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Effects of long-range transport of air pollutants on nitrogenous organic matters in mountain background region of Southeast China: Sources and influencing factors identified by observation and modal calculation

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Abstract

Nitrated aromatic compounds (NACs), a major component of brown carbon (BrC), have a significant role in the atmosphere's ability to absorb light. Despite this, the sources and major influencing variables of the mountain background atmosphere are mostly lacking. The current work is based on a thorough field investigation of NACs from fine particle samples taken in 2014 and 2015 at the peak of Mt. Wuyi (1139 meters above sea level) and includes a thorough examination of the seasonal fluctuations in their composition, sources, and significant influencing factors. As a result of the air masses traveling mostly via northern heating zones, the total abundance of nine quantifiable NACs increased significantly in the winter (3.9 ± 1.5 ng m^{-3}) and autumn (2.1± 0.94 ng m^{-3}), whereas it decreased in the spring (1.3 ± 0.75 ng m^{-3}) and summer (0.97 ± 0.36 ng m^{-3}). The most prevalent NAC species during the year was 4-nitrocatechol (25.8%), followed by 5-nitroguaiacol (17.6%). In addition, the majority of NACs (93%) were influenced by coal, biomass, and petroleum combustion over the entire year, according to the results of structural equation modeling (SEM). Pollutant movement had a significant impact on the atmospheric NACs at the peak of Mt. Wuyi, especially in the winter (93.4%) and spring (68.7%). Long-range transport of nitration reactions was the dominant style in the transport process during the winter (33.7%), while long-range transport of mixed sources was significant throughout the other seasons (14%–37%). In particular, for 4-nitrocatechol, NO_2 may enhance the generation of NACs with a major impact on their compositions. Under low-NO_x conditions, the

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formation of NACs was comparatively sensitive to NO_2, suggesting that NACs would become significant in the aerosol characteristics when nitrate concentrations decreased as a result of emission reduction measures.

1 Introduction

One of the most important constituents of BrC is nitrated aromatic compounds (NACs), which have an aromatic moiety and the -OH and -NO_2 functions (Desyaterik et al., 2013; Wu et al., 2020). Nitrophenols (NPs), nitrosalicylic acids (NSAs), nitroguaiacols (NGAs), and nitrocatechols (NCs) are the most common among various kinds of NACs. Due to their capacity to absorb light, they have received a lot of attention (Li et al., 2020c; Wang et al., 2018; Teich et al., 2017; Wang et al., 2016), and ~ 4% of the net water-soluble BrC absorption has been ascribed to them as documented by several earlier studies (Mohr et al., 2013; Zhang et al., 2013). Because of NACs' strong mutagenicity, cytotoxicity, and carcinogenicity, they manifest an influence on human health (Iinuma et al., 2010).

Various ambient atmospheres has been shown to have NACs, including rural (Liang et al., 2020; Teich et al., 2017; Lv et al., 2022), urban (Li et al., 2020b; Li et al., 2020c; Wang et al., 2019; Ren et al., 2022; Li et al., 2020a), suburban (Kitanovski et al., 2021), and mountain (Wang et al., 2018). They can not only originate from primary emissions, but also can be created *in-situ* by secondary formation. Biomass burning (Wang et al., 2017; Lin et al., 2017; Chow et al., 2015), traffic emissions (Lu et al., 2019a), and coal combustions (Lu et al., 2019b) are the key primary sources of NACs.

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Several works indicated that the primary cause of the generation of NACs is biomass burning (Lin et al., 2017; Wang et al., 2017; Mohr et al., 2013), whereas several other studies consider road traffic emissions as the primary cause of the origin of nitrophenols (Zhang et al., 2010). Secondary chemistry primarily classified as the nitration of aromatic compounds, may occur in both aqueous and gas phases (Li et al., 2020c; Harrison et al., 2005; Wang et al., 2019). According to recent research, phenolic VOCs being oxidized by the nitrate radical (NO_3•) at night may also function as a notable source of nitrophenols and additional BrC species (Mayorga et al., 2021). Even though researchers have started to study NACs, very little is known regarding the relative significance of their corresponding primary and secondary sources. The fundamental variables affecting the generation of NACs are also little known because only a few investigations have been conducted thus far, in particular within China.

Field observations in both clean and polluted environments are essential for better identifying elements that have previously gone unnoticed and for confirming the mechanistic understanding attained from research on smog chambers. These studies are nonetheless concerning, particularly those carried out in environments with low concentrations of anthropogenic pollutants like NO_x. In our earlier research, we examined how biomass burning affects biogenic secondary organic aerosol (BSOA) production from long-haul travel and how biogenic volatile organic compounds (BVOCs) contribute to the generation of BSOA in high mountain locations (Mt. Wuyi). Nine NACs (NPs, NGAs, NCs, and NSAs) in the $PM_{2.5}$ were studied in the current study, to better understand ambient characteristics of NACs, their chief primary sources,

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and the principal factors influencing their secondary development, particularly the effect of long-range transport of air pollutants. $PM_{2.5}$ samples that were collected over an entire year on Mt. Wuyi's summit were measured using GC-MS. The outcome of the current research offers useful insight into the information characteristics of NACs via seasonal variation in sources, and they can provide insightful information about the potential influences on the second generation of NACs in background environments that are relatively free of contaminants.

2 Experimental

2.1 Sample site and field observations

One national atmospheric background monitoring station is located at Mt. Wuyi station (27°35′N, 117°43′E, 1139 m a.s.l., Fig. 1). There are no evident sources of atmospheric pollution within 50 km^2 of the monitoring station, which is located at the southern tip of the Mt. Wuyi national reserve. As a result, it can accurately depict the atmospheric background conditions of southeast China's forest and mountain region. Due to its high altitude and active airstream, it can also be used to observe the effects of long-range transport. In this work, we used a high-volume air sampler (TE-6070V, Tisch Inc., USA) to gather $PM_{2.5}$ samples with an airflow equivalent to 1.063 m^3 min^{-1}. 49 $PM_{2.5}$ samples in total were taken over seven days. During the sampling, four blank specimens (one for individual seasons) were obtained. At the same time, we gathered data on conventional pollutants and weather-related pollutants, including temperature (T), relative humidity (RH), SO_2, NO_2, and O_3. Sample site and sampling

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information has been reported in detail in the literature (Ren et al., 2019).

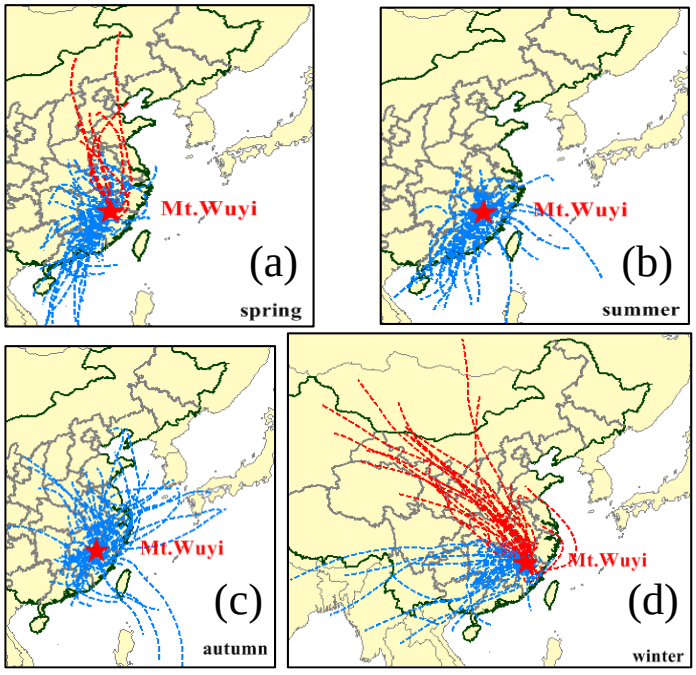

Fig. 1 Location of the sampling site (Mt. Wuyi: 27°35′ N, 117°43′ E; 1139 m a.s.l.) and 48 hour backward trajectories reaching the summit during the sampling (spring: March 20, 2014- June 4, 2014; summer: June 4, 2014- September 2, 2014; autumn: September 2, 2014-December 4, 2014; winter: December 4, 2014- February 25, 2015).

2.2 Chemical analysis

Organic compounds, for instance, nine NACs (including 3-methyl-4-nitrophenol (3M4NP), 4-nitrophenol (4NP), 2,4-dinitrophenol (2, 4-DNP), 4-nitroguaiacol (4NGA), 5-nitroguaiacol (5NGA), 4-nitrocatechol (4NC), 4-methyl-5-nitrocatechol (4M5NC), 3-nitro-salicylic acid (3NSA), 5-nitro-salicylic acid (5NSA)), fossil fuel *n*-alkanes (ff *n*-alkanes), PAHs, trehalose, and levoglucosan were identified in the samples. Elemental carbon (EC), organic carbon (OC) and some inorganic ions (i.e. SO_4^{2-}, NO_3^-,

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130 NH_4^+, K^+) were also the constituents of the samples. The procedures for sample
131 extraction and derivatization have been elaborated elsewhere (Ren et al., 2022; Ren et
132 al., 2019). Briefly stated, an aliquot of the filter was extracted with a mixture of
133 methanol and dichloromethane (DCM, 1:2) under ultrasonication for three times. The
134 extracts are concentrated and dried by using pure nitrogen, derivatized with N, O-bis-
135 (trimethylsilyl) trifluoroacetamide (BSTFA), and analyzed by using gas
136 chromatography equipped with mass spectroscopy (GC-MS, 7890A/5975C, Agilent
137 Co., USA). The GC separation was carried out on a DB-5MS fused silica capillary
138 column, and the GC oven temperature programmed from 50℃ (2min) to 120℃ with
139 15℃ min^{-1} and then to 300℃ with 5℃ min^{-1}, with a final isothermal hold at 300℃ for
140 16 min. The sample was injected in a splitless mode at an injector temperature of 280℃,
141 and scanned from 50 to 650 Daltons using electron impact (EI) mode at 70eV. Under
142 the Interagency Monitoring of Protected Visual Environments (IMPROVE)
143 thermal/optical reflectance (TOR) methodology, OC and EC were measured by a DRI
144 model 2001 Carbon Analyze (Atmoslytic Inc., Calabasas, CA, USA). OC collected by
145 filter membrane are first volatilized with the proceeding of temperature up to 580 ℃ in
146 the protection of He and determined. EC are analyzed then with the increasing of
147 temperature to 840℃ in the presence of He and O_2 by the NDIR non-dispersive infrared
148 CO_2 detector. Dionex-600 ion chromatography was used to quantify inorganic ions in
149 samples after extracted with Mili-Q pure water (Thermo Fisher Scientific Inc., USA).

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2.3 Model calculation

As a receptor model, Positive Matrix Factorization (PMF) (EPA PMF 5.0 version) has been extensively employed for the source distribution of atmospheric pollutants (Ren et al., 2022; Wu et al., 2020; Wang et al., 2018). To quantify the source apportionment for NACs including transport and local, the mass concentrations of SO_2, NO_2, CO, O_3, sulfate, nitrate, NH_4^+, K^+, ff-*n*-alkanes, PAHs, levoglucosan, trehalose 3M4NP, 4NP, 4NGA, 5NGA, 2,4-DNP, 4M5NC, 4NC, 5NSA, and 3NSA, were employed as input data. Q value and r, which were defined as the agreement between the model fit and the correlation between estimated and measured concentrations, respectively, are used to determine the appropriate factor number for modeling (Comero et al., 2009). In the current work, the model was iterated upon using a variety of combinations of the concentration data set and three to six covariates. The best solution was determined to be five components based on the Q value and r^2 (Table S1) values.

The direct and indirect effects of air pollutants variables on NACs were quantified by utilizing Structural equation modeling (SEM). Initially, a conceptual model of hypothetical linkages was developed using past and theoretical information. The measured data were then integrated into the model using the maximum-likelihood estimation technique. We identified the model that best fits the data by methodically deleting non-significant routes from the base model. The p-value, χ^2-test, goodness-of-fit index (GFI) and root mean square error of approximation (RMSEI) index were used to assess the model's suitability. The conceptual model was acceptable if the p-value > 0.05, Low RMSEA (<0.08), high GFI (>0.9), and low χ^2 values were regarded as

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positive model fits. AMOS 24.0 (IBM, Chicago, IL, USA) was used to analyze the above statistical analyses.

2.4 Quality assurance and quality control (QA/QC)

All glassware used were rinsed and baked at 450℃ for 8 h and further cleaned by using methanol, DCM and hexane immediately before using. Field blank sample analysis showed no serious contamination (less than 5% of real samples). GC/MS response factors of all organic species were used those of the authentic standards. The recovery experiment was done by spiking the standard solution onto blank filters (n=3) and analyzed using the above procedure. Recoveries of the quantified organic compounds were generally between 80% and 110%. Data reported here were all corrected for the blanks.

3 Results and discussion

3.1 Meteorological Features and Air masses

From March 2013 through February 2015, a total of four seasons were covered by the sampling campaign. In the area under investigation, the four seasons are typically referred to as spring (March through May), summer (June through August), autumn (September through November), and winter (December through February). The rise in temperatures starts in March, and peaks in July (25 °C), before falling to a minimal value of 2.9 ℃ in January–February. When determining the origin of air masses at a certain location, air mass backward trajectories are taken into account. The Hybrid

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Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) model supplied 48-hour air mass backward trajectories for this study. Although prior research has shown that atmospheric aerosols could potentially not follow the results trajectories due to gravitational settling and scavenging processes (Chen and Siefert, 2004), the air mass backward trajectories furnish important background information on airstreams as well as the plausible origins of the air mass that has been sampled (Chen and Chen, 2008). The source regions of primary aerosol gathered from an area located at a distance from the source location, have been also identified using air mass backward trajectories (Chiapello et al., 1997; Wang et al., 2013; Wang et al., 2014). The 48-hour backward trajectories (Fig. 1) show that during the sample, winds from the north were reaching the top, particularly in winter (Fig. 1d), when there were large concentrations of air pollutants due to anthropogenic emissions. Our prior research has shown that these anthropogenic pollutants considerably increased the generation of biogenic secondary organic aerosols (BSOA) (Ren et al., 2019). This explains why some anthropogenic pollutants, such as SO_2, NO_2, ff-*n*-alkanes (fossil fuel markers), PAHs (coal and fossil fuel markers), levoglucosan (biomass burning markers), SO_4^{2-}, NO_3^-, and others were typically higher in winter or autumn (Table 1).

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Table 1. Concentrations (ng m^{-3}) of organic compounds in $PM_{2.5}$ samples in Mt. Wuyi during the sampling time.

	spring (n=11)	summer (n=13)	autumn (n=13)	winter (n=12)
$PM_{2.5}$ (μg m^{-3})	16±5.5 (7.6-24)	14±7.8 (4.9-32)	20±7 (8.3-31)	21±7.8 (5-32)
T (℃)	16±3.6 (8.2-21)	23±1.3 (21-25)	17±4.7 (9.6-23)	6.4±2.8 (2.9-11)
RH (%)	78±9.7 (57-89)	79±6.5 (67-91)	75±9.2 (60-92)	64±16 (43-96)
SO_2 (μg m^{-3})	1.7±1.2 (0.5-4)	0.9±0.74 (0.21-2.8)	3.1±2 (0.58-6.5)	6.7±3.9 (0.42-14)
NO_2 (μg m^{-3})	4.2±2.1 (1.8-9.1)	1.7±1.3 (0.31-4.5)	4±1.9 (1.1-8.2)	6.2±2.3 (1.5-10)
CO (mg m^{-3})	0.42±0.07 (0.31-0.55)	0.27±0.08 (0.18-0.45)	0.43±0.09 (0.27-0.58)	0.46±0.07 (0.36-0.58)
O_3 (μg m^{-3})	104±12 (89-121)	82±25 (62-142)	93±20 (68-127)	83±20 (34-109)
OC (μg m^{-3})	2.2±1.2 (0.98-4.7)	1.6±0.86 (0.49-3.7)	3.1±1.5 (0.84-6.1)	4.6±1.9 (0.91-7.3)
EC (μg m^{-3})	0.51±0.11 (0.35-0.68)	0.48±0.20 (0.15-0.83)	0.56±0.15 (0.29-0.78)	0.69±0.13 (0.43-0.89)
Inorganic components (ng m^{-3})				
SO_4^{2-}	6.2±2.2 (2.6-9.8)	5.0±3.9 (1.2-15)	7.6±2.9 (2.8-11)	6.3±3.0 (1.1-13)
NO_3^-	0.06±0.11 (NA[a]-0.39)	0.01±0.02 (0.002-0.06)	0.19±0.39 (0.008-1.5)	1.3±1.1 (0.07-4.2)
NH_4^+	1.7±0.55 (0.75-2.3)	1.4±1.2 (0.3-4.5)	2.3±0.99 (0.72-3.8)	2.2±1.2 (0.36-5.1)
K^+	0.21±0.1 (0.08-0.42)	0.13±0.14 (0.03-0.46)	0.28±0.15 (0.06-0.49)	0.39±0.15 (0.08-0.59)
Nitrated aromatic compounds (ng m^{-3})				
4-nitrophenol (4NP)	0.18±0.13 (0.04-0.49)	0.05±0.04 (0.01-0.16)	0.32±0.28 (0.04-1.1)	0.74±0.34 (0.14-1.3)
3-methyl-4-nitrophenol (3M4NP)	0.03±0.03 (0.01-0.09)	0.05±0.02 (0.03-0.08)	0.04±0.02 (0.02-0.09)	0.06±0.04 (0.01-0.12)
2,4-dinitrophenol (2,4-DNP)	0.06±0.03 (0.03-0.13)	0.06±0.03 (0.03-0.14)	0.08±0.03 (0.03-0.14)	0.09±0.05 (0.03-0.18)
4-nitroguaiacol (4NGA)	0.07±0.03 (0.03-0.10)	0.07±0.03 (0.03-0.14)	0.07±0.03 (0.02-0.14)	0.05±0.02 (0.03-0.09)
5-nitroguaiacol (5NGA)	0.21±0.10 (0.06-0.37)	0.29±0.13 (0.07-0.48)	0.32±0.11 (0.11-0.51)	0.22±0.1 (0.07-0.42)
4-nitrocatechol (4NC)	0.34±0.31 (0.07-1.1)	0.14±0.07 (0.03-0.27)	0.64±0.48 (0.13-1.7)	1.6±0.87 (0.27-3.0)

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4-methyl-5-nitrocatechol (4M5NC)	0.20±0.08 (0.09-0.33)	0.19±0.06 (0.11-0.31)	0.34±0.1 (0.2-0.53)	0.39±0.19 (0.1-0.73)
3-nitrosalicylic acid (3NSA)	0.07±0.05 (0.03-0.2)	0.04±0.02 (0.01-0.08)	0.09±0.04 (0.04-0.18)	0.19±0.08 (0.04-0.31)
3-nitrosalicylic acid (5NSA)	0.12±0.10 (0.04-0.39)	0.07±0.04 (0.02-0.17)	0.23±0.13 (0.08-0.53)	0.55±0.29 (0.08-1.1)
NACs	1.3±0.75 (0.52-3.1)	0.97±0.36 (0.34-1.7)	2.1±0.94 (0.72-4.0)	3.9±1.5 (1.3-6.3)
Other organic components (ng m^{-3})				
Fossil fuel *n*-alkanes (ff-*n*-alkanes)	6.3±3.1 (2.7-12)	3.2±1.3 (1.5-6.1)	9.3±4.7 (3.9-20)	18±5.6 (5.7-28)
PAHs	1.5±0.86 (0.59-3.1)	0.54±0.30 (0.23-1.3)	2.1±1.1 (0.68-4.2)	4.5±1.8 (1.2-6.5)
Levoglucosan	15±17 (3.8-62)	4.2±1.7 (1.3-7.5)	23±13 (5.7-41)	52±21 (20-86)
Trehalose	0.63±0.25 (0.29-1.1)	0.87±0.41 (0.25-1.5)	0.49±0.33 (0.23-1.3)	0.36±0.14 (0.12-0.65)

[a] NA: not available.

3.2 Abundance and seasonal variations of NACs

Table 1 lists the measured concentrations of the major $PM_{2.5}$ constituents, and Fig.2 shows the seasonal fluctuations of the nine NACs throughout the year. Nine different NACs' average concentrations varied significantly throughout the year, with winter having the greatest levels (3.9± 1.5 ng m^{-3}), followed by autumn (2.1± 0.94 ng m^{-3}), spring (1.3± 0.75 ng m^{-3}), and summer (0.97± 0.36 ng m^{-3}). The total NACs concentrations in the current and earlier works have been compared in Table 2. The total NACs concentration in this study was significantly lower in comparison to that predicted for urban sites in China, particularly in winter and autumn, such as in Beijing (20± 12 ng m^{-3} in autumn, 74± 51 ng m^{-3} in winter) (Li et al., 2020c), Jinan (9.8± 4.2 ng m^{-3} in autumn, 48± 26 ng m^{-3} in winter) (Wang et al., 2018), Xi'an (17± 12 ng m^{-3} in winter) (Wu et al., 2020), and Hong Kong (12± 14 ng m^{-3} in winter) (Chow et al.,

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226 2015). Moreover, as compared to the levels in rural and background sites during
227 summertime in China, the levels in this work were also much lower, for instance,
228 Wangdu (Wang et al., 2018), Yucheng, (Wang et al., 2018), Mt.Tai (Wang et al., 2018),
229 and Xianghe (Teich et al., 2017). In comparison with the studies abroad, the total NAC
230 concentrations in this investigation were also comparatively lower than the
231 measurements in winter, such as in the UK (Mohr et al., 2013), Germany (Teich et al.,
232 2017), Slovenia (Kitanovski et al., 2012) and Belgium (Kahnt et al., 2013).
233

Table 2. Measured concentrations of nitrated aromatic compounds in domestic and foreigh researches over the last decade.

Sampling site	Sampling period	Aerosol Type	NAC Species[a]	Concentrations (ng m^{-3})	References
Mt. Wuyi, China	Spring, 2014 Summer, 2014 Autumn, 2014	$PM_{2.5}$	①②③④⑤⑥⑦⑧⑨	1.3 ± 0.75 0.97 ± 0.36 2.1 ± 0.94	This study
Beijing, China	Winter, 2014-2015 Apr., 2017 Jul., 2017	$PM_{2.5}$	①②③④⑤⑥⑦⑧⑨	3.9 ± 1.5 8.6 ± 6.7 8.5 ± 3.9	Ren et al., 2022
Beijing, China	Sep. -Nov.,2017 Dec., 2017-Feb.,2018	$PM_{2.5}$	①②③④⑥⑦⑧⑨	20 ± 12 74 ± 51	Li et al., 2020
Beijing, China	May-Jun., 2016	$PM_{2.5}$	①②⑥⑦⑩⑪⑫⑬	6.6	Wang et al., 2019
Xi'an, China	Jan., 2017 Jul.-Aug., 2017	$PM_{2.5}$	①②③④⑤⑥⑦⑧⑨	17 ± 12 0.40 ± 0.27	Wu et al., 2020
Jinan, China Yucheng, China Wangdu, China	Nov. 2013-Jan., 2014 Sep., 2014 Jun., 2014 Jun., 2014	$PM_{2.5}$	①②⑥⑦⑧⑨⑩⑪⑫	48 ± 26 9.8 ± 4.2 5.7 ± 2.8 5.9 ± 3.8	Wang et al., 2018
Mt.Tai, China Wangdu, China Xianghe, China	Jul.-Aug., 2014 Jun., 2014 Jul.-Aug., 2013	PM_{10}	①②③⑧⑨⑩⑬⑭	2.5 ± 1.6 9.2 3.6	Teich et al., 2017
Hong Kong, China	Spring, 2010-2012 Summer, 2010-2012 Autumn, 2010-2012	$PM_{2.5}$	①②⑥⑦⑩⑪⑫⑬	2.7 ± 3.6 2.2 ± 4.9 6.5 ± 6.9	Chow et al., 2015
TROPOS,	Winter, 2009-2012 Jan.-Feb., 2014	PM_{10}	①②②③⑧	12 ± 14 16	Teich et al.,

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Germany			⑨⑩⑬⑭		2017
Melpitz, Germany	Jan.-Feb., 2014			12	
	Jul., 2014			0.3	
Waldstein, Germany	Jul., 2014		⑧⑨	0.4	
Detling, UK	Jan.-Feb., 2012	PM_1	①③⑥⑦⑮	19	Mohr et al., 2013
Hamme, Flanders, Belgium	Spring, 2010	PM_{10}	①⑥⑦ ⑪⑫⑬	3.8	Kahnt et al., 2013
	Summer, 2010			2.2	
	Autumn, 2010			13	
	Winter, 2010			32	
Ljubljana, Slovenia	Dec., 2010-Jan., 2011	PM_{10}	①②③④⑤ ⑥⑦⑧⑨⑩ ⑪⑫	150	Kitanovski et al., 2012
	Aug., 2010			0.9	

[a] ①4-nitrophenol ②3-methyl-4-nitrophenol ③2,4-dinitrophenol ④4-nitroguaiacol ⑤5-nitroguaiacol ⑥4-nitrocatechol ⑦4-methyl-5-nitrocatechol ⑧3-nitro-salicylic acid ⑨5-nitro-salicylic acid ⑩2-methyl-4-nitrophenol ⑪3-methyl-5-nitrocatechol ⑫3-methyl-6-nitrocatechol ⑬2,6-dimethyl-4-nitrophenol ⑭ 3,4-dinitrophenol ⑮ 4-methyl-2-nitrophenol

234

235 For each NAC species, NPs (including 4NP, 3M4NP, 2, 4-DNP) (Fig. 2a), NCs
236 (4NC, 4M5NC included) (Fig. 2c), and NSAs (including 3NSA, 5NSA) (Fig. 2d) have
237 the same seasonal trends as the total NACs. However, on the contrary, there were no
238 obvious seasonal trends for NGAs (including 4NAG and 5NGA) (Fig. 2b). 4NC was
239 on average, the most abundant species throughout the year (25.8%), followed by 5NGA
240 (17.6%) (Fig. S1), with different proportions of molecular composition in different
241 seasons (Fig. 3). 4NC was the only NACs species that accounted for more than 20% in
242 spring (23.7%), autumn (27%), and winter (39.7%). The most prevalent compound over
243 the summer was 5NGA (28.7%), followed by 4M5NC (20.9%). These findings
244 contrasted with those of earlier studies on urban areas, which often revealed that 4NP
245 had the greatest levels, followed by 4NC (Li et al., 2020c; Wang et al., 2018; Wang et
246 al., 2019). These variations can be due to the various sources and NAC generation

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processes found in various situations.

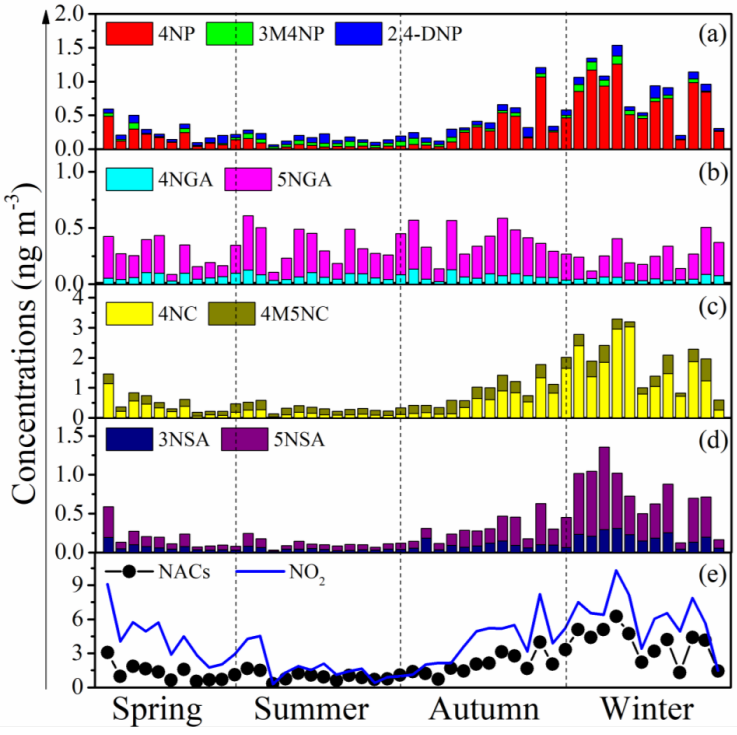

Fig.2 Temporal variations of each NACs species (4NP: 4-nitrophenol; 3M4NP: 3-methyl-4-nitrophenol; 2,4-DNP: 2,4-dinitrophenol; 4NGA: 4-nitroguaiacol; 5NGA: 5-nitroguaiacol;4NC: 4-nitrocatechol; 4M5NC: 4-methyl-5-nitrocatechol; 3NSA: 3-nitrosalicylic acid; 5NSA: 5-nitrosalicylic acid).

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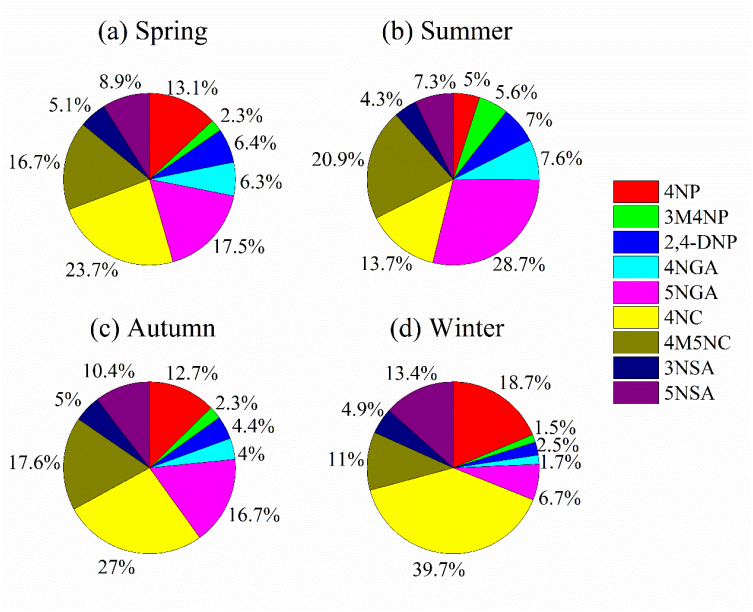

Fig.3 Relative contribution of each NACs species during the sampling time (4NP: 4-nitrophenol; 3M4NP: 3-methyl-4-nitrophenol; 2,4-DNP: 2,4-dinitrophenol; 4NGA: 4-nitroguaiacol; 5NGA: 5-nitroguaiacol;4NC: 4-nitrocatechol; 4M5NC: 4-methyl-5-nitrocatechol; 3NSA: 3-nitrosalicylic acid; 5NSA: 5-nitrosalicylic acid).

3.3 Influence factors and sources of NACs

For further clarification regarding the influencing factors and sources of NACs, the interrelation between total and individual NAC species and the related pollutants were analyzed based on the results of Pearson correlations depicted in Table 3 (for the whole campaign) and Tables S3-6 (for the four seasons), including $PM_{2.5}$, SO_2, NO_2, O_3, and other chemical components. It is noteworthy that total NACs and all identified NACs species manifested strong correlations with $PM_{2.5}$ in the whole year, indicating that they are important components of $PM_{2.5}$. There were good relationships between NACs and primary pollutants in the whole year, such as SO_2 ($r=0.859$, $p<0.01$), ff-*n*-

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alkanes (r=0.927, p<0.01), PAHs (r=0.927, p<0.01), levoglucosan (r=0.931, p<0.01), and K^+ (i.e., a BB tracer, r=0.817, p<0.01) (Table 3). Furthermore, the model calculation results of SEM indicate ff-*n*-alkanes, SO_2, and levoglucosan would account for 93% of NACs (Fig. 4a). All of these connections indicated that burning emissions throughout the year, such as the burning of coal (Lu et al., 2019b), biomass (Wang et al., 2017; Lin et al., 2017; Chow et al., 2015), and burning of petroleum (Lu et al., 2019a), had a substantial impact on NACs.

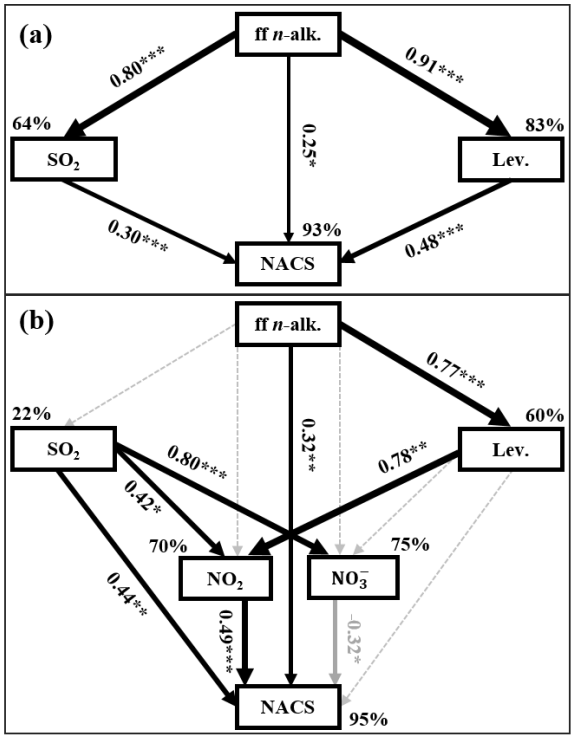

Fig. 4 Structural equation model (SEM) demonstrating the effects of ff *n*-alk., SO_2, Lev. and NO_2 on annual (a) or winter (b) mean NACs. The model fits the data well (χ^2 =0.235, df=1, p=0.628, GFI=0.999, RMSEA=0.000 (a), χ^2 =0.690, df=2, p =0.708, GFI=0.980, RMSEA=0.000 (b)). Black solid arrows indicate significant positive relationships, gray solid arrows indicate significant negative relationships and black dashed arrows indicate nonsignificant path coefficients. The width of arrows is proportional to the strength of path coefficients. Numbers on arrows are standardized path coefficients (equivalent to correlation

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coefficients), asterisks following the numbers imply significant relationships (*p < 0.05, **p < 0.01, ***p < 0.001). Percentages (R^2) close to endogenous variables indicate the variance explained by the ff *n*-alk., SO_2, Lev. and NO_2.

Additionally, total NACs also showed strong correlations with NO_2 (r=0.862, p<0.01), SO_4^{2-} (r=0.396, p<0.01), NO_3^- (r=0.757, p<0.01), NH_4^+ (r=0.524, p<0.01), probably suggesting that the secondary formation of NACs was also important in the campaign. Here, the NACs concentration was strongly associated with NO_2, especially in the winter (Fig. 2e), and correlated better than other secondary tracers (Table 3), suggesting that NO_2 is a relatively importance component in the creation of NACs. According to earlier research, the photochemical production of NACs is related to the oxidation of aromatics in the presence of NO_2, including the •OH oxidation and the NO_3• oxidation (Cai et al., 2022; Ren et al., 2022; Yi Chen et al., 2022; Finewax et al., 2018).

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Table 3. Pearson correlations between individual NAC species and meteorological parameters, aerosol components, and gas pollutants during the whole campaign (n = 49).

	NACs	4NP	3M4NP	2,4-DNP	4NGA	5NGA	4NC	4M5NC	3NSA	5NSA
$PM_{2.5}$	0.657**	0.649**	0.376**	0.359*	0.308*	0.521**	0.501**	0.703**	0.561**	0.564**
SO_2	0.859**	0.887**	0.520**	0.299*	-0.184	-0.053	0.781**	0.637**	0.748**	0.889**
NO_2	0.862**	0.834**	0.329*	0.347*	-0.142	0.103	0.845**	0.543**	0.762**	0.774**
O_3	0.146	0.145	0.028	0.024	0.308*	0.403**	0.029	0.348*	0.174	0.102
ff- *n*-alkanes	0.927**	0.942**	0.364*	0.475**	-0.140	0.090	0.841**	0.732**	0.834**	0.880**
PAHs	0.927**	0.944**	0.486**	0.347*	-0.205	-0.049	0.857**	0.661**	0.838**	0.942**
Levoglucosan	0.931**	0.885**	0.299*	0.392**	-0.207	0.113	0.884**	0.721**	0.881**	0.860**
K^+	0.817**	0.805**	0.308*	0.363*	0.109	0.330*	0.707**	0.736**	0.709**	0.732**
SO_4^{2-}	0.396**	0.412**	0.281	0.285*	0.411**	0.516**	0.250	0.502**	0.272	0.305*
NO_3^-	0.757**	0.829**	0.448**	0.322*	-0.225	-0.108	0.701**	0.486**	0.618**	0.766**
NH_4^+	0.524**	0.560**	0.314*	0.321*	0.276	0.443**	0.385**	0.547**	0.373**	0.442**

**Significant correlation at the 0.01 level.

*Significant correlation at the 0.05 level.

Based on the results of the PMF model, this work identified five styles of sources during the campaign to further qualitatively and quantitatively the effects of transportation and local sources of various pollutants emissions on NACs at the summit of Mt. Wuyi. These sources have been shown in Fig. 5 and Fig. 6. As the first source factor, levoglucosan loading was larger in this component profile than it was in other factor profiles due to the long-range transport of biomass burning, also with other high loading anthropogenic primary organic markers, included ff-*n*-alkanes, PAHs, SO_2, and NO_2 (Fig. 5a). Since there was no obvious anthropogenic source at the summit of Mt. Wuyi, this source was assumed to originate from the transmission process. Long-range

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transport of mixed sources, with the highest loading of SO_2, NO_2 and K^+, as well as anthropogenic primary organic markers, was identified as the second source factor during the transmission process, including primary and secondary emissions (Fig. 5b). The third source factor namely long-range transport of nitration reaction showed high concentrations of NO_3^- (Fig. 5c). Long-range transport of coal combustion was identified the fourth source factor, with high levels of SO_2 (Fig. 5d). Local sources were recognized as the last source factor, with relatively high levels of O_3 and low levels of anthropogenic pollutants (e.g. SO_2, NO_2, ff-*n*-alkanes, PAHs, levoglucosan) (Fig. 5e). It is noteworthy that trehalose also showed relatively high levels because this component is a naturally existing carbohydrate in vegetations, which were abundant in the sampling site.

For the whole campaign year, atmospheric NACs at the summit of Mt. Wuyi was substantially affected by the transport of air pollutants (67%), including long-range transport of mixed sources (21.9%), biomass burning (18.3%), coal combustion (16.5%) and nitration reaction (10.3%). While the impact of local sources accounted for only 33% (Fig.5a). The influence of local sources on NACs mainly took place in summer (Fig. 7c), while the other seasons were mainly influenced by the transport of air pollutants (Fig. 7b, d, e). Moreover, these sources had obviously different seasonal variation characteristics (Fig. 6). Long-range transport of biomass burning, nitration reaction, and coal combustion were much more intense in winter than in other seasons (Fig. 6a, c, d). Spring, autumn, and winter saw the most long-range transport of mixed sources, whereas later summer and early autumn had the least amount of it (Fig. 6b). In

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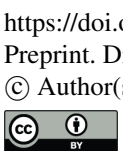

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spring, summer, and autumn, contributions from local sources were higher than they were in winter (Fig. 6e).

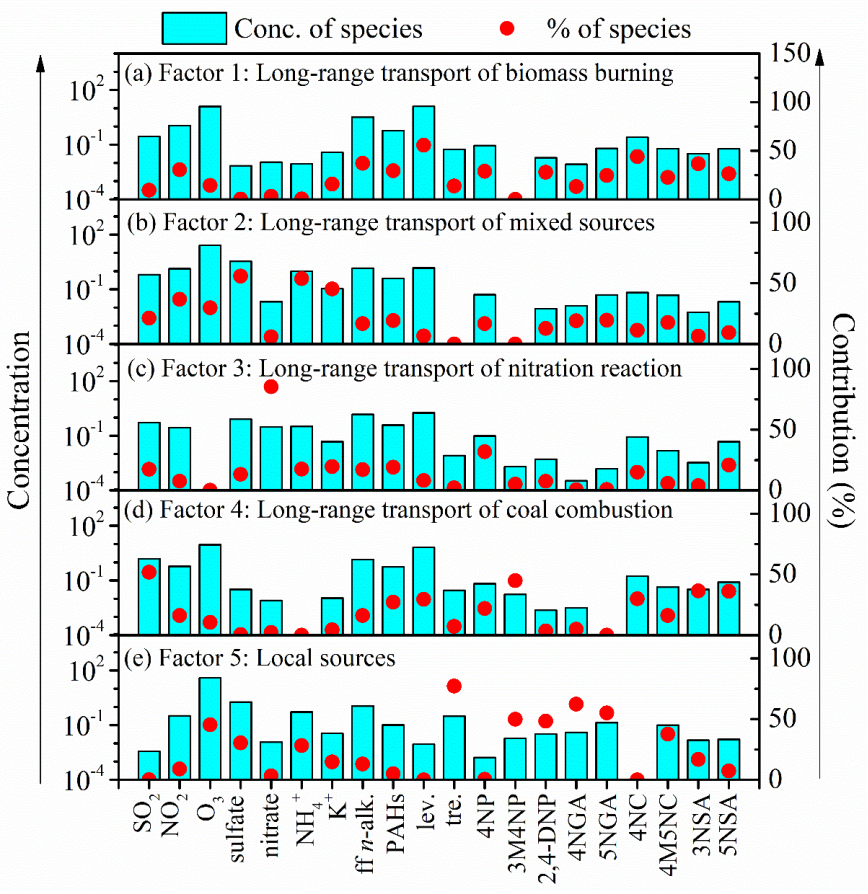

Fig.5 Source profiles of NACs obtained from PMF analysis (ff *n*-alk.: ff *n*-alkane. lev.: levoglucosan. tre.: trehalose).

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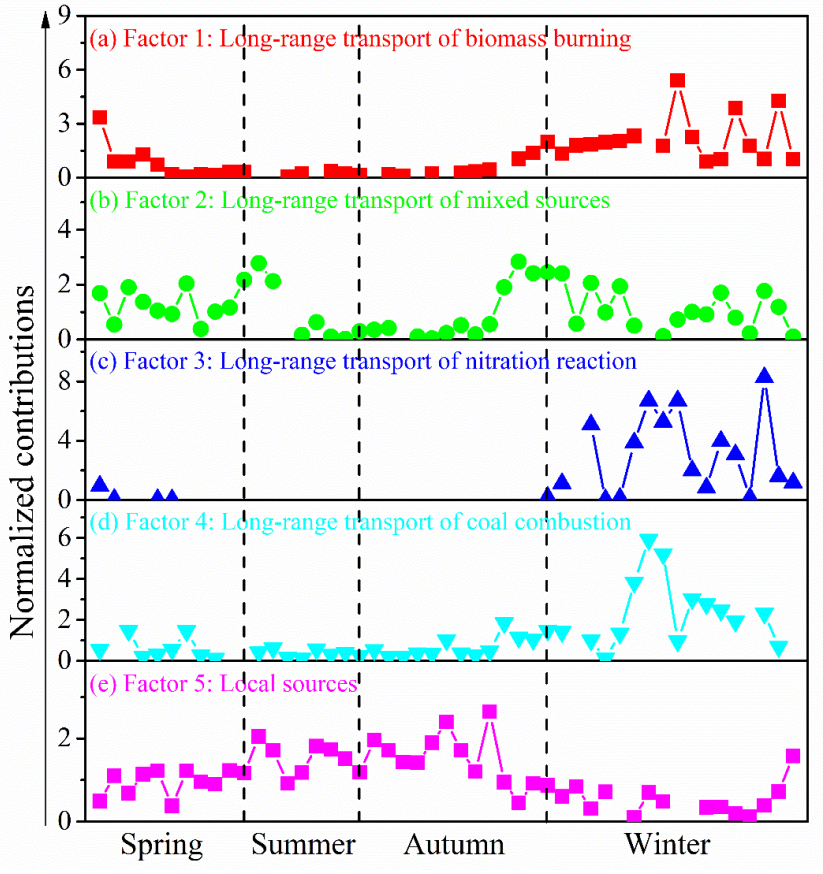

Fig. 6 Time variations of normalized contributions of each source.

During springtime, long-range transport of mixed sources had the biggest influence on NACs, followed by the local sources, which accounted respectively for 37.1% and 31.3% of the total (Fig. 7b). For total NACs, the correlation coefficient (Pearson r) was strong with SO_2, ff-*n*-alkanes, PAHs, levoglucosan, and K^+ ($r>0.73$, $p<0.01$), and the total NACs correlated well with NO_2, O_3, NO_3^-, and NH_4^+ ($r>0.70$, $p<0.01$) (Table S2). The outcome indicated that NACs originate not only from primary emissions but also from the secondary formation. Furthermore, The Pearson r for levoglucosan ($r=0.933$, $p<0.01$) and NO_2 ($r=0.945$, $p<0.01$) were higher in comparison

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to other parameters, suggesting that the burning of biomass and NO_2 had significant effects on NACs at the summit of Mt. Wuyi in spring.

During summertime, local sources were the largest contributors to NACs, with the relative contributions accounting for more than 65% of the total (Fig. 7c). The correlation coefficient (Pearson r) of total NACs was strong with NO_2 (r=0.869, p<0.01), O_3 (r=0.786, p<0.01), SO_4^{2-} (r=0.884, p<0.01), NO_3^- (r=0.678, p<0.05), and NH_4^+ (r=0.881, p<0.01) (Table S3), further suggesting that the secondary formation contributes significantly to the summertime NACs at the summit of Mt. Wuyi. The secondary formation has been identified as a major cause of the origin of atmospheric nitrated phenols, particularly in the summer, during the various field and modeling investigations conducted recently (Yuan et al., 2016; Mayorga et al., 2021; Xie et al., 2017; Cai et al., 2022; Wang et al., 2019). The strong associations between O_3 and NACs further support the significance of photochemical oxidation for NACs. In addition, Cai et al. discovered that in the summer metropolitan Shanghai, the majority of NACs were enhanced via photo-oxidation (Cai et al., 2022).

During autumn, the relative contributions of each source of NACs were similar to those observed in spring. Local sources and long-range transport of mixed sources made almost equal contributions to NACs, which accounted for 28% and 27.1%, respectively (Fig. 7d). Long-range transport of biomass burning also made a relatively large contribution to NACs (22.3%). There was still a strong correlation between NACs and NO_2 (r=0.886, p<0.01). It is noteworthy that the correlation coefficient (Pearson r) of total NACs was stronger with SO_2 (r=0.805, p<0.01) and SO_4^{2-} (r=0.615, p<0.05), and

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weaker with O_3 (r=0.165) in autumn than with the same in spring (Table S4). The findings revealed that at the summit of Mt. Wuyi in autumn, the proportional contribution of coal combustion was rising and the impact of photochemical reaction was declining.

During wintertime, long-range transport of nitration reaction was the largest contributor for NACs (33.7%), followed by long-range transport of biomass burning (27.5%) and coal combustion (23.6%) (Fig. 7e). The total NACs correlated better with NO_2 (r=0.879, p<0.01) than any other parameters (Table S5), thereby pointing towards significant involvement of NO_2 in NACs formation. According to earlier research, coal combustion and biomass burning had a greater contribution to NACs in the winter (Cai et al., 2022), with direct emissions from biomass burning in the range of 0.4 to 11.1 mg kg^{-1} (Iinuma et al., 2007; Wang et al., 2017). Furthermore, earlier research suggested that the detection of increased amounts of particulate phenols could be significantly attributed to coal combustion activities. The emission factors ranged from 0.2 to 10.1 mg kg^{-1} for bituminite, anthracite, lignite chunks, and briquettes. The residential coal combustion resulted in a net emission of 178 ± 42 Mg of fine particles of nitrated phenols, according to statistics of domestic coal consumption in a total of 30 provinces in Chinese in 2016 (Lu et al., 2019b).

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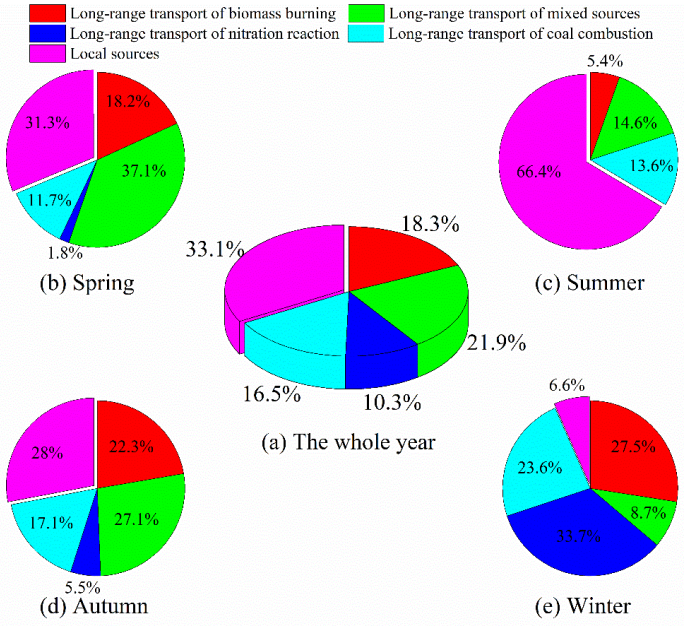

Fig. 7 Relative contributions of each source for NACs in different seasons.

3.4 Impact of NO_2 on NACs

Although NACs are highly affected by primary emissions, the secondary formation was also a very important source of particulate NACs, and NO_2 was a very important factor during the process (Ren et al., 2022; Cai et al., 2022). Studies have revealed that there is a closer link between NACs and NO_2 for samples taken at night, further pointing to the importance of NO_3•-initiated oxidation in the generation of NACs at night (Wang et al., 2018; Li et al., 2020c; Cai et al., 2022). According to the previous research, the intermediate formed when phenol reacts with either •OH during in the daytime or NO_3• during the night produces phenoxy radical (C_6H_5O•), which is where nitrophenol is produced (Berndt and Bge, 2003). The total measured NACs and NO_2 in our study displayed comparable temporal fluctuations (Fig. 2e), and they

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revealed strong correlations in the course of the entire campaign (r=0.879, p<0.01). The concentrations of nitrate (NO_3^-) and total NACs as a function of NO_2 abundance, and the fluctuations of [NACs] / [NO_3^-] mass ratios were plotted in Fig. 8 to examine the impact of NO_2 abundance further on the second generation of NACs and the current form. According to earlier investigations, box whisker plots (Fig.6a, c) typically showed higher NACs and NO_3^- concentrations with increasing NO_2 abundance (Cai et al., 2022; Wang et al., 2018; Ren et al., 2022). Additionally, the encouraging effect of NO_2 was more pronounced in winter than in other seasons (Fig. 8b), perhaps because winter has much higher NO_x abundance with higher VOC precursor oxidation capacity (Cai et al., 2022). Based on the results of SEM, the influence of the weight of NO_2 on NACs was significantly greater than that of other factors in winter, such as ff *n*-alkane and SO_2, although they all had significant effects on NACs (Fig. 4b). Fig .6d shows the variations of [NACs] / [NO_3^-] mass ratios during the whole campaign. This ratio was much higher in comparison to that observed in urban sites (Cai et al., 2022; Wang et al., 2018; Ren et al., 2022), would suggesting NACs were more likely generated in the background site at low NO_x levels. According to certain studies conducted in urban centers, when NO_2 levels were high (NO_2>30ppb), the NO_2 excess would be further oxidized to generate inorganic nitrate, which would lead to a change in the relative dominance of organic and inorganic compounds. When NO_2 was scarcer, a higher portion of NO_2 was covered into organic nitrogen (Cai et al., 2022; Wang et al., 2018). Here, the NO_2 levels on the submit of Mt. Wuyi were much lower than those in the urban's atmosphere, with the ratio of [NACs] / [NO_3^-] highest during summer than in

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other seasons (Fig. 8d), all indicating that the formation of organic nitrated aerosols was relatively sensitive to NO_2 at the low-NO_x level. Additionally, NO_2 may encourage the synthesis of NACs and have a major impact on their composition, particulars for NCs (Fig. 9a). When NO_2 levels were above 8ppb, 4NP and 4NC both contributed more to the total NACs, and the concentrations of NACs were at their maximum levels at those levels (Fig. 9b).

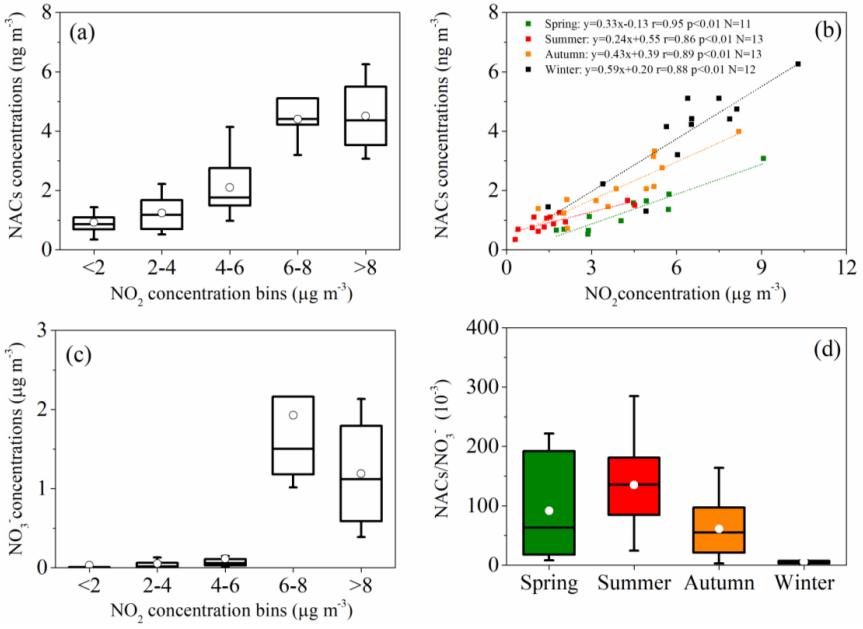

Fig. 8 Concentrations of NACs (a, b), nitrate (NO_3^-) (c) as a function of NO_2 concentration bins, and NACs / NO_3^- ratios (d) during the whole sampling time. The mean values are represented by the markers and the 25th and 75th percentiles are represented by whiskers.

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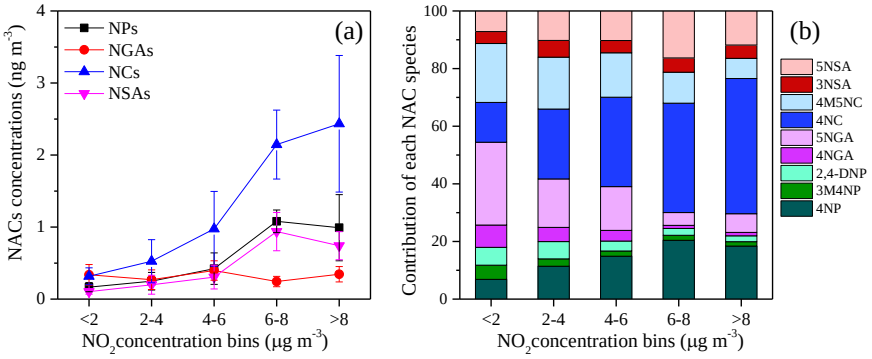

Fig. 9 Concentrations of NACs (a) and (b) contribution of each NACs species as a function of NO_2 concentration bins. (NPs: 4NP, 3M4NP, and 2,4-DNP; NGAs: 4NGA and 5NGA; NCs: 4NC and 4M5NC; NSAs: 3NSA and 5NSA).

Different levels of NO_2 may have different effects on nitrate aerosols in different atmospheric conditions, especially at high NO_x levels, although previous studies had come to a consensus that organic nitrated aerosols were relatively sensitive to NO_2 under low levels. In Beijing, our prior research had shown that at NO_2 concentrations above 30ppb, inorganic nitrates were converted more quickly during the day, while at the night, there was a shift in the corresponding products of oxidation to predominantly organic ones (Ren et al., 2022). The transition from organic- to inorganic-dominated products takes place in line with the switch from low- to high-NO_x regimes according to Wang et al., (2019), with low-NO_x conditions being predominated by organic-dominated products and a switch from majorly organic-entities to inorganic ones at high-NO_x conditions (NO_2 ~ 25 ppb for the night and NO_2 ~20 ppb for the day). Inorganic nitrate predominated among the NO_x oxidation products in high-NO_x concentrations (NO_2>30ppb), according to Cai et al., (2022). These variations could be caused by different precursor kinds and concentrations, as well as other variables. Additional and more thorough research is required to fully understand the quantitative

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impact of NO_2 on nitrate aerosols under various atmospheric conditions using laboratory simulation and field measurements.

4 Summary and conclusion

NACs from samples of fine particle were examined at the peak of Mt. Wuyi in 2014 and 2015. Nine quantified NACs manifested a significant rise in overall abundance in the winter and autumn, partly as a result of air masses traveling primarily through northern heating regions. Over the year, 4-NC was the most prevalent species. The majority of NACs were impacted by the primary emissions such as coal, biomass and petroleum combustion. The transport of contaminants had a significant impact on the atmospheric NACs at the peak of Mt. Wuyi, particularly in the winter and spring. Under low-NO_x conditions, the production of organic nitrated aerosols was relatively responsive to NO_2. For obtaining a more quantitative understanding of the influence of NO_2 on nitrate aerosols under diverse atmospheric settings, additional thorough examination through laboratory modeling and field measurements is required.

Data availability

The field observational and the lab experimental data used in this study are available from the corresponding author upon request (Gehui Wang via ghwang@geo.ecnu.edu.cn).

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Author contributions

GW designed the research; JT and ZZ collected the samples; YR conducted the experiments; YR and JW analyzed the data and wrote the paper; GW, JW and HL contributed to the paper with useful scientific discussions and comments.

Competing interests

The authors declare that they have no conflict of interest.

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