

Chemical characteristics and environmental drivers of nitrogen-containing organic aerosol formation in coastal and inland urban atmospheres in Myanmar

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Abstract:

Nitrogen-containing organic compounds (NOCs) are important light-absorbing constituents of atmospheric PM_{2.5} and can substantially influence aerosol radiative forcing, air quality, and climate. Previous studies have mainly focused on the source

apportionment and concentrations levels of NOCs, while the mechanisms governing their formation and particle-phase partitioning remain insufficiently constrained, particularly in tropical regions. Here, we aim to elucidate regional differences in NOCs characteristics in Myanmar, with emphasis on how relative humidity (RH) and precursor species influence their formation pathways. We report the first molecular-level spatio-temporal characterization of NOCs in Myanmar, identifying 1064 organic compounds in ESI⁻ mode, with NOCs contributing 14-21% of molecular formulas and 13-35% of total mass. Organic nitrates (ONs) dominated CHON species across all sites, with higher abundances in Mandalay than in Yangon. Two ubiquitous nitrophenols, nitrocatechol (C₆H₅NO₄) and dimethyl nitrocatechol (C₈H₉NO₄), showed strong covariance but a distinct relationship of their particle-phase C₈H₉NO₄/C₆H₅NO₄ ratio with RH. CHemistry with Aerosol Microphysics in Python (PyCHAM) box model simulations reveal that increasing RH enhances aerosol water content, to which C₈H₉NO₄ and C₆H₅NO₄ respond differently because of differences in their partitioning thermodynamics. Increased photochemistry in summertime further promotes C₆H₅NO₄ formation. These two processes, in addition to gas-phase precursor concentration, can explain the observed RH relationship and demonstrate that the C₈H₉NO₄/C₆H₅NO₄ ratio is sensitive, by comparable extents, to: partitioning thermodynamics, photochemistry and precursor supply. These findings provide new constraints on nitrophenol evolution in humid tropical environments and improve interpretation of NOC sources and aging processes, thereby supporting more accurate assessments of their regional and global radiative impacts.

Keywords: nitrogen-containing organic compounds; nitrophenolic compounds; relative humidity effects; gas-to-particle partitioning; aging

1.Introduction

Nitrogen-containing organic compounds (NOCs) are abundant and important constituents of atmospheric aerosols (Li et al., 2025), accounting from around 10% up

to 60% of the total aerosol nitrogen under typical urban (Yu et al., 2025; Yu et al., 2021), and playing a significant role in the global nitrogen cycle (Ma et al., 2024). In addition, NOCs have been identified as important precursors of secondary organic aerosol (SOA), thereby contributing to air pollution, and posing potential risks to human health (Smith et al., 2009; Abudumutailifu et al., 2024).

Over the past decade, research on NOCs has mainly focused on source apportionment and concentrations levels (Lin et al., 2010; Samy et al., 2013; Priestley et al., 2018), and Yu et al. (2024) reported that biomass burning and secondary formation are dominant NOCs sources. Observational studies conducted in urban, rural, marine and forested environments have demonstrated pronounced spatial variability in the molecular composition and relative abundances of aerosol NOCs (Samy and Hays, 2013; Jiang et al., 2022; Lin et al., 2012a; Xu et al., 2023; Zeng et al., 2020; Geng et al., 2009). Such variability is largely attributed to the diversity of emission sources and the heterogeneity of formation mechanisms of aerosol NOCs (Ma et al., 2024). Furthermore, subsequent oxidation or nitration of certain NOCs by ozone (O_3), hydroxyl radical (OH), and nitrogen oxides (NO_x) can exacerbate the health risks associated with organic aerosols (Bandowe and Meusel, 2017).

In recent years, increasing attention has been directed toward the formation mechanisms of NOCs, for example, Ma et al. (2024) elucidated how fresh and aged biomass fuels emit distinct classes of NOCs during combustion. Organic nitrates (ONs) and nitrophenols are two classes of NOCs that have attracted considerable research attention. Aerosol-phase ONs play an important role in the atmospheric fate of NO_x and O_3 production (Lelieveld et al., 2016), and several analytical techniques have been developed for their direct quantification in both the gas and particle phases. For instance, Aruffo et al. (2022) and Rollins et al. (2012) applied thermal dissociation laser-induced fluorescence (TD-LIF) to measure ONs in chamber experiments and field observations. Xu et al. (2017) estimated the mass concentration of organic nitrogen in Beijing using aerosol mass spectrometry (AMS), whereas Yu et al. (2019) quantified ON mass concentrations in PM_{10} based on measurements from a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS).

Nitrophenols are important components of brown carbon, formed through both primary emissions from combustion processes and secondary atmospheric chemistry (Desyaterik et al., 2013; Harrison et al., 2005). Time-of-flight mass spectrometer (ToF-MS), High Performance Liquid Chromatography (HPLC), and Gas Chromatography-Mass Spectrometry (GC-MS) have been widely employed to detect nitrophenols in cloud water and aerosol samples, as well as to investigate their sources, concentrations and formation mechanisms (Desyaterik et al., 2013; Harrison et al., 2005). Yu et al. (2019) identified three biogenic volatile organic compounds (VOCs) (α -pinene, limonene, and camphene) and one anthropogenic VOC (styrene) as key precursors contributing to the formation of particulate ONs in urban site in China. Biomass burning not only acts an important primary source of nitrophenols but also provides critical precursors for their secondary formation (Harrison et al., 2005; Laskin et al., 2015). However, owing to the limited commercial availability of nitrophenol standards, most studies have been restricted to the quantitative analysis of only a limited number of nitrophenolic compounds (Cai et al., 2022; Cao et al., 2023).

Previous ultra-high-performance liquid chromatography coupled with orbitrap mass spectrometry (UHPLC-Orbitrap MS) studies have successfully characterized the molecular composition of atmospheric NOCs and nitroaromatic compounds in urban environments such as Beijing (Li et al., 2020; Wang et al., 2022). However, comparable molecular-level investigations remain largely unavailable in Southeast Asia, particularly in Myanmar, a region strongly influenced by severe air pollution and frequent biomass burning (Zhang et al., 2022; Nway et al., 2020). Existing studies in Myanmar have mainly focused on the mass concentrations, chemical composition, and source apportionment of atmospheric particulate matter (Zhang et al., 2022; Zhang et al., 2024b), whereas systematic investigations into the characteristics and formation pathways of atmospheric NOCs remain limited. This study aimed to characterize the spatial variability of NOCs in ambient PM_{2.5} samples collected from Yangon and Mandalay, Myanmar, using UHPLC-Orbitrap MS. In addition, the formation-related processes of high-abundance nitrophenolic compounds were investigated, with particular emphasis on the influences of relative humidity (RH) and precursor

availability on their secondary formation. Molecular-level identification of aerosol NOCs provides critical insights into their precursors, sources, and formation pathways, thereby enhancing our understanding of atmospheric NOCs drivers.

2. Materials and methods

2.1 Sample collection

PM_{2.5} samples were collected at two major urban sites in Myanmar, Yangon and Mandalay (Fig. S1), during 2016 and 2017. In Yangon, sampling was conducted using a medium-volume PM_{2.5} sampler (flow rate was 0.3 m³ min⁻¹, Guangzhou Mingye Huanbao Technology Company, China) deployed on the rooftop of a six-story building (about 20 m above the ground) in Hlaing Township (16°51'30"N, 96°8'0"E), located in the northwestern urban area. In Mandalay, samples were collected on the rooftop of a three-story building situated in a mixed residential and commercial area of Chan-aye-thazan township (21°58'0"N, 96°5'0"E). Daily PM_{2.5} samples were collected during both winter and summer periods, including winter campaigns from 4-22 December 2016 in Yangon and from 26 December 2016 to 16 January 2017 in Mandalay, as well as summer campaigns from 10-29 April 2017 in Yangon and from 20 March to 7 April 2017 in Mandalay. In total, 72 PM_{2.5} samples were obtained. Detailed descriptions of the sampling procedures can be found in Zhang et al. (2022).

2.2. Instrumental analysis

2.2.1 Determination of water-soluble organic nitrogen

The mass concentration of water-soluble organic nitrogen (WSON) in atmospheric particulate matter was calculated as the difference between the concentration of water-soluble total nitrogen (WSTN) and that of water-soluble inorganic nitrogen (WSIN), i.e., $WSON = WSTN - WSIN$, where WSIN was calculated as $WSIN = [NO_3^-]/62 \times 14 + [NH_4^+]/18 \times 14$. Here, $[NO_3^-]$ and $[NH_4^+]$ denote the mass concentrations of nitrate and ammonium, respectively, measured by ion chromatography. The mass

concentration of WSTN was determined using a UV–visible spectrophotometer (TU-1901, China).

Quality assurance and quality control (QA/QC) procedures were implemented throughout the analyses. For the determination of water-soluble inorganic ions, one procedural blank was analyzed for every 20 samples. In addition, duplicate analyses were performed for 10% of the samples during instrumental measurements, and the relative difference between duplicate measurements was generally less than 5%. For WSTN determination, one duplicate sample was analyzed for every 10 samples, with relative differences between duplicate measurements also below 5%. Spike recovery tests were conducted to evaluate analytical accuracy, and the recoveries generally ranged from 90% to 110%. Furthermore, the concentrations of target species in field blank samples were less than 5% of those measured in ambient samples, indicating negligible effects on the quantified concentrations.

2.2.2 GC-MS analysis of organic compounds

20 μ L methyl- β -D-xylanopyranoside (MXP) was spiked onto the filters (30 cm²) as an internal standard. The filters were subsequently subjected to ultrasonic extraction with 20 mL of dichloromethane/methanol (1:1 v/v) for 20 minutes at room temperature for three times. The combined extracts were concentrated to approximately 2-3 mL using a rotary evaporator, followed by filtration and derivatization with 100 μ L of N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, with 1% trimethylchlorosilane as catalyst) and 20 μ L of pyridine at 75 °C for 45 min. Prior to injection, hexamethylbenzene was added as an injection standard to evaluate the recovery of the target compounds, which ranged from 80% to 120%.

The extracts were analyzed using GC-MS (Agilent 5975 MSD coupled with Agilent 6890 GC) to determine levoglucosan mass concentrations. The GC oven was programmed to start at 60 °C for 2 min, ramped to 300 °C at 5 °C min⁻¹, and held isothermally at 300 °C for 10 min. Detailed descriptions of the GC-MS settings and analytical procedures are provided in previous publications ([Feng et al., 2013](#); [Zhong et al., 2021](#)).

2.2.3 UHPLC-MS analysis of polar organic compounds

A 12 cm² section of each sampling filter was ultrasonically extracted with 3 mL of methanol and 30 µL of ethylene diamine tetraacetic acid (EDTA) for 30 minutes, with ice added to the water bath to prevent temperature increases and decomposition of organic compounds. After standing for 15 minutes, the extract was filtered through a 0.45 µm PTFE syringe filter. The residual filter was subsequently extracted twice (using 2 mL of methanol with 20 µL of EDTA and 1 mL of methanol with 10 µL of EDTA, respectively). All filtered extracts were combined and evaporated to near dryness under a slow stream of high-purity nitrogen, then redissolved in 100 µL of water and acetonitrile mixture ($V:V = 1:1$). The redissolved solution was centrifuged at >11,000 rpm for 20 minutes, and 5 µL of the supernatant was injected for analysis using UHPLC (Dionex 3000, Thermo Scientific, USA) - Orbitrap MS (Thermo Scientific, USA).

3-Nitrophenol (3-NP) was utilized to estimate the semi-quantitative concentrations of the detected compounds based on peak areas (unit: ng m⁻³). To assess the reliability of the semi-quantitative approach, the summed concentrations of all detected organic compounds were compared with independently measured water-soluble organic carbon (WSOC) concentrations. A strong correlation was observed (Fig. S2, $r = 0.88$), indicating that the semi-quantified molecular data reasonably capture the temporal variability of WSOC. It should be noted that the semi-quantitative approach adopted in this study is intended primarily to compare relative abundance patterns and temporal variations among compound classes rather than to provide absolute concentrations. Detailed information for the HPLC separation setup, UHPLC-Orbitrap MS data analysis and quantification procedures can be founded in [Text S1](#) and [Figs. S3-S4](#). The instrument was calibrated weekly to ensure that the mass resolution in negative mode (ESI⁻) was below 2 ppm. Blank samples were processed and analyzed in the same way for deduction of background effects.

2.3. Box modeling

Observation interpretation was augmented through application of the CHemistry with Aerosol Microphysics in Python (PyCHAM) box model ([O'Meara et al., 2021](#)) version 5.6.0 (available at <https://github.com/simonom/PyCHAM>). The model used v3.3.1 of

the Master Chemical Mechanism (Rickard, 2025) to solve gas-phase chemistry, including gas-phase inorganics and the following gas-phase VOCs: methane, propane, α -pinene, benzene, ethylbenzene, m,o,p-xylene (Bloss et al., 2005; Jenkin et al., 1997; Jenkin et al., 2003; Saunders et al., 2003). The model treats gas-particle partitioning dynamically with thermodynamics driven by the Kelvin term, component mole fraction (Raoult's law), particle-phase solubility and pure component vapor pressures, as described in O'Meara et al. (2021). It was run in Eulerian mode. Assuming zero-dimensional representation of a $1*1*1$ km box, and a 3 m s^{-1} horizontal wind vector, gave an air change rate of $3 \times 10^{-3} \text{ s}^{-1}$. Observations of NO_x , O_3 , RO_2 and HO_2 from urban Asian sites were used to set representative influx rates of NO_x and aliphatic parent VOCs (Aung et al., 2019; Tan et al., 2018; Nelson et al., 2021).

Since the gas-particle partitioning of aromatic oxidation products was investigated here, specifically $\text{C}_6\text{H}_5\text{NO}_4$ and $\text{C}_8\text{H}_9\text{NO}_4$, influx rates of their parent VOCs (benzene for $\text{C}_6\text{H}_5\text{NO}_4$ and ethylbenzene and o,m,p-xylene for $\text{C}_8\text{H}_9\text{NO}_4$) were particularly important for accurately identifying drivers of particle-phase aromatic oxidation products. For summer in Yangon, rates were set to give aromatic parent VOC concentrations consistent with observations from May 2017 in Yangon (Aung et al., 2019). However, Zhang et al. (2022) show that the prevailing source of air is maritime during Yangon summer and continental for Yangon winter and Mandalay winter and summer, resulting in substantially lower particle-phase organic carbon loading during Yangon summer. Furthermore, we know from Nelson et al. (2021) that benzene concentrations in southern Asian cities can reach 10 ppb, eight times more than the 1.2 ppb maximum reported for Yangon summer by Aung et al. (2019).

Additionally, Myanmar is a major biomass-burning region (Amnuaylojaroen and Parasin, 2023); Continental air is more prone to influence from open fire burning (e.g. agricultural residues and tropical forest) than maritime air, levoglucosan concentrations (Yangon winter: 629.6 ng m^{-3} , Yangon summer: 461.1 ng m^{-3} , Mandalay winter: 827.6 ng m^{-3} , Mandalay summer: 553.0 ng m^{-3}), a well-established tracer for biomass burning, were significantly higher at the inland site (Mandalay), indicating stronger influence from biomass combustion (Fig. S5). Whilst both $\text{C}_6\text{H}_5\text{NO}_4$ and

C₈H₉NO₄ were well correlated with levoglucosan in both cities (Fig. S5), indicating a biomass burning source for both, the emission ratios of the precursors vary substantially between urban biomass burning, with ratios around 3:1 for C₈H₉NO₄: C₆H₅NO₄ precursors (Krugly et al., 2014), and tropical forest or agricultural residue burning, which have ratios of 1:3 and 1:2, respectively (Andreae, 2019). Therefore, for all locations and times, the same influx rates of C₈H₉NO₄ precursors was used (those constrained against observations for Yangon summer), however, the C₆H₅NO₄ precursor influx rate was set three times greater in Mandalay winter and summer than in Yangon summer and two times higher in Yangon winter than in Yangon summer, ratios consistent with the relative organic carbon loadings reported in Zhang et al. (2022).

For PyCHAM simulations, RH, temperature, and seed particle concentration were constrained against Zhang et al. (2022). The pure component saturation vapour pressures of C₆H₅NO₄ and C₈H₉NO₄ were constrained by the observations of Fredrickson et al. (2022) who report a c^* for C₆H₅NO₄ of the order $10^1 \mu\text{g m}^{-3}$. Using the Nannoolal et al. (2008) method for vapour pressure prediction from the UManSysProp toolkit (Topping et al., 2016), the vapour pressure of C₈H₉NO₄ compounds was estimated to be an order of magnitude lower than for C₆H₅NO₄, and was therefore set at $10^0 \mu\text{g m}^{-3}$. For other organics the Nannoolal et al. (2008) method was used to estimate pure component vapour pressures. The different particle-phase solubilities were not directly measured, but were represented through activity coefficients following previous studies of structurally similar aromatic nitro-compounds (Lee et al., 2000). The C₆H₅NO₄ molecule contains hydroxyl and nitro functional groups that enhance polarity and hydrogen-bonding interactions with aerosol water, and was therefore assumed to behave relatively close to ideal solution conditions. In contrast, C₈H₉NO₄ contains additional non-polar organic functionality, which is expected to increase non-ideal interactions and reduce effective aqueous-phase solubility. Solubility was assumed to vary linearly with particle water mole fraction, consistent with Kholod et al. (2011). Consequently, for both C₆H₅NO₄ and C₈H₉NO₄ the activity coefficient was assumed to be unity at zero particle water mole fraction,

whilst for $\text{C}_6\text{H}_5\text{NO}_4$ diluted by water, the activity coefficient was set to 10, and for $\text{C}_8\text{H}_9\text{NO}_4$ it was set to 3000. The combination of different volatilities and solubilities of $\text{C}_6\text{H}_5\text{NO}_4$ and $\text{C}_8\text{H}_9\text{NO}_4$ in a thermodynamic simulation of gas-particle partitioning presents the potential for different sensitivities to varying particle-phase water content, which is quantitatively investigated in the results.

The model does not explicitly include the organic oxidation products entering the simulated box, similarly it cannot spatially distinguish between precursors of SOA that were emitted directly from sources within the box and those transported in from sources outside. Nevertheless, the model and its setup, including a non-zero air change rate for representative transport losses, allow investigation of the processes driving particle-phase organic composition in the observed areas. The results and implications below are therefore constrained to this ability.

The HO_2 uptake coefficient to particles was set to 0.2 following Jacob. (2000) Gas-phase HONO influx rate was assumed to vary linearly with gas-phase water content, and tuned to give HONO values comparable to those observed in Delhi in 2017 by Pawar et al. (2024) with a maximum of $4.8 \times 10^{-17} \text{ mol s}^{-1}$ for $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ of gas-phase water during Yangon summer.

Testing showed the model required around 9 hours of spin-up (starting from midday local time) before mass concentrations of all components, including radicals, were within 5 % of their concentration 24 hours later, and therefore results were taken over the 24 hours of simulation from 9-33 hours through the simulation. Unless otherwise stated, PyCHAM results are arithmetic means over these 24 hours. Natural light intensity was determined by setting the day of year and relevant latitude and longitude following the parameterisation of Hayman. (1997). All relevant PyCHAM input files, and key outputs, are archived at <https://github.com/simonom/PyCHAM/releases/tag/v5.7.8>.

2.4. Data analysis

The Van Krevelen (VK) diagram is widely used to illustrate the evolutionary pathways of organic mixtures to infer the potential sources of organic aerosols by

classifying known categories of natural and anthropogenic organic compounds (Xie et al., 2021; Bianco et al., 2018). Based on the H/C and O/C ratios, the VK diagram can be divided into seven regions corresponding to common classes of compounds identified in dissolved organic matter (Table 1): (A) lipids-like compounds, (B) aliphatic/peptides-like compounds, (C) carboxylic-rich alicyclic molecules (CRAMs-like structures), (D) carbohydrates-like compounds, (E) unsaturated hydrocarbons, (F) aromatic structures, and (G) highly oxygenated compounds (HOC).

Table 1 Stoichiometric ranges of VK classes (Bianco et al., 2018)

Rank	Class	H/C	O/C
A	Lipids-like	$1.5 < H/C \leq 2.0$	$0 \leq O/C \leq 0.3$
B	Aliphatic/peptides-like	$1.5 < H/C \leq 2.2$	$0.3 < O/C \leq 0.67$
C	CRAMs-like structures	$0.67 < H/C \leq 1.5$	$0.1 \leq O/C < 0.67$
D	Carbohydrates-like	$1.5 < H/C \leq 2.5$	$0.67 < O/C < 1.0$
E	Unsaturated hydrocarbons	$0.67 < H/C \leq 1.5$	$O/C < 0.1$
F	Aromatic structures	$0.2 \leq H/C \leq 0.67$	$O/C < 0.67$
G	Highly Oxygenated Compounds (HOC)	$0.6 < H/C \leq 1.5$	$0.67 \leq O/C \leq 1.0$

The aromaticity index (AI) is a parameter used to represent the density of C=C double bonds in organic molecules. Koch et al. (2006) proposed a modified formula for AI that excludes the potential contribution of heteroatoms to C=C bond density (Equation 1). $AI \geq 0.67$ is generally considered indicative of condensed aromatic structures, whereas $AI > 0.50$ indicates the presence of aromatic structures. When the calculated AI value is less than zero, it is set to zero. The equation for calculating AI is given as follows (Koch and Dittmar, 2006):

$$AI = \frac{1 + C - \frac{1}{2}O - S - \frac{1}{2}(N + H)}{C - \frac{1}{2}O - N - S} \quad (1)$$

3. Results and discussion

3.1 Characteristics of molecules in ESI⁻ modes

The identified organic compounds were classified into six categories based on molecular composition: CHO, CHON, CHONS, CHN, CHNS, and CHOS. CHONS-compounds represent species containing only C, H, O, N, and S in the ESI⁻ mode, and the other categories are defined analogously. CHN and CHNS compounds were rarely detected in the ESI⁻ mode.

The number of organic compounds identified in the ESI⁻ mode ranged from 562 to 1,318, with an average of 1,064 molecular formulas. Among these, CHO species accounted for the largest proportion (46-67%), followed by CHOS (13-25%) and CHON (14-21%). Similar molecular composition patterns have been reported in a wide range of atmospheric environments. Sun et al. (2025) summarized observations from urban, forest, and remote regions worldwide and showed that CHO compounds generally dominate atmospheric organic matter, followed by CHON and/or CHOS compounds. Consistent with this review, a wintertime study in Beijing using UHPLC-Orbitrap MS also identified CHO, CHON, and CHOS as the three most abundant molecular classes (Wang et al., 2022). These results suggest that the predominance of these compound classes is a common feature of atmospheric organic matter, although their relative contributions may vary depending on local emission sources and atmospheric processing.

The total mass concentration of organic compounds detected in the ESI⁻ mode was $279.7 \pm 87.6 \text{ ng m}^{-3}$. Specifically, the mass concentrations of CHO-, CHON-, and CHOS- compounds were $164.3 \pm 39.0 \text{ ng m}^{-3}$, $62.3 \pm 31.8 \text{ ng m}^{-3}$, and $43.8 \pm 18.6 \text{ ng m}^{-3}$, respectively (Table S1). Their corresponding contributions to the total concentration ranged from 49-73% for CHO species, 13-35% for CHON species, and 8-22% for CHOS species. Although the number proportion of CHON compounds was lower than that of CHOS species, their contribution to the total mass concentration was comparatively higher, indicating that CHON compounds possess higher average molecular abundances and play a non-negligible role in the overall organic aerosol mass.

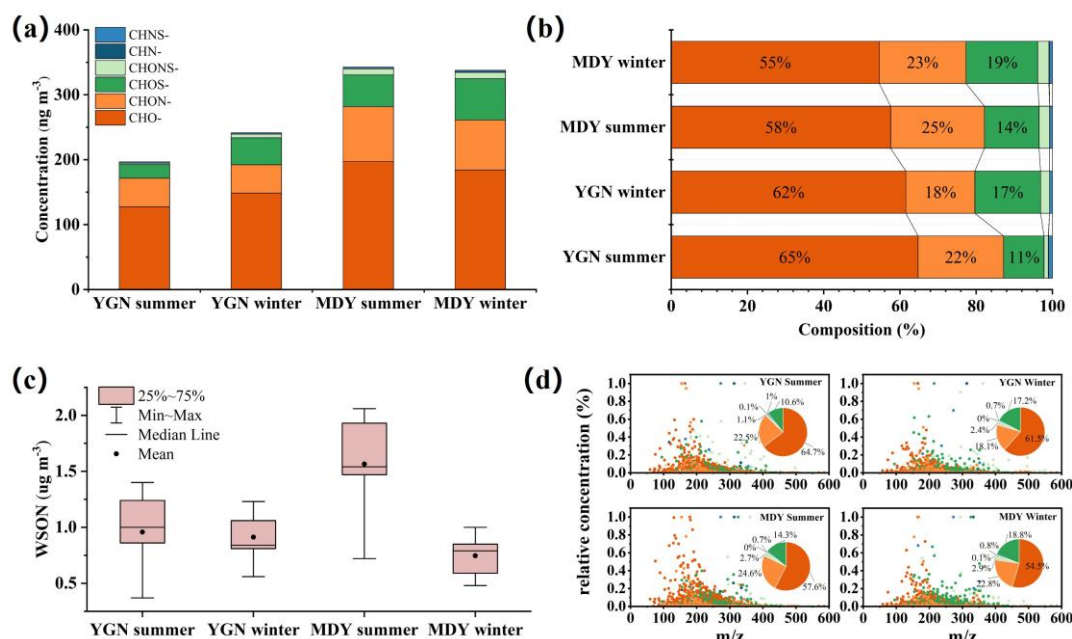


Figure 1 Molecular characteristics of organic matter in Yangon (YGN) and Mandalay (MDY). **a.** Semi-quantitative concentrations of CHO, CHON, CHOS, CHONS, CHN, and CHNS species detected in both cities during summer and winter in the ESI⁻ mode. **b.** Percentage contributions of CHO, CHON, CHOS, CHONS, CHN, and CHNS species to the total molecular mass concentrations in both cities during summer and winter in the ESI⁻ mode. **c.** Mass concentration of WSON in both cities during summer and winter. **d.** Reconstructed mass spectra of organic compounds derived from extracted ion chromatograms in the ESI⁻ mode. The vertical axis represents the semi-quantitative normalized concentration of each compound. The pie charts illustrate the seasonal average concentration contributions of different molecular species.

Significant differences in the mass concentrations and compositions of various compound classes were observed between the two cities (Fig. 1a and Fig. 1b, Table S2). In the ESI⁻ mode, the mass concentrations of all compound types in PM_{2.5} were higher in Mandalay than in Yangon during both winter and summer, consistent with the spatial distribution patterns of organic carbon (OC) (Zhang et al., 2024a).

The concentration proportion of CHO compounds was consistently higher in Yangon than in Mandalay (Yangon summer: 65%, Yangon winter: 62%, Mandalay summer: 58%, Mandalay winter: 55%). In contrast, CHON compounds accounted for a lower proportion in Yangon compared to Mandalay (Yangon summer: 22%, Yangon winter: 18%; Mandalay summer: 25%, Mandalay winter: 23%). The spatial distribution of CHOS concentration contributions exhibited a pattern similar to that of CHON, with higher fractions observed in Mandalay (Yangon summer: 11%, Yangon winter: 17%;

Mandalay summer: 14%, Mandalay winter: 19%). Notably, the mass concentration of WSON, particularly during the MDY summer period, was substantially higher than those observed in the other three sampling periods (Fig. 1c). The results of the t-test showed that the WSON mass concentration in MDY summer was significantly different from that in YGN summer and MDY winter, with *p* values lower than 0.05 for both comparisons. These results indicate a statistically significant enhancement of WSON during the MDY summer period, and the underlying causes of the elevated WSON levels in MDY summer warrant further investigation. The reconstructed mass spectra of PM_{2.5} samples collected in Yangon and Mandalay during winter, and summer are shown in Fig.1d. The molecular weights of the detected compounds were primarily distributed between 100 and 400, with majority of signal intensities concentrated between 100 and 200.

3.2 Spatial distribution characteristics of NOCs

3.2.1 Spatial distribution of organic nitrates

The formation of organic nitrates (ONs) enhances the partitioning of semi-volatile compounds into the particulate phase, thereby promoting SOA growth (Ng et al., 2007). Consequently, ONs are recognized as an important class of atmospheric compounds. In all Myanmar samples, 69-87% (mean: 77%) of CHON molecules met the structural criterion of containing at least one -ONO₂ functional group ($O/3N \geq 1$) and were preliminarily identified as ONs (Lin et al., 2012b; Wang et al., 2016). This result is consistent with the findings of Lin et al. (2012a), who reported that ONs constitute a major subclass of CHON- compounds in PM_{2.5}.

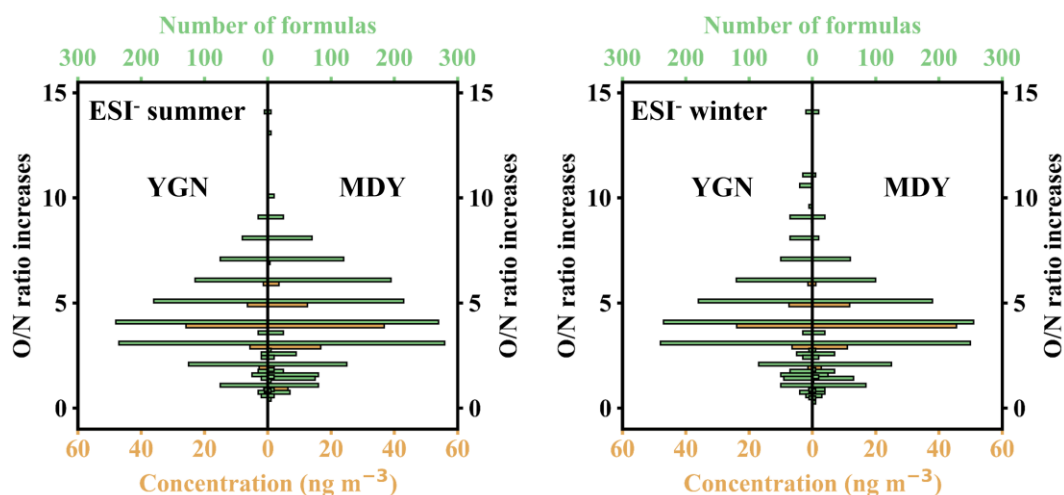


Figure 2 Classification of CHON compounds into subgroups based on O/N ratios in the ESI mode. Yellow and green colors indicate the ONs mass concentrations (ng m^{-3}) and number of species in each subgroup, respectively.

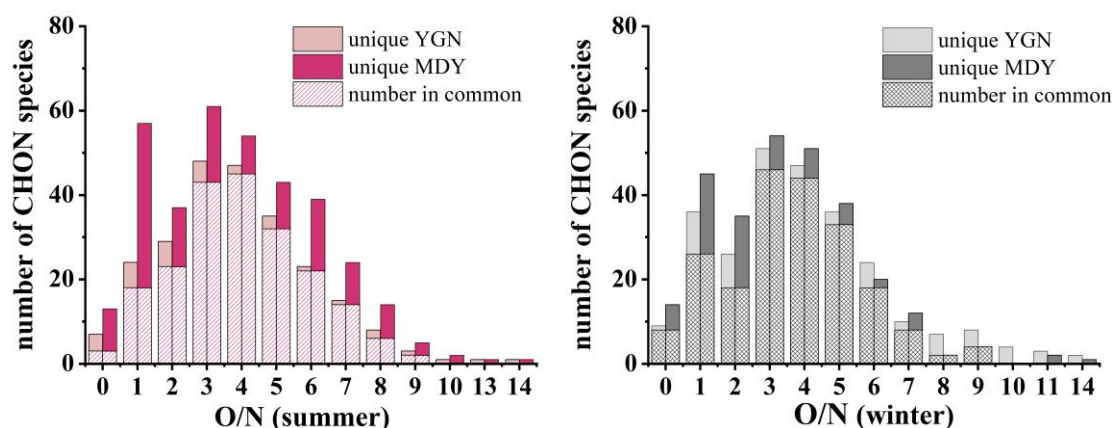


Figure 3 Numbers of common and region-specific compounds in MDY and YGN binned by O/N ratio. Number in common refers to the number of CHON compounds detected in both YGN and MDY, whereas unique YGN and unique MDY denote the numbers of CHON compounds detected exclusively in YGN and MDY, respectively.

As shown in Fig. 2, CHON compounds were classified into 32 subgroups according to their O/N ratios. A total of 245 CHON compounds were detected in the Yangon summer samples, of which 75.1% were identified as ONs. 263 CHON compounds were detected in Yangon winter samples, with ONs accounting for 73.0% of the total CHON molecular species. Similarly, 351 and 278 CHON compounds were identified in the Mandalay summer and Mandalay winter samples, with ONs constituting 69.5% and 66.2%, respectively. The contributions of ONs to the total

CHON compound mass concentrations in PM_{2.5} were 89.5%, 91.5%, 84.4%, and 90.6% for Yangon summer, Yangon winter, Mandalay summer, and Mandalay winter, respectively. The remarkably high proportions of ONs in both molecular number and mass concentration indicate that ONs represent a dominant subgroup within CHON compounds.

In Fig. 2, pronounced differences in ON mass concentrations between the two sites are observed. The mass concentrations of ONs with O/N ratios higher than 3 in MDY were substantially higher than those in YGN (39.6 ng m⁻³, 40.0 ng m⁻³, 71.2 ng m⁻³, and 69.7 ng m⁻³ for Yangon summer, Yangon winter, Mandalay summer, and Mandalay winter, respectively). In contrast, the comparable overall mass contributions of ONs between the two sites were mainly attributable to the relatively higher mass concentrations of compounds with O/N < 3 in MDY than in YGN (4.7 ng m⁻³, 3.7 ng m⁻³, 13.1 ng m⁻³, and 7.3 ng m⁻³ for Yangon summer, Yangon winter, Mandalay summer, and Mandalay winter, respectively). Further examination of CHON molecular formulas (Fig. 3) shows that, for most O/N ratio bins, the number of CHON compounds detected exclusively in MDY aerosols was higher than that detected exclusively in YGN aerosols, a pattern that was particularly pronounced in summer. These results indicate substantial differences in aerosol composition between the two cities, especially during MDY summer, exhibiting a more distinct molecular profile (Figs. 1c and 3).

3.2.2 Spatial distribution characteristics of nitrophenols

To more accurately identify types of NOCs, compounds containing aromatic rings were screened by combining AI values with the VK diagram. Molecular formulas that simultaneously met the criteria of O/N ≥ 3 (as nitrophenols contain at least one nitro group (-NO₂) and one hydroxyl group (-OH), corresponding to a minimum theoretical O/N ratio of 3) and AI > 0.5 were classified as potential nitrophenolic compounds. These compounds were primarily distributed across Zones C, F, and G of the VK diagram (Figs. 4 and 5). Bianco et al. (2018) reported that compounds with CRAMs-like structures (Zone C) may be associated with photochemical processing in aerosols,

whereas HOC (Zone G) represent a group of extensively oxidized organics. Consequently, these two types of compounds are predominantly formed via secondary oxidation processes. Notably, mass concentration of these two compounds was higher in the Mandalay samples than in Yangon (Yangon summer: 40.2 ng m⁻³, Yangon winter: 40.1 ng m⁻³, Mandalay summer: 78.4 ng m⁻³, Mandalay winter: 71.4 ng m⁻³), suggesting that secondary formation processes play a more prominent role in PM_{2.5} in Mandalay than in Yangon.

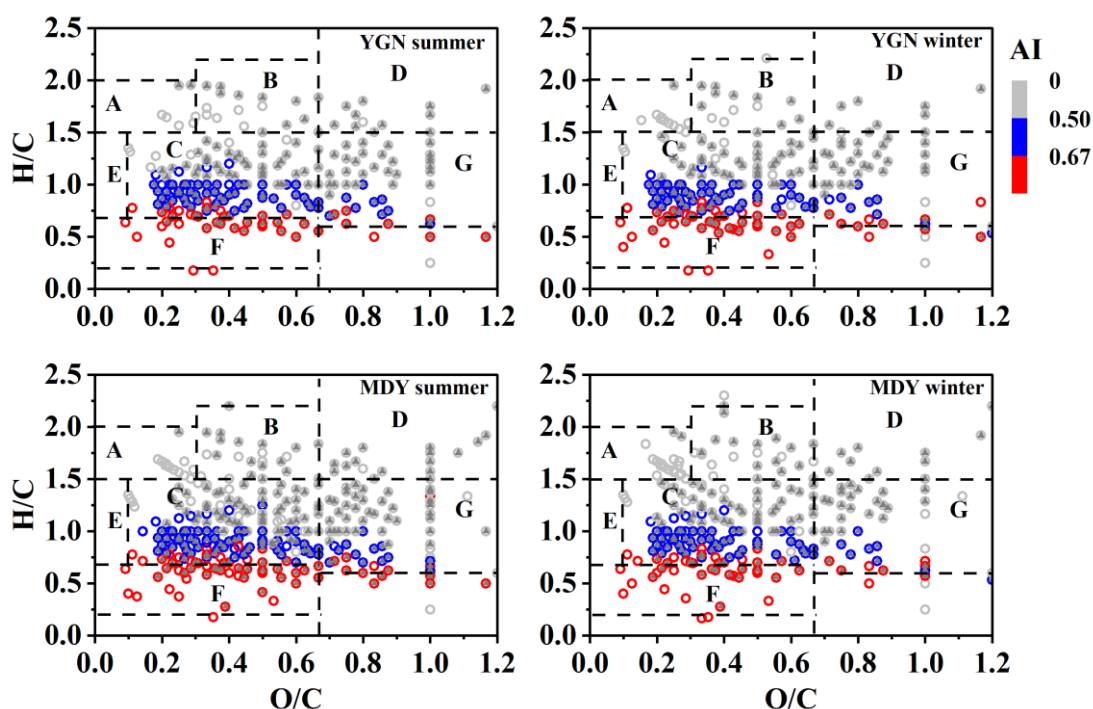


Figure 4 CHON- Van Krevelen (VK) diagram for the identified compounds. According to the H/C and O/C ratios, organic compounds are classified into seven categories (A-G). Color bars represent the aromaticity index (AI), while grey triangles denote compounds with O/N $\geq$ 3.

The number of nitrophenolic compounds accounted for a relatively high proportion within Zone C (approximately 35%), with higher proportion observed in Yangon than in Mandalay during both seasons (Fig. 5). In Zone G, number of nitrophenolic compounds represented about 20% of all identified species. During summer, the number proportion of nitrophenolic compounds in Zone G was higher in Yangon (22.9%) than in Mandalay (19.4%), whereas in winter, the trend was reversed, with Mandalay exhibiting a higher proportion (19.5%) compared to Yangon (16.3%).

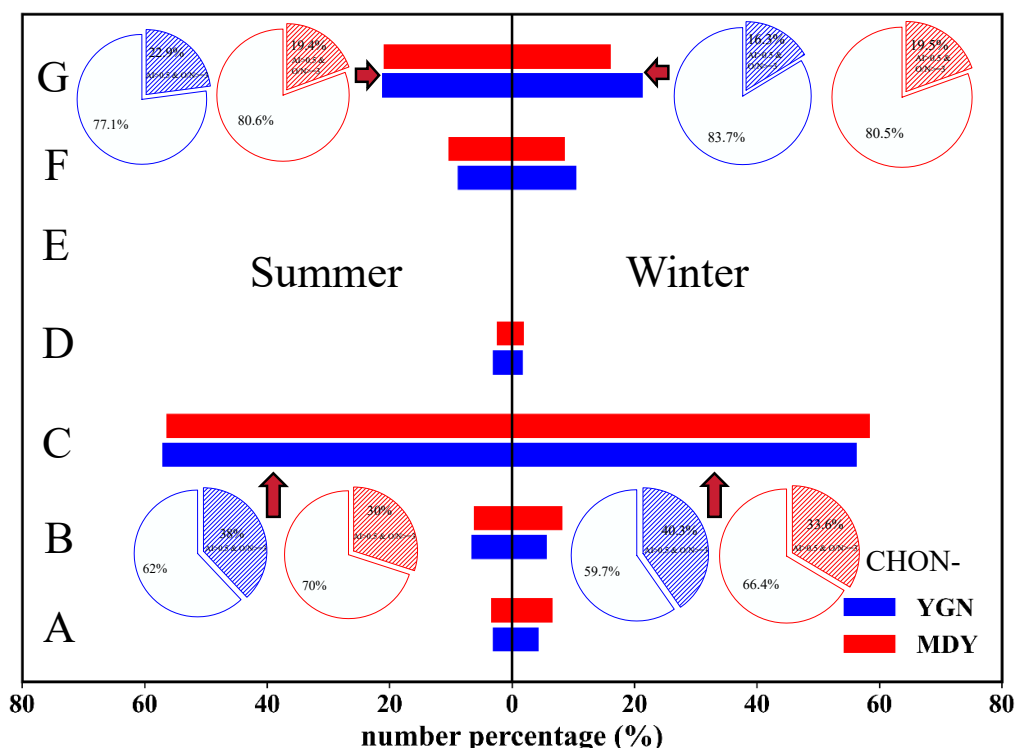


Figure 5 Percentage of CHON- subfraction groups (A-G). Shaded sections in the pie charts represent the number proportion of nitrophenolic compounds within each corresponding subgroup. Blue denotes the Yangon site, while red represents the Mandalay site.

3.3 $C_8H_9NO_4$ and $C_6H_5NO_4$

3.3.1 High detection efficiency NOCs

Compounds detected in all samples (detection frequency of 100%) were defined as common peaks. A total of 35 CHON compounds were identified as common peaks, and their reconstructed mass spectra were generated (Fig. S6). Among these, the two most abundant compounds corresponded to the molecular formulas $C_6H_5NO_4$ (m/z 154.01477) and $C_8H_9NO_4$ (m/z 182.04609), which were located in Zones G and C of Fig. 4, respectively. Based on literature reports, NIST library analysis, and the strong positive correlations of these compounds with levoglucosan ($r = 0.76$ and 0.73 for $C_8H_9NO_4$ and $C_6H_5NO_4$, respectively. Fig. S5), $C_6H_5NO_4$ and $C_8H_9NO_4$ were inferred to be nitrocatechol (Herich et al., 2011; Simoneit et al., 1991; Lin et al., 2018) and dimethyl nitrocatechol (Claeys et al., 2012; Kourtchev et al., 2016), respectively.

Correlation analysis revealed a strong positive relationship between $C_6H_5NO_4$ and $C_8H_9NO_4$, suggesting that these two compounds share similar sources. However, under $RH < 50\%$, the ratio of $C_8H_9NO_4/C_6H_5NO_4$ mass concentration changes with RH (Fig. 6). Samples collected during the Mandalay summer exhibited a relatively lower $C_8H_9NO_4/C_6H_5NO_4$ that coincided with a lower RH compared to the other sampling periods. According to our previous study (Zhang et al., 2022), the backward trajectories during both winter and summer in Mandalay were highly similar, indicating that the observed RH differences cannot be attributed to variations in air-mass transport. Collectively, these findings indicate that the formation of $C_6H_5NO_4$ and $C_8H_9NO_4$ is strongly associated with RH. The PyCHAM box model is applied to further investigate the factors influencing the formation of these two compounds.

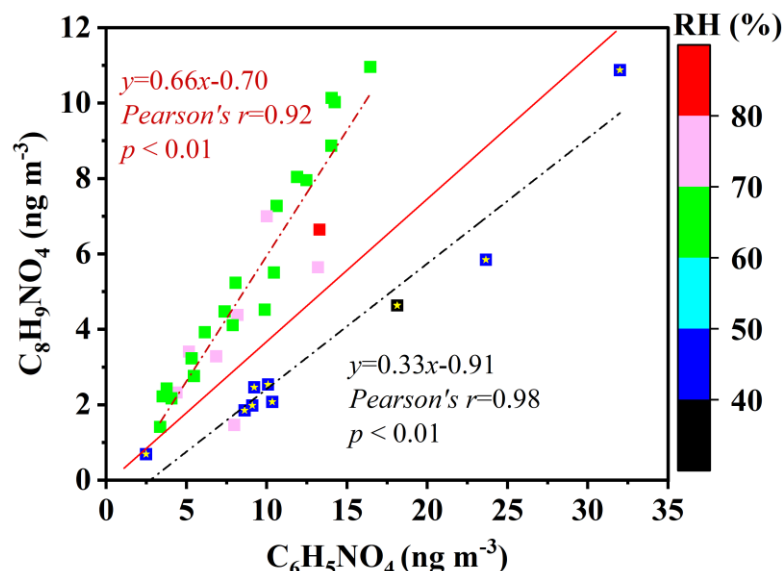


Figure 6 The correlation between $C_6H_5NO_4$ and $C_8H_9NO_4$. Color bar is relative humidity. Yellow stars represent MDY summer samples.

3.3.2 RH effect on $C_8H_9NO_4/C_6H_5NO_4$

Following application of the constraints to box modelling described in Section 2.3, six simulations were conducted to investigate the drivers of varying particle-phase $C_8H_9NO_4/C_6H_5NO_4$ ratio, three for Yangon and three for Mandalay. In Mandalay, the RH changed substantially between seasons, whilst simulated influx rates of precursors remained constant, whilst in Yangon, the RH was relatively consistent but simulated influx rates of precursors changed with season. To help probe the effect of varying

photochemistry between seasons, one of the Yangon simulations is a hypothetical scenario where the photochemistry was set to winter but the precursor influx was set to summer conditions (Fig. S7).

The resulting simulations of particle-phase $\text{C}_8\text{H}_9\text{NO}_4$ and $\text{C}_6\text{H}_5\text{NO}_4$ reproduce the observed trend of increasing $\text{C}_8\text{H}_9\text{NO}_4/\text{C}_6\text{H}_5\text{NO}_4$ ratio with increasing RH (Fig. 7). Several factors are at play in the simulated results of Fig. 7, the increase in gas-phase OH concentration from winter to summer (photochemistry effect), the increasing influx rate of benzene from a minimum in Yangon summer to a moderate value in Yangon winter and a maximum for both seasons for Mandalay, the changing partitioning thermodynamics for $\text{C}_8\text{H}_9\text{NO}_4$ and $\text{C}_6\text{H}_5\text{NO}_4$ due to the changing absorptive molar concentration of particles and changing water mole fraction that affects solubility as explained in Section 2.3.

The effect of HO_2 uptake to particles and of HONO influx rate dependence on gas-phase water content was tested by turning off HO_2 uptake and by setting HONO influx rate to constant across simulations. Neither process showed a significant change to the trend of increasing $\text{C}_8\text{H}_9\text{NO}_4/\text{C}_6\text{H}_5\text{NO}_4$ ratio with increasing RH.

Considering first just the Mandalay results (Fig. 7a), for which the influx rates of $\text{C}_6\text{H}_5\text{NO}_4$ and $\text{C}_8\text{H}_9\text{NO}_4$ precursors were constant across all RH, modelled $\text{C}_8\text{H}_9\text{NO}_4/\text{C}_6\text{H}_5\text{NO}_4$ changes from 0.69 to 0.54 as RH changes from 80 to 60 %, whilst observations report a change from 0.59 to 0.48. Because both 80 and 60 % were during the winter period, the modelled change is not due to changing actinic flux, similarly although the decrease in gas-phase water content from 80 to 60 % RH leads to a slight decrease in OH concentration, the change in consumption of the parent VOCs is negligible, therefore photochemistry does not explain the change in ratio. The only remaining explanation for the ratio changes available to the model is changes to the particle phase due to changed partitioning thermodynamics. The decrease in particle-phase concentration of $\text{C}_8\text{H}_9\text{NO}_4$ from 80 to 60 % RH is 30 %, whilst the decrease is 10 % for $\text{C}_6\text{H}_5\text{NO}_4$. Therefore, the greater sensitivity of $\text{C}_8\text{H}_9\text{NO}_4$ to changing partitioning thermodynamics, which results from changes to both absorptive particle concentration and particle-phase solubility, results in changed $\text{C}_8\text{H}_9\text{NO}_4/\text{C}_6\text{H}_5\text{NO}_4$.

Variations in sensitivity are dependent on the product of component activity coefficient and vapour pressure, which gives an effective volatility or c^*_{eff} . For $\text{C}_8\text{H}_9\text{NO}_4$, c^*_{eff} changes from 2400 to 1800 $\mu\text{g m}^{-3}$ between 80 and 60 % RH, whilst for $\text{C}_6\text{H}_5\text{NO}_4$ c^*_{eff} changes from 82 to 64 $\mu\text{g m}^{-3}$. These effective volatilities can be divided by the component molar masses to give units of mol m^{-3} and combined with the total absorptive molar concentration ($c_{n,\text{abs}}$) of the particle phase in an equation for equilibrium gas-particle partitioning (Pankow 1994) to demonstrate the different thermodynamic sensitivity of the two components:

$$\xi_i = \left(1 + \frac{c^*_{n,i,\text{eff}}}{c_{n,\text{abs}}}\right)^{-1}, \quad (2)$$

where ξ is the equilibrium condensing fraction of component i and n is the molar concentration. Using the simulated $c_{n,\text{abs}}$ of 3.59×10^{-6} and 7.28×10^{-6} mol m^{-3} for the 60 and 80 % RH scenarios, respectively, gives a factor change in ξ ($\xi_{i,80\%RH}/\xi_{i,60\%RH}$) of 1.33 for $\text{C}_8\text{H}_9\text{NO}_4$ and 1.04 for $\text{C}_6\text{H}_5\text{NO}_4$.

Whilst partitioning thermodynamics continues to act to decrease condensation of $\text{C}_8\text{H}_9\text{NO}_4$ and $\text{C}_6\text{H}_5\text{NO}_4$ as RH decreases from 60 % in Mandalay winter to 40 % in Mandalay summer, the particle-phase loading of both $\text{C}_8\text{H}_9\text{NO}_4$ and $\text{C}_6\text{H}_5\text{NO}_4$ actually increases, driven by the increased OH concentration that results from enhanced photochemistry. $\text{C}_6\text{H}_5\text{NO}_4$ appears to be particularly sensitive to changing atmospheric oxidizing capacity, as its relative increase is greater than that of $\text{C}_8\text{H}_9\text{NO}_4$, with fractional increases of 140 and 70 % respectively. Analysis of simulated rates of production and destruction at midday shows a production enhancement of factor 2.33 for $\text{C}_6\text{H}_5\text{NO}_4$ going from 60 to 40 % RH, whilst the factor for $\text{C}_8\text{H}_9\text{NO}_4$ is 1.62 and for both components the rate of chemical destruction is relatively minor so that dilution dominates losses.

The Yangon results are all for 70 % RH, and therefore have similar partitioning thermodynamics. For Yangon results, two factors are therefore at play, changing influx rates (Section 2.3 and Fig. S7) and changing photochemistry. Moving from Yangon summer to winter, photochemical changes act to increase $\text{C}_8\text{H}_9\text{NO}_4/\text{C}_6\text{H}_5\text{NO}_4$, as seen and explained above for Mandalay results between 40 and 60 %. The photochemistry

effect for Yangon is isolated from the influx rate effect by the hypothetical result in Fig. 7b, and indeed predicts increased $C_8H_9NO_4/C_6H_5NO_4$ from Yangon summer. However, both measurements and non-hypothetical simulation (for the latter changed photochemistry and changed precursor influx rates are at play) results show a slight decrease in $C_8H_9NO_4/C_6H_5NO_4$. Taking the hypothetical and non-hypothetical simulation results for Yangon winter together shows that the opposing effects of changes in photochemistry and precursor influx rates on $C_8H_9NO_4/C_6H_5NO_4$ broadly compensate one another for the non-hypothetical Yangon winter simulation.

The box modelling results and above explanations have shown that changes in partitioning thermodynamics that are driven by changes in aerosol water content, which are driven by changes in RH, exert a physical influence over $C_8H_9NO_4/C_6H_5NO_4$, since $C_8H_9NO_4$ is more sensitive to the effect. However, atmospheric oxidizing capacity has also been identified as playing an influential role in explaining the observed changes in $C_8H_9NO_4/C_6H_5NO_4$. The box modelling results are consistent with observed changes in the BeP/(BeP+BaP) ratio ((where BeP (Benzo[e]pyrene) and BaP (Benzo[a]pyrene) data were taken from our previous study (Zhang et al., 2024b, Fig. S8). The BeP/(BeP+BaP) ratio has been widely used as an indicator of aerosol aging (Křůmal et al., 2013). Fig. S8 shows the highest BeP/(BeP+BaP) ratios for Mandalay summer and Yangon summer, supporting the box model result that photochemistry varies substantially between seasons. Because of the difference in sensitivity to changing oxidizing capacity between $C_8H_9NO_4$ and $C_6H_5NO_4$, when all else is constant, the $C_8H_9NO_4/C_6H_5NO_4$ acts as an indicator of aerosol aging. However, the spread of points in Fig. S8, particularly for Yangon summer and Mandalay summer, indicates that aerosol aging alone cannot fully explain the variability in $C_8H_9NO_4/C_6H_5NO_4$. The box-model simulations suggest that RH-dependent partitioning, precursor emissions, and photochemical processing all contribute to the observed variability.

Considering the modelling and observation results discussed in this section, two factors are suggested to contribute to the significantly greater WSON in Mandalay summer in Fig. 1. First, the high degree of oxidation of organics due to enhanced photochemistry relative to the winter scenarios. Second, the high concentration of

precursors for relatively soluble oxidation products relative to Yangon summer (see Section 2.3 for discussion of why $C_6H_5NO_4$ is expected to be more water soluble than $C_8H_9NO_4$). However, a more thorough investigation involving more NOCs would be needed to test this hypothesis.

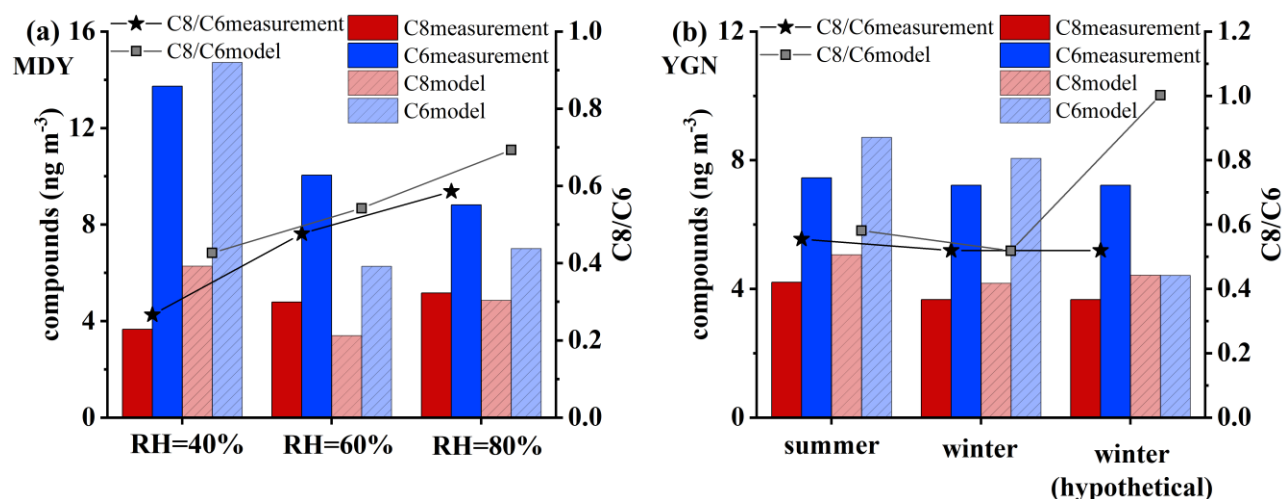


Figure 7 (a) Concentration distributions of $C_8H_9NO_4$ and $C_6H_5NO_4$ under different RH conditions in Mandalay. (b) Concentration distributions of $C_8H_9NO_4$ and $C_6H_5NO_4$ during Yangon summer, winter and winter hypothetical. Dark-colored bars represent the observed mass concentrations, while light-colored bars indicate the mass concentrations simulated by the model.

4. Atmospheric implications

This study provides new insights into the molecular characteristics and formation controls of NOCs in urban aerosols influenced by biomass burning. The results demonstrate that ONs and nitrophenolic compounds constitute major components of NOCs. By combining molecular-level observations with aromatic emission rates from combustion of varying biomasses and box model simulations, we show that variations in the formation of nitrophenolic compounds can be influenced by changing RH, variations in precursor concentrations, and seasonal changes to photochemistry. Our results are consistent with previous studies identifying biomass burning as an important source of aromatic precursors and nitrophenolic compounds (Salvador et al., 2021; Wang et al., 2020), whilst providing additional investigation of how RH and

photochemical conditions can influence molecular-level partitioning and transformation of nitrophenolic compounds in tropical urban atmospheres.

We found that enhanced photolysis acts to increase particle-phase $\text{C}_6\text{H}_5\text{NO}_4$ in particular, but that changes to influence from open biomass burning can exert a comparable change to particle-phase $\text{C}_6\text{H}_5\text{NO}_4$ concentration. Seasonal changes in open biomass burning influence, represented by changed model influx rates, are supported by changes to air mass back trajectories in Zhang et al. (2022) that show a shift from maritime to continental influence from Yangon summer to Yangon winter. The simulated effect of changing precursor availability for Yangon is sufficiently great to indicate that varying precursor concentration could drive changes also seen in Mandalay, however we did not have the data to justify changing precursor influx rates between Mandalay simulations, in contrast to changes in photochemistry and RH that were justified for Mandalay.

Meanwhile, particle-phase $\text{C}_8\text{H}_9\text{NO}_4$ concentrations were shown to be relatively sensitive to changing RH, via partitioning thermodynamics. These findings indicate the importance of accurately representing emissions, photochemistry, and gas-particle partitioning thermodynamics in predicting particle-phase composition and abundance in chemical transport models, and we note that the latter two processes are in principle represented by the BAT-VBS framework (Serrano Damha et al., 2024). While this study focuses on Myanmar, the identified controls of RH on gas-particle partitioning and of atmospheric oxidizing capacity on nitrophenol formation are fundamental atmospheric processes likely relevant to other humid and photochemically active regions. Nevertheless, regional differences in precursor abundance and emission profiles may modulate the sensitivity of particle-phase nitrophenolic compounds to these processes. As nitrophenolic compounds are important constituents of biomass-burning-derived brown carbon, the demonstrated sensitivity of their abundance to RH and photochemical conditions may also contribute to uncertainties in estimates of brown carbon radiative forcing. However, due to the limited availability of standards, quantitative analysis was only possible for few nitrophenolic compounds. Future work

should include more comprehensive laboratory simulations to better constrain the effects of RH and OH on the formation and degradation of nitrophenolic compounds.

Data availability. The data supporting the findings of this study are publicly available at the Zenodo (<https://doi.org/10.5281/zenodo.20328885>).

Author contributions. JF and YM designed the research. NZ conducted the measurements. NZ, JF, SO, ZL, JW and EA analysed the data. NZ, JF, SO, YM, XG, WL, PC, PDC, JW and EA reviewed and commented on the paper. NZ and SO wrote the paper.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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