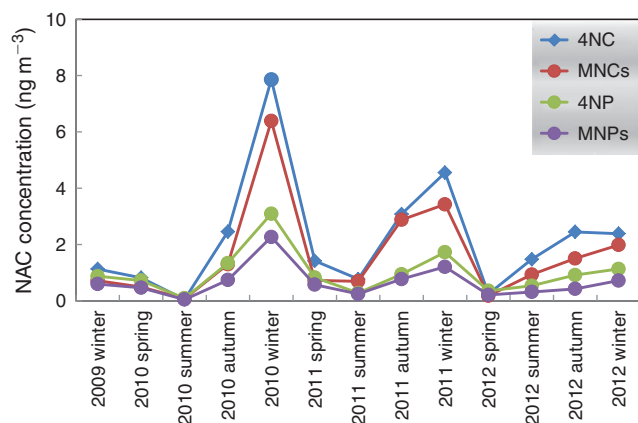
Analyte	Winter				Spring			Summer			Autumn		
	2009 (n = 12)	2010 (n = 17)	2011 (n = 24)	2012 (n = 4)	2010 (n = 12)	2011 (n = 13)	2012 (n = 8)	2010 (n = 17)	2011 (n = 27)	2012 (n = 22)	2010 (n = 9)	2011 (n = 9)	2012 (n = 10)
4NC (ng m <sup>-3</sup> )	1.13	7.86	4.55	2.39	0.823	1.42	0.245	0.056	0.775	1.48	2.46	3.08	2.45
4M5NC (ng m <sup>-3</sup> )	0.260	2.17	1.28	0.532	0.161	0.242	0.051	0.010	0.206	0.254	0.442	0.876	0.441
3M6NC (ng m <sup>-3</sup> )	0.128	0.385	0.280	0.107	0.088	0.127	0.082	0.055	0.107	0.051	0.090	0.229	0.131
3M5NC (ng m <sup>-3</sup> )	0.330	3.84	1.87	1.35	0.244	0.362	0.050	0.013	0.382	0.629	0.768	1.77	0.936
4NP (ng m <sup>-3</sup> )	0.879	3.10	1.73	1.13	0.725	0.831	0.358	0.094	0.282	0.539	1.342	0.945	0.918
3M4NP (ng m <sup>-3</sup> )	0.089	0.270	0.147	0.071	0.063	0.069	0.030	0.012	0.026	0.022	0.091	0.064	0.039
2M4NP (ng m <sup>-3</sup> )	0.510	2.00	1.06	0.650	0.405	0.507	0.183	0.036	0.221	0.296	0.652	0.710	0.390
2,6D4NP (ng m <sup>-3</sup> )	0.017	0.10	0.031	0.010	0.011	0.013	0.010	0.002	0.017	0.008	0.016	0.025	0.005
Levogluconan (ng m <sup>-3</sup> )	43.88	180.50	125.53	78.27	38.15	49.28	19.87	7.24	37.90	59.86	93.75	57.92	44.61
Mannosan (ng m <sup>-3</sup> )	3.37	17.43	13.97	6.04	2.83	6.75	1.27	0.412	2.66	3.30	6.19	5.44	3.51
PM <sub>2.5</sub> (µg m <sup>-3</sup> )	30.93	54.91	34.21	32.17	39.30	38.77	26.12	15.60	23.28	22.52	44.47	31.52	57.20
OC (µg m <sup>-3</sup> )	6.53	11.44	8.49	8.23	5.37	5.77	4.67	3.65	4.96	5.26	9.27	7.63	9.12
EC (µg m <sup>-3</sup> )	2.30	2.61	1.62	2.29	1.98	2.05	1.93	2.06	1.83	2.28	2.03	1.57	2.47
SO <sub>4</sub> <sup>2-</sup> (µg m <sup>-3</sup> )	9.18	13.04	8.11	8.16	8.15	10.82	8.07	3.99	7.16	6.06	15.15	9.42	17.09
NO <sub>3</sub> <sup>-</sup> (µg m <sup>-3</sup> )	2.24	6.22	3.69	2.91	2.54	2.68	1.41	0.250	1.06	1.31	2.22	2.07	3.14

be quite variable across different winter seasons. The winter season of 2009 (mid-November 2009 to mid-March 2010) and 2012 (mid-November 2012 to mid-March 2013) was not fully covered by this study, which was limited to the 3 calendar years (2010, 2011 and 2012). This leaves two complete winter

seasons (2010 and 2011) for comparison. The NAC concentration levels in winter 2010 were on average 85 % higher than that in winter 2011. The large variations were very likely linked to the biomass combustion source strength or the different meteorological conditions.

### Inter-species correlations

Strong correlations were found among the NACs measured in this study (Table 5) with correlation coefficients ( $R$ ) larger than 0.75 except for 2,6D4NP, which might be associated with higher measurement uncertainties because of its very low atmospheric concentrations. One sample (TW110110) was considered an outlier because of the extremely high NAC concentrations



**Fig. 3.** Seasonal variations of the nitroaromatic compounds (NACs) 4-nitrocatechol (4NC), methyl-nitrocatechols (MNCs), 4-nitrophenol (4NP), methyl-nitrophenols (MNPs) during the study period.

( $\Sigma\text{NAC} = 70.6 \text{ ng m}^{-3}$ ). The chemical speciation data obtained for this sample is proved to be valid but the high NAC concentrations would bias the regression analysis. Therefore, this sample was not included when studying the inter-species correlations. It is noted that the correlations within each subgroup, i.e. NCs and NPs, are even stronger than those between the subgroups. This might be attributable to (1) the semi-volatile characteristics of NPs which lead to a temperature-dependent partitioning between gas- and particle-phases<sup>[38]</sup> or (2) multiple sources of NPs (both primary and secondary). Nevertheless, the high correlations among NACs strongly suggest similar sources or formation processes.

Correlation analysis was further conducted between NACs and other measured PM components or species (Table 6). Total NACs are found to be highly correlated with levoglucosan, mannosan and  $\text{NO}_3^-$  ( $R = 0.82, 0.83$ , and  $0.71$  respectively) and also moderately correlated with  $\text{K}^+$  ( $R = 0.59$ ), suggesting their association with biomass burning sources. Fig. S2, Supplementary material, and Table 7 show the correlations between two subgroups of NACs and levoglucosan,  $\text{NO}_3^-$  and  $\text{K}^+$  in different seasons. This result is similar to that reported by Iinuma et al.<sup>[28]</sup> for measurements of MNCs and levoglucosan in 45  $\text{PM}_{10}$  samples made at a rural village site in Germany ( $R = 0.86$ ). Interestingly, both NPs and NCs correlated better with levoglucosan during winter, spring and autumn than in summer. On the other hand, correlations between NAC subgroups with  $\text{NO}_3^-$  and with  $\text{K}^+$  were the strongest in summer among all the seasons.

**Table 5.** Correlations between individual nitroaromatic compounds measured in particulate matter of  $2.5 \mu\text{m}$  or less in aerodynamic diameter samples at Tsuen Wan from 2010 to 2012 (TW110110 excluded)

4-Nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC), 3-methyl-5-nitrocatechol (3M5NC), 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 2,6-dimethyl-4-nitrophenol (26D4NP)

	4NC	4M5NC	3M6NC	3M5NC	4NP	3M4NP	2M4NP	2,6D4NP
4NC	1.00							
4M5NC	0.94	1.00						
3M6NC	0.84	0.91	1.00					
3M5NC	0.94	0.95	0.89	1.00				
4NP	0.87	0.75	0.67	0.74	1.00			
3M4NP	0.85	0.82	0.77	0.75	0.91	1.00		
2M4NP	0.89	0.84	0.77	0.84	0.93	0.93	1.00	
2,6D4NP	0.54	0.59	0.53	0.51	0.57	0.66	0.64	1.00

**Table 6.** Correlations between nitroaromatic compounds (NACs) and measured aerosol components for particulate matter of  $2.5 \mu\text{m}$  or less in aerodynamic diameter ( $\text{PM}_{2.5}$ ) samples at Tsuen Wan from 2010 to 2012 (TW110110, TW110282 and TW120914 excluded)

Organic carbon (OC), elemental carbon (EC), nitrophenols (NPs) and nitrocatechols (NCs)

	$\text{PM}_{2.5}$	$\text{NH}_4^+$	$\text{K}^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$	OC	EC	Levoglucosan	Mannosan	NPs	NCs	$\Sigma\text{NACs}$
$\text{PM}_{2.5}$	1.00												
$\text{NH}_4^+$	0.74	1.00											
$\text{K}^+$	0.72	0.71	1.00										
$\text{NO}_3^-$	0.75	0.73	0.68	1.00									
$\text{SO}_4^{2-}$	0.76	0.95	0.64	0.57	1.00								
$\text{C}_2\text{O}_4^{2-}$	0.78	0.68	0.62	0.61	0.70	1.00							
OC	0.73	0.71	0.73	0.71	0.61	0.61	1.00						
EC	0.25	0.17	0.09	0.18	0.16	0.22	0.43	1.00					
Levoglucosan	0.51	0.47	0.72	0.64	0.32	0.38	0.72	0.06	1.00				
Mannosan	0.46	0.45	0.63	0.71	0.26	0.33	0.60	-0.03	0.90	1.00			
NPs	0.60	0.60	0.66	0.82	0.42	0.43	0.80	0.24	0.83	0.83	1.00		
NCs	0.42	0.46	0.55	0.66	0.28	0.34	0.63	0.16	0.79	0.80	0.87	1.00	
$\Sigma\text{NACs}$	0.47	0.50	0.59	0.71	0.32	0.37	0.69	0.18	0.82	0.83	0.92	0.99	1.00

One hypothesis is that the anhydrosugars are more related to fresh emissions of biomass burning whereas NACs are secondarily formed from biomass burning-emitted precursors and associated with more aged aerosols. As a result, NACs and levoglucosan were better correlated during winter and the two transitional seasons when biomass burning activities in the continent could affect Hong Kong directly by pollutants transported by northerly winds. In summer with southerly winds prevailing, air masses influenced by biomass burning emissions could have been mixed and processed to a larger extent before arriving at Hong Kong.

Among all the samples, two samples (TW110828 and TW120914) were found to have very high levoglucosan concentrations (408 and 802 ng m<sup>-3</sup>), an unexpected result for summer samples that initially puzzled us. Later it was found that these 2 days coincided with the Chinese Yu Lan Ghost Festival (the 7th month in the Chinese lunar calendar) during which traditional events such as incense and joss paper burning were held in a sports field within 50 m of the sampling site. High concentration levels of levoglucosan led to the ratios of [ $\Sigma$ NACs]/[levoglucosan] on these 2 days (0.03 and 0.01 respectively) being much lower than the average value throughout the study period (0.08). No NAC concentration spike was instantly observed under the circumstance of strong biomass burning emissions (high levoglucosan level) because a certain time was needed for subsequent chemical processing to form NAC products. Results from these

two incidental samples serve as unique evidence for the predominantly secondary origin of NACs.

In addition, higher NAC concentrations were found with elevated night time NO<sub>2</sub> levels (Fig. 4), whereas when daytime NO<sub>2</sub> was also considered, the correlations were significantly weakened. This may hint that night time oxidation, e.g. oxidation involving the NO<sub>3</sub> radical,<sup>[39]</sup> is important in the secondary formation of NACs. In a previous study by Claeys et al.,<sup>[29]</sup> they reported during an intensive biomass burning event, the concentration level of 4NC at night time was a factor of 5 higher than at daytime, consistent with our observation of positive association of NACs with night time NO<sub>2</sub>.

In summary, the cumulative evidence suggests that NACs observed at our study site are mostly secondary formation products of biomass burning emissions.

### Source origins of NACs

To better understand the source origins of the NACs, attempts were made to associate NAC speciation with different tracked air mass derived by the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT4) model. The meteorological data field input was obtained from the online Global Data Assimilation System (GDAS) one-degree archive. Seventy-two-hour back trajectories were calculated by the National Weather Service's National Centers for the Environmental Prediction (NCEP) model data available in the Air Resources Laboratory (ARL) archives in National Oceanic and Atmospheric Administration (NOAA). The selection of the 72-h back trajectory length is supported by the lifetimes of different secondary species.<sup>[40]</sup> Every single day in the period of 2010–2012 was tested by the model in order to obtain nine representative clusters of air mass origins for the TW sampling site (Fig. 5a).

For individual sampling days, 24-hourly trajectories were calculated and examined in order to assign them into different clusters. The cluster-associated NAC speciation is shown in Fig. 5b. In general, higher levels of NACs together with anhydrosugars were found to be from the continent (clusters 2, 3 and 5) and lower in the maritime air masses (clusters 6, 7 and 8) and coastal air masses (cluster 1). The highest NAC concentrations were associated with cluster 3 when the air masses were coming from the west. The satellite-derived fire counts (Fig. S3, Supplementary material) reveal that large-scale burning in South-east Asia could be responsible for the high NAC levels observed in Hong Kong.

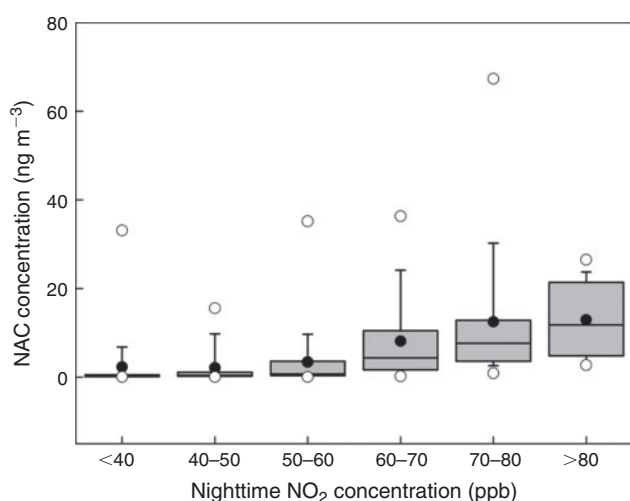
### Conclusions

An analytical method based on LC-MS was characterised for the quantitative determination of a group of NACs in ambient PM<sub>2.5</sub> samples. A total of 184 PM<sub>2.5</sub> samples collected over a 3-year period for an urban site in Hong Kong were analysed. The highest seasonal concentration of the total NACs was recorded in winter ( $12.2 \pm 13.5$  ng m<sup>-3</sup>), which nearly doubled that of the second most abundant season (autumn,  $6.5 \pm 6.9$  ng m<sup>-3</sup>). Much lower NAC levels were found in spring and summer months ( $2.7 \pm 3.6$  and  $2.2 \pm 4.9$  ng m<sup>-3</sup> respectively). The strong correlations among individual NACs suggest that they primarily come from similar sources or formation processes. NACs were also found to highly correlate with anhydrosugars, suggesting that they are related to biomass burning sources. The season-dependent correlations of NACs v. levoglucosan and NACs v. NO<sub>3</sub><sup>-</sup> support the hypothesis that unlike anhydrosugars, which are freshly emitted from biomass combustions, NACs are

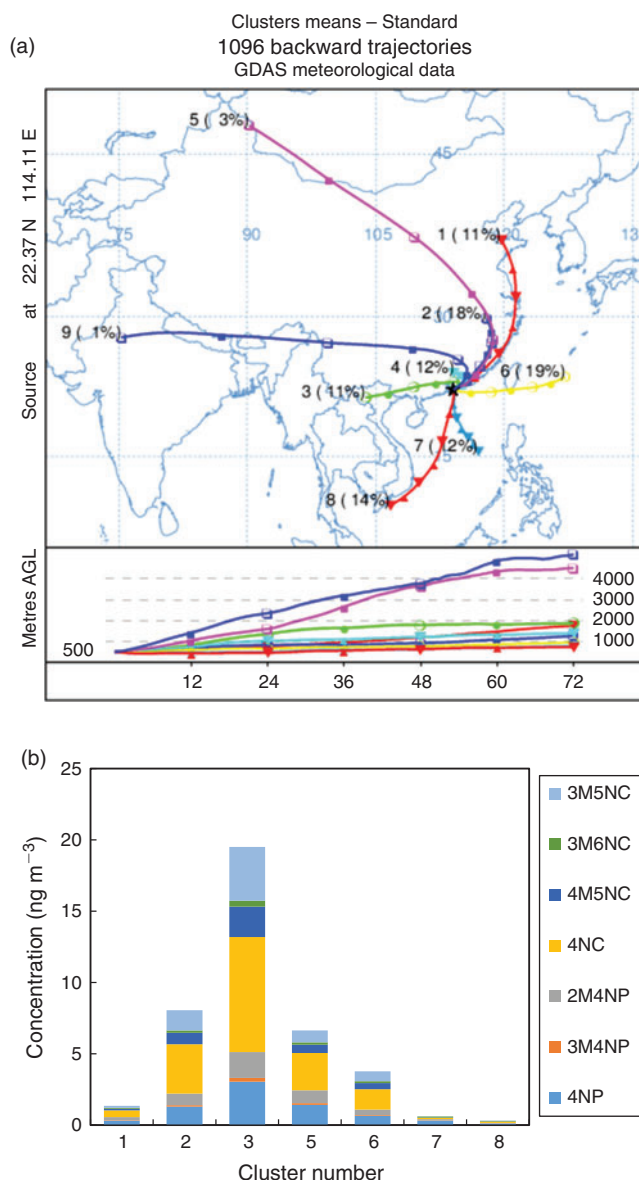
**Table 7. Correlations between nitroaromatic compound subgroups (nitrophenols (NPs) and nitrocatechols (NCs)) and levoglucosan, nitrate and water-soluble potassium in different seasons**

Correlation	Winter	Spring	Summer	Autumn
NPs v. levoglucosan	0.77	0.80	0.45 <sup>A</sup>	0.85
NCs v. levoglucosan	0.83	0.71	0.57 <sup>A</sup>	0.48
NPs v. NO <sub>3</sub> <sup>-</sup>	0.76	0.74	0.90	0.51
NCs v. NO <sub>3</sub> <sup>-</sup>	0.55	0.61	0.85	0.45
NPs v. K <sup>+</sup>	0.48	0.72	0.66	0.58
NCs v. K <sup>+</sup>	0.45	0.56	0.61	0.22

<sup>A</sup>TW110110, TW110828 and TW120914 were excluded.



**Fig. 4.** Nitroaromatic compound (NAC) concentrations (ng m<sup>-3</sup>) v. night time NO<sub>2</sub> concentration bins (ppb). Closed circles within boxes represent mean values, open circles represent 5 and 95 percentiles, and whiskers represent 25 and 75 percentiles.



**Fig. 5.** (a) Clusters of air mass origins derived from backward trajectory analysis by Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT4) model (3-year average,  $n = 1096$ ) and (b) nitroaromatic compound speciation (3-methyl-5-nitrocatechol (3M5NC), 3-methyl-6-nitrocatechol (3M6NC), 4-methyl-5-nitrocatechol (4M5NC), 4-nitrocatechol (4NC), 2-methyl-4-nitrophenol (2M4NP), 3-methyl-4-nitrophenol (3M4NP), 4-nitrophenol (4NP)) for different air mass origins.

secondarily formed through further oxidation of certain biomass burning emission constituents (e.g. phenol and substituted phenols) and therefore more associated with aged PM mass. Observation of high levoglucosan but low NACs in two incidental samples collected on days influenced by nearby festival biomass burning further supports their secondary formation hypothesis.

Backward trajectory cluster analyses were conducted for the sampling period in order to better understand the air mass origins. NAC abundance associated with different clusters of air mass together with the fire count data further support our understanding of the biomass burning activities and air pollutant transport in this region.

## Supplementary material

A figure demonstrating the matrix effects on sensitivities of NACs and corresponding numerical results, the inter-species correlations among NACs and between NACs with levoglucosan,  $\text{NO}_3^-$ , and  $\text{K}^+$ , and the fire map during the sampling period are available as Supplementary material (see [http://www.publish.csiro.au/?act=view\\_file&file\\_id=EN15174\\_AC.pdf](http://www.publish.csiro.au/?act=view_file&file_id=EN15174_AC.pdf)).

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**Supplementary material**

**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**

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**Table S1. Matrix effects on sensitivities of individual nitroaromatic compounds (slope  $\pm$  standard error (correlation coefficient,  $R^2$ ))**

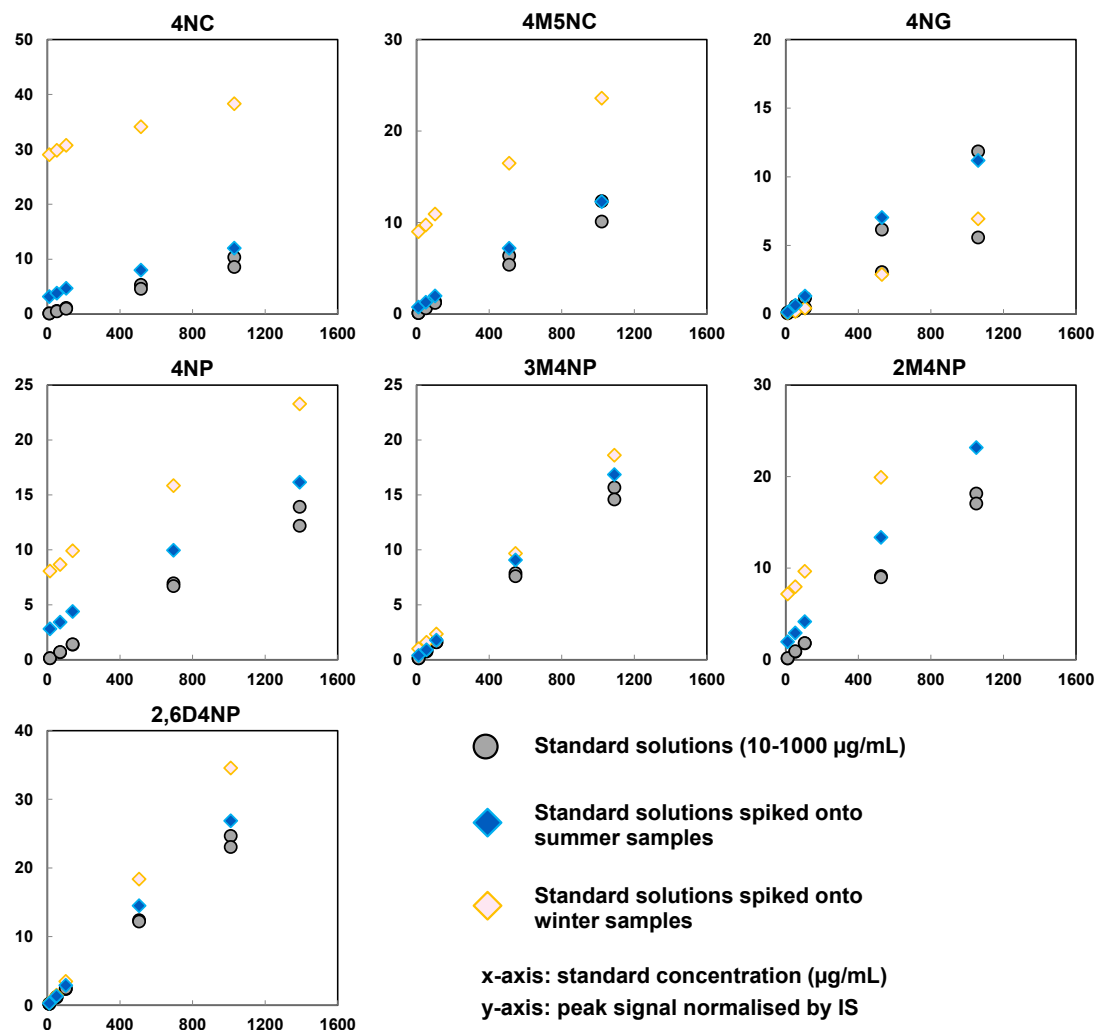
Standard (STD), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 4-nitroguaiacol (4NG), 4-nitrophenol (4NP), 3-methyl-4-nitrophenol (3M4NP), 2-methyl-4-nitrophenol (2M4NP), 2,6-dimethyl-4-nitrophenol (26D4NP)

Compound	Summer sample		Winter sample	
	STD	STD + matrix	STD	STD + matrix
4NC	0.0083 $\pm$ 0.0002 (0.999)	0.0084 $\pm$ 0.0004 (0.994)	0.0100 $\pm$ 0.0001 (1.000)	0.0088 $\pm$ 0.0005 (0.992)
4M5NC	0.0099 $\pm$ 0.0002 (0.999)	0.0115 $\pm$ 0.0004 (0.996)	0.0121 $\pm$ 0.0001 (1.000)	0.0143 $\pm$ 0.0003 (0.999)
4NG	0.0054 $\pm$ 0.0002 (0.997)	0.0108 $\pm$ 0.0008 (0.984)	0.0012 $\pm$ 0.0001 (1.000)	0.0066 $\pm$ 0.0003 (0.993)
4NP	0.0088 $\pm$ 0.0002 (0.998)	0.0097 $\pm$ 0.0002 (0.998)	0.0100 $\pm$ 0.0000 (1.000)	0.0110 $\pm$ 0.0002 (0.999)
3M4NP	0.0134 $\pm$ 0.0002 (1.000)	0.0155 $\pm$ 0.0003 (0.999)	0.0144 $\pm$ 0.0000 (1.000)	0.0164 $\pm$ 0.0001 (1.000)
2M4NP	0.0163 $\pm$ 0.0003 (1.000)	0.0205 $\pm$ 0.0005 (0.998)	0.0174 $\pm$ 0.0000 (1.000)	0.0239 $\pm$ 0.0004 (0.999)
2,6D4NP	0.0229 $\pm$ 0.0004 (0.999)	0.0268 $\pm$ 0.0006 (0.998)	0.0245 $\pm$ 0.0001 (1.000)	0.0346 $\pm$ 0.0007 (0.999)

**Table S2. Correlations between  $m/z = 182$  and individual nitrocatechols (NC) and total nitroaromatic compounds (NACs) measured in particulate matter of 2.5  $\mu\text{m}$  or less in aerodynamic diameter ( $\text{PM}_{2.5}$ ) samples at Tsuen Wan from 2010 to 2012**

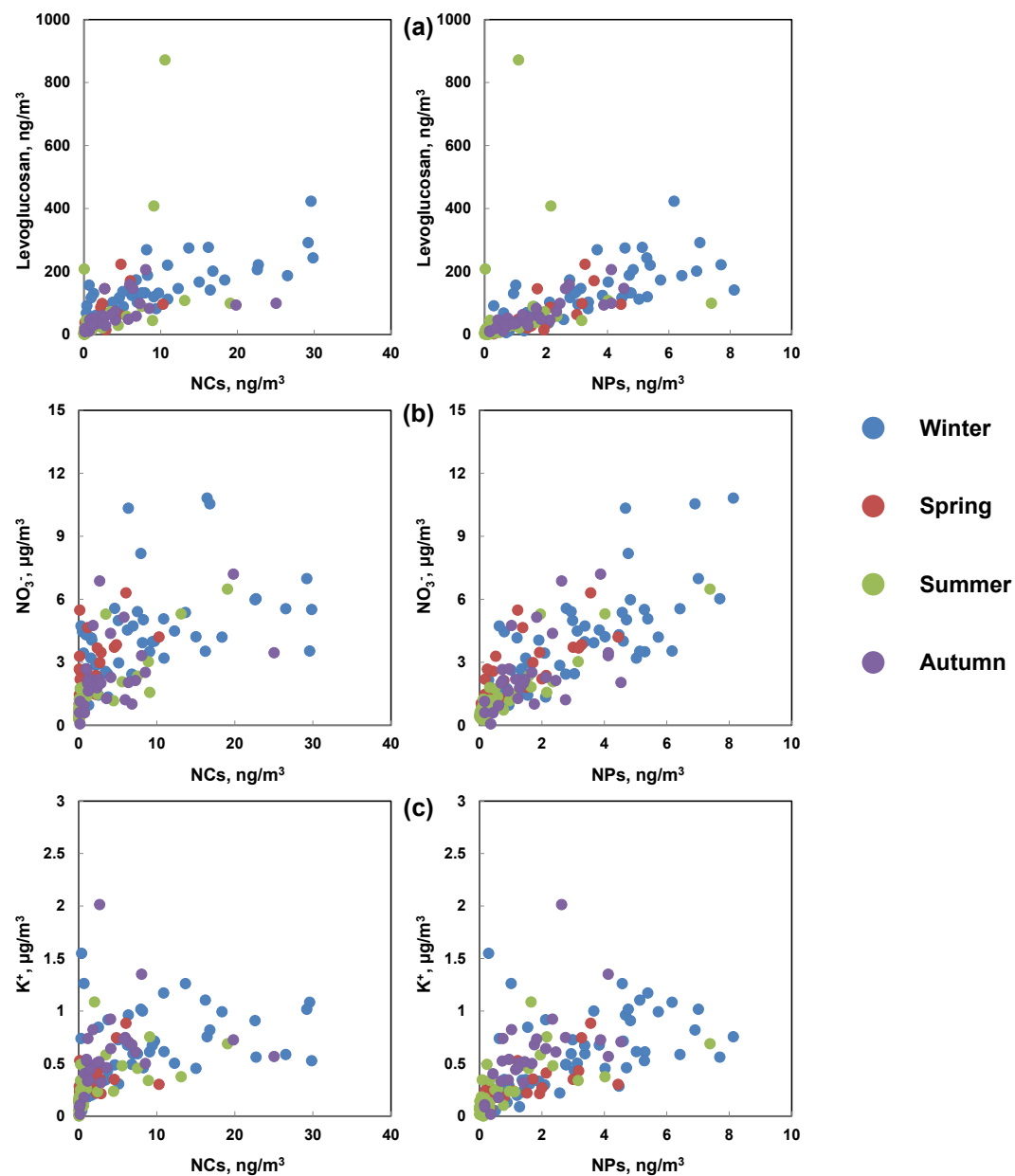
4-Nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-methyl-6-nitrocatechol (3M6NC) and 3-methyl-5-nitrocatechol (3M5NC)

$m/z$	4NC	4M5NC	3M6NC	3M5NC	$\Sigma\text{NACs}$
182(1)	0.74	0.68	0.63	0.67	0.76
182(2)	0.84	0.70	0.65	0.73	0.84
182(3)	0.82	0.89	0.74	0.75	0.82
182(4)	0.86	0.93	0.85	0.84	0.87
182(5)	0.87	0.91	0.86	0.97	0.89

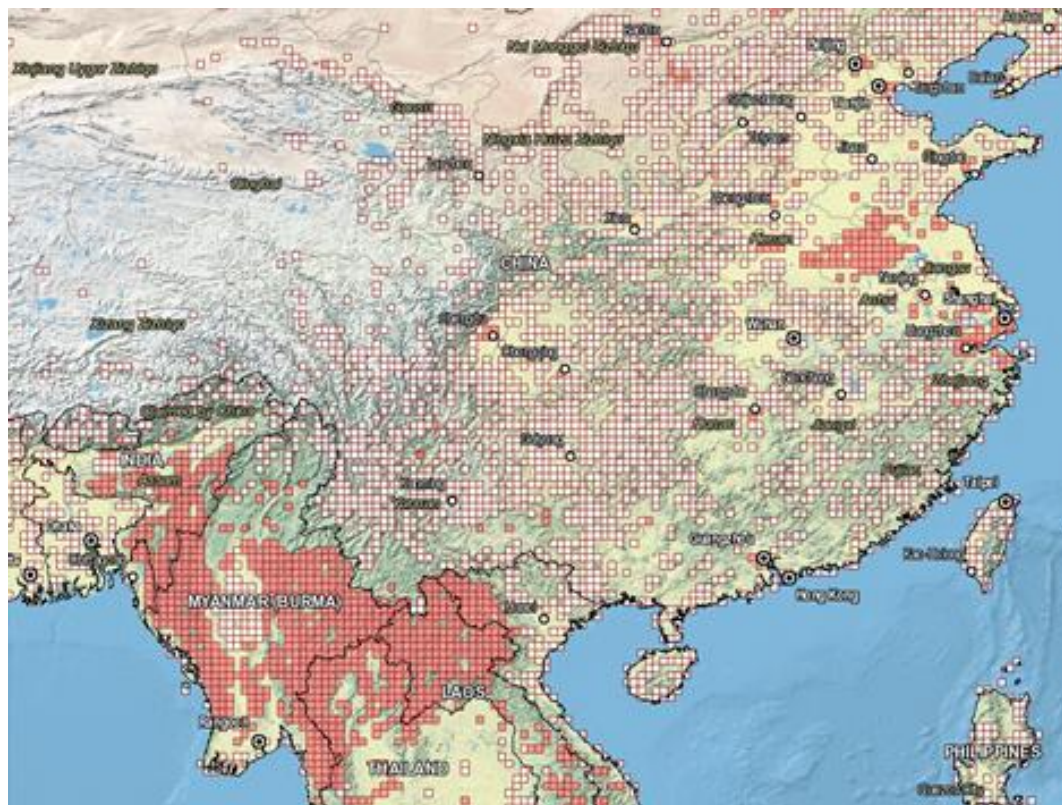


**Fig. S1.** Nitroaromatic compound (NAC) standards of five concentration levels spiked onto aerosol filters show comparable linear regression slopes (listed in Table S1). One summer and one winter filter samples were used in this matrix effect experiments. The set of standard addition points associated with the winter filter matrix generally form linear curves of higher intercepts because of the higher level of NACs present in the winter filter.





**Fig. S2.** Correlations between nitroaromatic compounds (NACs) and (a) levoglucosan, (b) NO<sub>3</sub><sup>-</sup>, and (c) K<sup>+</sup> for particulate matter of 2.5 µm or less in aerodynamic diameter (PM<sub>2.5</sub>) samples collected at Tsuen Wan from 2010 to 2012.



**Fig. S3.** Fire counts during the sampling period (2010–2012) in this study (data were retrieved from MODIS active fire detection by NASA Fire Information for Resource Management System (FIRMS)).