Responses to referee's Comments:

Referee comments are in red color, responses are in green color and changes in the manuscript are in blue color.

Referee 1:

Comments: Md. Al-amin Hossen et al. report new data sets on phenolic precursors identified in brown carbon (BrC) sampled in the megacity of Dhaka. The new data found by using different state-of-the-art instruments such as scanning electron microscopy and infrared spectrometry is of great importance. In addition, they improve the understanding of BrC formation in highly populated regions. However, the novelty of the results and the applied laboratory methods such as the nitration experiment lack a scientific standard to being published in ACP as a research article. Hence, I agree with the editor's suggestion to publish this manuscript as a 'Measurement report' if the addressed revisions below are taken care of:

Response: We thank the reviewer for his thorough reading of our manuscript and valuable comments and suggestions. We have addressed every comment and made subsequent changes to the manuscript. We believe the manuscript has greatly improved after incorporating the reviewer suggestions.

Major comments

1. I believe the definition of BrC is not correctly introduced and hence, I suggest the authors review such parts of the text. Here is one examples: Abstract and line 48: Brown carbon is not the only OA particle type absorbing light: Please carefully read the definitions e.g. here: https://pubs.acs.org/doi/pdf/10.1021/cr5006167?ref=article_openPDF and rephrase.

Response: Thank you for your suggestion. I have rewritten the definition of brown carbon both in the abstract and on line 48 as follows, according to your suggestion and also cite this article in the text of the manuscript:

Abstract

Light-absorbing organic carbon, collectively known as brown carbon (BrC), significantly influence climate and air quality, particularly in urban environments like Dhaka, Bangladesh. Despite their significance, the contributions and transformation pathways of phenolic compounds—major precursors of brown carbon (BrC)—are still insufficiently understood in the South Asian megacities. This study addresses this gap by investigating the surface morphology of $PM_{2.5}$, quantifying seven phenolic BrC precursors, and exploring the aqueous-phase formation pathway of nitrophenols at two urban sites (Dhaka South and Dhaka North) from July 2023 to January 2024. Phenolic compounds, including phenol, methylphenols, methoxyphenol, hydroxyphenol, and nitrophenol were identified and quantified using gas chromatography–flame ionization detection (GC-FID). $PM_{2.5}$ surface morphology and elemental composition were analyzed via Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (FESEM-EDX), and functional groups were characterized using Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR). Results revealed that $PM_{2.5}$ particles were predominantly spherical or chain-like with carbonaceous elements (C, O, N, S), mineral dust, and trace metals. The dominant functional groups included aromatic conjugate double bond, carbonyl, and nitro group. Aqueous-phase nitration of 2-hydroxyphenol under acidic conditions, analyzed via UV-Vis spectroscopy, demonstrated an alternative nitrophenol formation pathway. Among the detected compounds, 2-hydroxyphenol and 4-nitrophenol showed the highest average concentrations (2.31±1.39 and 2.20±1.21 $\mu g\ m^{-3}$, respectively). Seasonal variations showed elevated nitrophenol levels during winter, especially in Dhaka South (4.54±2.94 $\mu g\ m^{-3}$). These findings highlight the quantification of phenolic precursors and the role of aqueous-phase reactions in BrC formation, providing valuable insights for future atmospheric modeling and air quality management strategies in South Asia.

Lin 48 is now rewritten as follows:

Brown carbon (BrC) is a type of organic carbon that absorbs light at shorter wavelengths, such as 300-400 nm (Laskin et al., 2015).

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, https://doi.org/10.1021/cr5006167, 27 May 2015.

2. Especially the Methods section needs thorough revision on English grammar and check when to use past or present tense (past for experimental steps, present tense for general valid statements). E.g.:

Response: Thank you for your comment. We carefully read the manuscript for English checking and also used Grammerly for the English correction according to your suggestion.

2.1. Line 125: change ‘for obtaining’ to ‘to obtain’

Response: Thank you for your suggestion. We have changed the sentence as follow:

To obtain a high-resolution SEM image each sample was kept in a desiccator for 1 hour and then freeze-dried for 6 hours to completely remove the moisture. Next, a small section of the filter was precisely severed and arranged on a sample holder using carbon nano tape.

2.2. Line 126: change ‘freeze-drying’ to ‘freeze-dried’

Response: Thank you for your suggestion. We have changed “freeze-drying” to “freeze-dried” as follow:

To obtain a high-resolution SEM image each sample was kept in a desiccator for 1 hour and then freeze-dried for 6 hours to completely remove the moisture. Next, a small section of the filter was precisely severed and arranged on a sample holder using carbon nano tape.

2.3. Line 152: change ‘to identification and quantification’ to ‘to identify and quantify’

Response: Thank you for your suggestion. We have changed the sentence as follows:

To identify and quantify of phenolic precursors of BrC half of each sample filter paper was cut into small pieces and taken into a conical flask. Then added 30.0 mL of solvent 1:1 (dichloromethane: ethylacetate) and kept to soak overnight for better extraction. After 24 hours, each sample was sonicated for 40 min at 30°C followed by shaking for 40 min in an orbital shaker.

2.4. Please use a table for the chemical reagent on line 195

Response: Thank you for your suggestion. We have added a table for the reagent using the formation experiment of the nitroaromatic compound in the manuscript as follows:

Table-1: List of required reagents for the laboratory experiments to study the formation of nitro-aromatic compounds.

S/N	**Reagents**	**Required Concentration**
1.	Catechol (1,2-dihydroxybenzene), $C_6H_4(OH)_2$	1 mM
2.	Sodium Nitrite, $NaNO_2$	1 mM
3.	Sulfuric Acid, H_2SO_4	0.1 M
4.	Ammonia Buffer (pH~8) & 6% H_2O_2	Used for alkaline conditions
5.	Hydrogen Peroxide, H_2O_2	6%

3. Please review the caption of all Figures and mention the abbreviations again so that one can understand the Figure without reading the main text. Also, it might facilitate to follow Figure 1 if you shortly summarize the main flows in the text after line 117.

Response: Thank you for your suggestion. We have revised the captions of all figures by replacing abbreviations with their full forms to ensure clarity. In addition, we have added a short description of the flow chart in Figure 1 in the main text after line 117 according to your suggestion as follows:

In total, 26 samples, including blanks, were collected from each site. The $PM_{2.5}$ mass was determined by calculating the difference between the weight of the blank filter and the $PM_{2.5}$-loaded filter. The total volume of air passing through the filter was calculated using the difference between the initial and final readings of the gas meter. After sampling, each sample were wrapped in aluminum foil, stored in a desiccator to regulate humidity, and finally preserved in a refrigerator at 4°C until further analysis. The flow diagram is given below (Fig. 1).

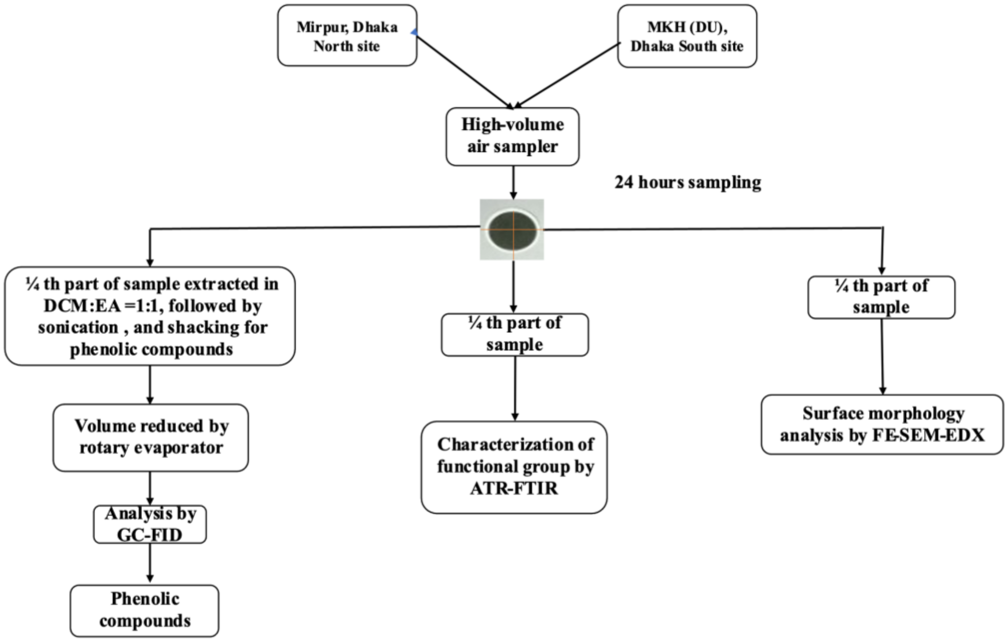


Fig.1: Schematic diagram of the overall sampling and analysis procedure from July 2023 to January 2024 at the Dhaka North site and the Dhaka South site

Fig. 1 illustrates the sampling and analysis workflow. In short, $PM_{2.5}$ samples were collected for 24 hours from two locations in Dhaka city. Each $PM_{2.5}$-loaded filter was divided into four equal parts. One-quarter was extracted and analyzed for phenolic precursors of brown carbon using gas chromatography–flame ionization detection (GC-FID). Another quarter was used to identify functional groups via attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-

FTIR). A further quarter was examined for surface morphology and elemental composition using field emission scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (FESEM-EDX).

4. The paragraphs starting on line 222 reads like part of the Introduction. It does not describe or explain results you obtained but introduces aerosol nucleation theory. Please carefully revise this. Similarly, the first paragraph from line 248 and the first paragraph from line 341 on describe a method and not results.

Response: Thank you for your comment. We have removed this line and rewritten the section 3.1 as follows:

3.1 Morphological Study of $PM_{2.5}$

In this research investigated the surface elements that are most prevalent in the Earth's atmosphere. The chemical components of $PM_{2.5}$ were categorized into distinct categories according to their morphology, as indicated by the SEM images (Fig. 2a–c). It shows that $PM_{2.5}$ particles exhibit predominantly irregular, aggregate, and chain-like morphologies. Most individual particles are ≤ 2.5 µm, while aggregates and chain-like structures range from 1.88 µm to 4.99 µm (Fig. 2c). Such coarse aggregates indicate particle growth through coagulation/agglomeration of smaller particles and the condensation of vapors onto pre-existing seed particles, rather than formation by fresh homogeneous nucleation (Lee et al., 2019). Lots of pre-existing particles in the atmosphere are released from the combustion event of biomass in our daily life, fossil fuel, and emissions from vehicles, and other sources. As a result, the gaseous pollutants in the atmosphere (NO_x, SO_x, NH_3, etc) undergo heterogeneous condensation on the surface of the pre-existing particle to form aggregates, chain-like aerosols of sulfate and nitrate. The morphology of the particles in $PM_{2.5}$ including diameter and shape are similar in Dhaka

North and Dhaka South sites but the surface chemical compositions are varied with season and sampling locations. The observed surface morphologies of aerosol particles, including irregular, aggregate, and chain-like structures, play a significant role in the formation and optical properties of BrC. These morphologies provide a large reactive surface area that facilitates the heterogeneous adsorption and condensation of gaseous phenolic precursors and other organic compounds onto existing particles. Such interactions promote the chemical aging processes like nitration and oxidation, which enhance the light-absorbing capacity characteristic of BrC (Hossen et al., 2025).

Hossen, M. A. amin, Roy, S., Nahian, S., Zaman, S. U., Selim, A., and Salam, A.: Spectral characteristics of water-soluble Brown carbon and it's radiative impacts on the atmosphere of Dhaka, Bangladesh, Atmos Environ, 351, 121185, https://doi.org/10.1016/J.ATMOSENV.2025.121185, 2025.

Similarly, the first paragraph from line 248 on describes a method and not results.

Response: Thank you for your comment. We agreed with the reviewer and removed the paragraph (with line 248) from the manuscript.

The first paragraph from line 341 on describes a method and not results.

Response: Thank you for your comment. We have removed the paragraph from section 3.4.3 and transferred it to the methodology section 2.6. Correlation Analysis as follows:

2.6. Correlation Analysis

The degree and direction of a linear relationship between two variables (in this case, compounds) are measured by Pearson's correlation coefficient or r. The r-value is between -1 and 1: r=1 (perfectly positive correlation), r=-1(perfectly negative correlation), r=0 no correlation. r > 0.7

means strongly correlation, 0.3 > r > 0.7 means moderately correlation, and 0.3 > r means weak correlation (Hauke and Kossowski, 2011).

5. What does Fig. 4 add to the story? It seems that Fig. 4 shows redundant data already depicted in Fig.3. Please explain or delete one.

Response: Thank you for your comment. We agree that Fig. 4 presents data that overlaps with Fig. 3. To avoid redundancy and improve clarity, we have removed Fig. 4 from the revised manuscript.

6. I have a hard time to understand how section 3.5 fits into this manuscript. May you elaborate on this new production mechanism of nitro-aromatic compounds and put it into atmospheric context such as its relevance? It may help if you show the differences between your newly discovered pathway and the one(s) elaborated in the literature.

Response: Thank you for your thoughtful comment. In the revised manuscript, we have replaced section 3.5 in the methodology (Section 2.7: Nitration Experiment of Catechol to Formation of Light-Absorbing Product). We have elaborated Section 3.5 by providing a detailed explanation of the observed spectra, including the experiment conducted in an alkaline medium and its interpretation. Furthermore, we have compared our identified pathway with previously reported mechanisms in the literature and added this comparison to the last part of the Introduction to place our findings in a broader atmospheric context.

The revised section 3.5 is given below.

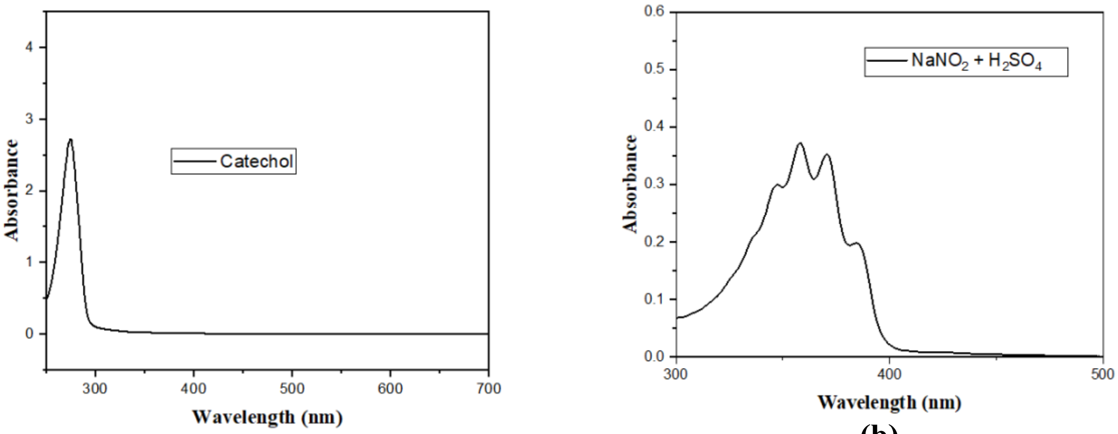
3.5 Formation of light-absorbing nitro-aromatic compounds

In our study, we quantified several common brown carbon (BrC) precursors in the ambient atmosphere. Among them, 2-hydroxyphenol and 4-nitrophenol were found in the highest amount in our sampling area, both of which are well-known products of biomass burning. To gain a better understanding of the possible formation processes of nitroaromatic compounds under atmospheric conditions, we conducted controlled aqueous-phase nitration experiments in the laboratory.

In these experiments, catechol (2-hydroxyphenol), selected because it was the most abundant precursor detected in our samples, was reacted with sodium nitrite under both acidic conditions (pH adjusted using H_2SO_4 and NaOH) and basic conditions (pH adjusted using ammonia buffer, with H_2O_2 added to enhance NO_2^- production) to form light absorbing nitro aromatic compound.

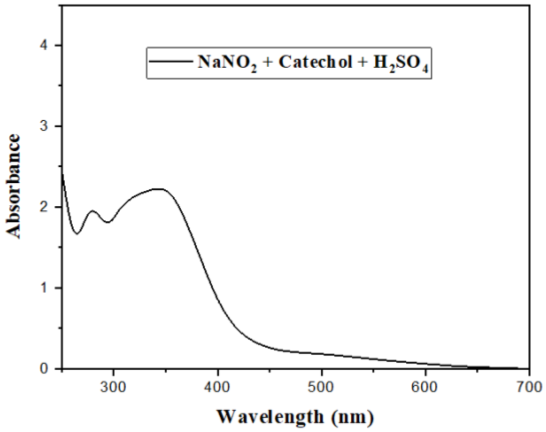
3.5.1. UV-visible light absorption properties of the catechol-nitrite reaction system

The catechol (2-hydroxyphenol) absorbs the UV-visible light at 280 nm (peak at 280 nm) (Scalzone et al., 2020). When it reacted with the sodium nitrite in the presence of H_2SO_4, the peak (λ_{max}) was shifted to a longer wavelength. This shift of λ_{max} indicated that there was an interaction between 2-hydroxyphenol and the nitrite ions in the reaction system (Fig.5).



(a)

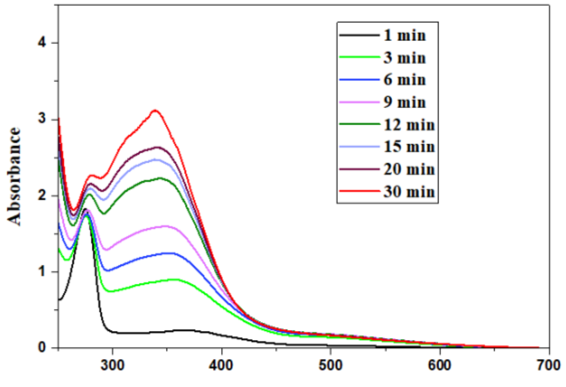
(b)



(c)

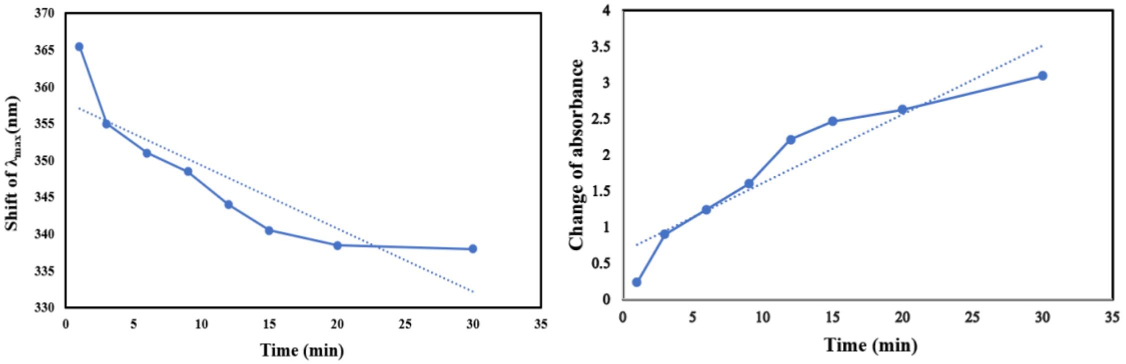
Fig.5: UV-visible spectra of (a) single catechol, λ_{max}=275 nm, (b) $NaNO_2 + H_2SO_4$, and (c) reaction system (catechol-nitrite)

The change of absorbance with time at pH=3.5 of the catechol-nitrite reaction system is represented in Fig.6. At pH=3.5 the absorbance gradually increases with time in the wavelength range from 300 – 700 nm and the λ_{max} shifted to a shorter wavelength with time increase. Initially, at 1 min the λ_{max} obtained at 355 nm then as time increased the absorbance increased gradually and the λ_{max} shifted to a shorter wavelength such as 338 nm after half an hour and no change further increase in time (Fig.6a). It is clear from this change that the nitro group has been added to the aromatic ring, leading to an increase in absorption and a shift in the position of the peak.



(a)

Time (min)	λ_{max}(nm)	Change of absorbance
1	365.5	0.236
3	355	0.899
6	351	1.246
9	348.5	1.598
12	344	2.216
15	340.5	2.466
20	338.5	2.628
30	338	3.094



(c) (d)

Fig.6: (a) Change of the absorbance with times of the reaction system containing 1 mM 2-hydroxyphenol and 1 mM $NaNO_2$ at pH=3.0. A distinct color denotes the duration of the sample run in the ultraviolet-visible spectrophotometer. The initial reactant contribution was subtracted from each spectrum. Table (b) Data for the shift of peak and change of absorbance, (c) Shift of λ_{max} with time, and (d) Change of absorbance with time

Fig. 6 shows the UV–Vis spectrum of the $NaNO_2$ and 2-hydroxyphenol reaction system in acidic medium shows a clear time-dependent evolution in absorbance over the 1–30 min period, indicating progressive formation of new light-absorbing species. At the early stage (1 min), the spectrum is dominated by the characteristic $\pi \rightarrow \pi^*$ transition of the aromatic ring near 270–280 nm with relatively low intensity in the higher wavelength region. As the reaction proceeds, both the main aromatic band and a second band in the 300–350 nm region gradually increase in intensity, with the latter showing a slight bathochromic shift. This hyperchromic effect and modest red-shift are consistent with the formation of nitro-substituted aromatic compounds such as o- or p-nitrophenol. The strong electron-withdrawing nature of the nitro group extends conjugation and enhances n→π* and charge-transfer transitions, leading to stronger and slightly longer wavelength absorption than the parent phenol. The continuous increase in absorbance with time, without any later decline, confirms the accumulation of these nitro-aromatic products in solution. This spectral change therefore provides strong evidence that the reaction proceeds through electrophilic aromatic substitution of 2-hydroxyphenol by nitronium ions generated from $NaNO_2$ in the acidic medium, yielding stable nitro-phenol derivatives with enhanced UV absorption.

Reaction in alkaline medium

At high pH, nitrite remains primarily in the form of NO_2^-, and the formation of electrophiles such as HONO, NO_2^+, or N_2O_3 is strongly suppressed. Although phenolates are highly activating toward substitution, the lack of these electrophilic species makes aromatic nitration largely ineffective. However, the presence of peroxide facilitates the formation of NO_2^+.

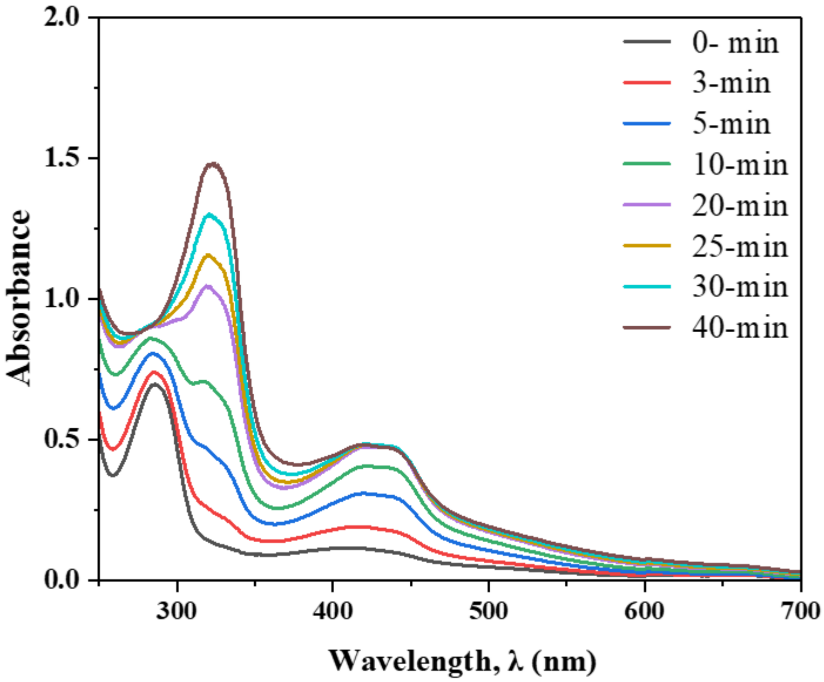


Fig. 8: UV-visible absorption spectra of the nitrite-catechol reaction system in alkaline medium pH~7-8 to form a light-absorbing nitro aromatic compound.

Fig. 8, the UV–Vis spectra of the $NaNO_2$–2-hydroxyphenol system in alkaline medium with H_2O_2 show a time-dependent evolution of absorption features, indicating the formation of light-absorbing products. Initially, the spectrum is dominated by the characteristic UV absorption of phenolate anions (~280–300 nm), but with reaction time (0–15 min) the peak intensity increases and a broad shoulder emerges and intensifies in the 400–450 nm region. This indicated the completed protonated form of nitrophenol (Syedd-León et al., 2020). This bathochromic shift and visible-range growth reflect the formation of conjugated nitroaromatic and quinone-like species with extended π-systems, likely via oxidation of phenolate by HO_2^-/oxidants and subsequent nitration by reactive nitrogen species from nitrite. The progressive increase in visible absorption is consistent with the generation of chromophoric, brown carbon-type products with potential atmospheric light-absorbing properties. These spectral changes strongly suggest nitro-substituted aromatic and quinone-type chromophores are forming in the system.

Under acidic conditions, nitrite generates the potent electrophile NO_2^+ (via HNO_2/HNO_2^+) and N_2O_3/NO^+ equilibria). The activated aromatic ring of phenol or catechol then undergoes rate-determining electrophilic attack by NO_2^+ to form the Wheland (σ) intermediate, directed ortho/para by the OH group(s). Subsequent deprotonation restores aromaticity, yielding the nitroaromatic product. The reaction mechanism of the nitration of aromatic compounds takes place through the reaction with an aqueous nitrite solution. Esteves et al., (2003) have also suggested that the exceedingly potent electrophile NO_2^+ facilitated the reaction at a low pH. The NO_2^+ electrophile attacks the benzene ring and forms a C-N bond. According to Wang et al., (2023) HONO acts as an electrophile in the aqueous nitration of catechol (2-hydroxybenzene). This explains the accelerated nitration rate in acidic environments, as HONO, being a stronger electrophile than NO_2^-, is more readily formed at lower pH levels.

Under alkaline conditions, nitration is generally unfavorable. At high pH, nitrite remains primarily in the form of NO_2^-, and the formation of electrophiles such as HONO, NO_2^+, or N_2O_3 is strongly suppressed. Although phenolates are highly activating toward substitution, the lack of these electrophilic species makes aromatic nitration largely ineffective. However, the presence of peroxide facilitates the formation of NO_2^+.

In the atmosphere, a similar pathway occurs inside aqueous aerosol droplets or cloud/fog water, where phenolic compounds (e.g., catechol) are taken up. These droplets adsorb NO_2 and interact with OH radicals under sunlight, generating reactive nitrogen species (HONO, NO_2^+, peroxynitrite) that nitrate and oxidize the phenolic precursors. This process yields nitro-aromatic and quinone-type chromophores, which extend absorption into the visible range (Yang, X., et al. 2023). Thus, the laboratory results directly mimic the aqueous-phase reactions in atmospheric droplets that lead to the formation of light-absorbing brown carbon.

Yang, J., Au, W. C., Law, H., Leung, C. H., Lam, C. H., & Nah, T. (2023). pH affects the aqueous-phase nitrate-mediated photooxidation of phenolic compounds: implications for brown carbon formation and evolution. *Environmental Science: Processes & Impacts*, *25*(2), 176-189. https://doi.org/10.1039/D2EM00004K

Moreover, we have added the following section in the introduction.

Previous studies have primarily emphasized gas-phase reactions between phenolic VOCs and NOx, followed by photochemical oxidation and subsequent partitioning into the particle phase (Hems et al., 2021; Laskin et al., 2015; Harrison et al., 2005). Li et al., (2020) shows the formation pathway of nitro aromatic compound via gas-phase reactions, occurring through $^*OH + NO_2$ in daytime and $^*NO_3 + NO_2$ at nighttime. Our results highlight an alternative pathway for the formation of nitroaromatic compounds in aqueous phase reaction in the laboratory through electrophilic substitution (mediated by NO_2^+ or HONO) under acidic or alkaline conditions in the absence of sunlight, with demonstrated applicability to biomass samples. Similarly, aerosol and cloud water can contain free-radical NO_2, and it converts to atmospheric HNO_2, which may undergo photo-oxidation to produce nitroaromatic compounds.

Harrison, M. A. J., Barra, S., Borghesi, D., Vione, D., Arsene, C., and Iulian Olariu, R.: Nitrated phenols in the atmosphere: A review, Atmos Environ, 39, 231–248, https://doi.org/10.1016/j.atmosenv.2004.09.044, 2005.

Hems, R. F., Schnitzler, E. G., Liu-Kang, C., Cappa, C. D., and Abbatt, J. P. D.: Aging of Atmospheric Brown Carbon Aerosol, https://doi.org/10.1021/acsearthspacechem.0c00346, 15 April 2021

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, https://doi.org/10.1021/cr5006167, 27 May 2015.

Li, X., Yang, Y., Liu, S., Zhao, Q., Wang, G., and Wang, Y.: Light absorption properties of brown carbon (BrC) in autumn and winter in Beijing: Composition, formation and contribution of nitrated aromatic compounds, Atmos Environ, 223, https://doi.org/10.1016/j.atmosenv.2020.117289, 2020.

Syedd-León, R., Sandoval-Barrantes, M., Trimiño-Vásquez, H., Villegas-Peñaranda, L. R., and Rodríguez-Rodríguez, G.: Revisiting the fundamentals of p-nitrophenol analysis for its application in the quantification of lipases activity. A graphical update, Uniciencia, 34, 31–42, https://doi.org/10.15359/RU.34-2.2, 2020.

Minor comments

1. Please check all abbreviations and use them throughout the text. I have found e.g. ‘brown carbon’ even though you have introduced its abbreviation. E.g.: line 89.

Response: Thank you for your valuable comment. We have carefully reviewed the manuscript and ensured that all abbreviations, such as brown carbon (BrC), are introduced at first use and used consistently throughout the text. Instances where the full term was previously used after introducing the abbreviation have now been replaced by the appropriate abbreviation to maintain clarity and consistency.

2. Please use ‘secondary organic aerosol (SOA) particles’ throughout the text and not ‘secondary organic aerosols (SOAs)' (e.g. line 26).

Response: Thank you for your suggestion. We have replaced the term ‘secondary organic aerosols (SOAs)' by ‘secondary organic aerosol (SOA) particles’. Now the new line is given below.

Light-absorbing secondary organic aerosol (SOA) particles, collectively known as brown carbon (BrC), significantly influence climate and air quality, particularly in urban environments like Dhaka, Bangladesh.

3. Please do not use abbreviations if not introduced already (e.g. line 35)

Response: Thank you for your suggestion. We have revised the manuscript and changed it as follows:

$PM_{2.5}$ surface morphology and elemental composition were analyzed via Field Emission Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (FESEM-EDX), and functional groups were characterized using Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR).

4. Please add column titles for Table 1.

Response: Thank you for your suggestion. We have added a column titles of Table 1 as follows:

Table-2: Primary band assignments for ATR-FTIR spectra of PM2.5 particulate matter

Range of Wavenumber	**Vibrational Assignment**
2500 – 2000 cm^{-1}	**$C \equiv N$ and $C \equiv C$ bond stretching**
1800 – 1650 cm^{-1}	Carbonyl ($C = O$) bond stretching
1600 – 1475 cm^{-1}	Aromatic ring stretching
1640-1550 cm^{-1}	Bending of aromatic N-H bond
1445 cm^{-1}	Bending of $-CH_3$, $-CH_2$ and stretching of aromatic ring
1355 – 1315 cm^{-1}	$R - ONO_2$ organic nitrate stretching
1440 – 1220 cm^{-1}	Bending of C-O-H
1200-1000 cm^{-1}	Stretching vibration of $C - O$
900 – 690 cm^{-1}	Out plane bending of aromatic ring

5. Line 43: Change ‘critical’ to ‘new’.

Response: Thank you for your suggestion. We have changed the sentence as follows:

These findings highlight the quantification of phenolic precursors and the role of aqueous-phase reactions in BrC formation, providing valuable insights for future atmospheric modeling and air quality management strategies in South Asia.

6. Line 55: Add a citation or combine both sentences.

Response: Thank you for your comment. We have combined both sentences as follows:

The two main sources of BrC were automobile emissions and biomass burning, with the composition of these emissions varying considerably depending on the fuel type and combustion conditions (Laskin et al., 2015).

7. Line 69: the citation is misplaced. Please review accordingly.

Response: Thank you for pointing it out. We have reviewed it and changed as follows:

According to the previous research, phenol and cresols (such as m-cresol, p-cresol, and o-cresol) can oxidize to produce nitrophenol and its derivatives (Harrison et al., 2005).

8. Line 72: change ‘a study’ to ‘studies'.

Response: Thank you for your suggestion. We have changed ‘a study’ to ‘studies' in the revised manuscript as follows:

Furthermore, studies conducted by Andreozzi et al., (2006) and Hummel et al., (2010) have demonstrated that the primary pathway for the creation of 3-nitrosalicylic acid and 5-nitrosalicylic acid in the aqueous phase is the nitration of salicylic acid.

9. Line 83: change ‘are comes’ to ‘come’

Response: Thank you for your suggestion. We have changed the sentence in the revised manuscript as follows:

In Bangladesh, most pollutants originate from vehicle emissions, solid waste burning, biomass burning, and brick kilns emission (Hossain et al., 2024; Kumar et al., 2021). All these are major sources of BrC. Therefore, studies on BrC composition, such as phenolic compounds and their derivatives, in Bangladesh are essential.

10. Please rephrase the sentence starting on line 85.

Response: Thank you for your suggestion. We have rephrased the sentence as follows:

In Bangladesh, most pollutants originate from vehicle emissions, solid waste burning, biomass burning, and brick kilns emission (Hossain et al., 2024; Kumar et al., 2021). All these are major sources of BrC. Therefore, studies on BrC composition, such as phenolic compounds and their derivatives, in Bangladesh are essential.

11. Line 91: add ‘we’ before ‘focused’.

Response: Thank you for your suggestion. We have changed the last part of the introduction as follows:

In Bangladesh, most pollutants originate from vehicle emissions, solid waste burning, biomass burning, and brick kiln emissions (Hossain et al., 2024; Kumar et al., 2021). All these are major sources of BrC. Therefore, studies on BrC composition—such as phenolic compounds and their derivatives—in Bangladesh are essential. In previous studies, Ankhy et al., (2024); Hossen et al., (2023); and Runa et al., (2022) determined the optical properties of BrC emissions from biomass burning as well as ambient air in Dhaka, Bangladesh, but did not investigate the individual composition of BrC. Previous studies have primarily emphasized gas-phase reactions between phenolic VOCs and NOx, followed by photochemical oxidation and subsequent partitioning into the particle phase (Hems et al., 2021; Laskin et al., 2015). Yang et al., (2021) reported that photooxidation of phenolic compounds forms BrC, and phenolic compounds are a major class of aromatic compounds known as BrC precursors. Li et al., (2020) show the formation pathway of nitro aromatic compounds via gas-phase reactions, occurring through $^*OH + NO_2$ in daytime and $^*NO_3 + NO_2$ at nighttime. Our study reports an alternative pathway for the formation of nitroaromatic compounds in aqueous-phase reactions through electrophilic substitution (mediated by NO_2^+ or HONO) under acidic or alkaline conditions in the absence of sunlight, with demonstrated applicability to biomass samples. The main focus of this work, however, is the quantification of phenolic precursors of BrC. Specifically, we investigate the surface composition of $PM_{2.5}$ and phenolic precursors in the atmosphere of Dhaka, Bangladesh, from July 2023 to January 2024, along with an experiment on the aqueous nitration of 2-hydroxyphenol, a common BrC precursor.

12. Line 93: delete ‘in the laboratory’.

Response: Thank you for your suggestion. We have removed “in the laboratory” from line 93 and updated the last part of the Introduction accordingly, as already noted in our response to comment 11.

13. Line 110: Change ‘concurrently’ to ‘simultaneously’.

Response: Thank you for your suggestion. We have changed change ‘concurrently’ to ‘simultaneously’ in line 110 as follows:

Sampling was conducted simultaneously at both locations (Dhaka South and Dhaka North sites) from July 2023 to January 2024. Each month, four samples were collected from both sites.

14. Line 207: Please revise the sentence.

Response: Thank you for your suggestion. We have revised the sentence as follows:

In this research, we investigated the most prevalent surface elements in the atmospheric particulate matter.

15. Line 209: Which panels in Fig. 2 are you referring to?

Response: Thank you for your question. We have rewritten this section 3.1, including line 209, as already mentioned in the response to comment 4. The panels referred to are Fig. 2(a–c).

16. The sentence on line 210 sounds like a repetition of the sentence above. Please revise.

Response: Thank you for pointing it out. We have rewritten this section 3.1, including line 210, as already mentioned in the response to comment 4.

17. Line 211: You cannot say PM2.5 particles. Either aerosol particles or PM2.5.

Response: Thank you for your suggestion. We have changed it to aerosol particles in the revised manuscript and rewritten section 3.1 already mentioned in the response to comment 4.

18. Panels a-c in Fig. 2: The font is too small. Either you get rid of all the text, or you enlarge the images. The size bar must be clearly readable. In addition, in panel e) one cannot see the description of the peaks in the spectrum and thus, the Fig. seems to be useless. Panel f) is a Table and not a Figure. Please revise.

Response: Thank you for your suggestion. We have enlarged the images in panels a–c to improve text and scale bar readability. The peak descriptions in panel e have been clarified for better visibility. Additionally, panel f has been revised and reformatted as a table instead of a figure.

19. Line 237: I can only follow this from Table 2f.

Response: Thank you for your comment. We have changed the sentence as follows:

Table 2f shows that the quantity of carbon (C) and oxygen (O) were very high in $PM_{2.5}$, along with varying amounts of minerals (Ca, Fe, K, Al), sulfur, nitrogen, and trace metals (As, Cr, Cd, Pb, Hg).

20. Line 241: What have the sulphur emissions with nitrogen in common? Otherwise, make two sentences, please.

Response: Thank you for your comment. We have revised the sentence for clarity and separated it into two sentences as follows:

Sulfur dioxide (containing S) is primarily emitted from coal combustion, while nitrogen dioxide (containing N) mainly originates from agricultural land and fertilizers.

21. Line 277: Which phenolic compound? You did not elaborate this until now.

Response: Thank you for your comment. We have now clarified and elaborated on the specific phenolic compounds identified in our study as follows:

The phenolic components serving as primary precursors of brown carbon include phenol, 4-nitrophenol, methoxy phenol, and cresols (m-cresol, p-cresol, and o-cresol). This detail has been added to the manuscript for better clarity.

22. Line 279: Again here, I am unsure why you add this here as you should talk about the results and not the introduction of and why you were looking for nitrophenols as SOA proxies.

Response: Thank you for your comment. We have removed line 279 from the manuscript.

23. Line 286: Please already explain this in the first sentence of this paragraph and add it to the caption of Fig. 3. Please also explain the meaning of the grey error bar and show how you derived it in the main text.

Response: Thank you for your insightful comments. We have revised the manuscript accordingly.

Line 286 : "In Dhaka South, the second-highest concentration was found to be 2-hydroxyphenol (catechol) with values of 1.34±0.31, 2.44±0.16, and 5.04±3.41 μg m^{-3} during the monsoon, post-monsoon, and winter seasons respectively while the values recorded at Mirpur were 1.43±0.07, 1.78±0.53, and 1.82±0.51 μg m^{-3} respectively (Table S7)".

The sentence on line 286 has been kept to provide specific seasonal concentration values for 2-hydroxyphenol (catechol) at Dhaka South and Mirpur, complementing the overall discussion of phenolic compounds in $PM_{2.5}$.

The meaning of the grey error bars in Fig. 3 represents the error bars, the standard deviation of the measured concentrations, indicating variability across samples. The formula used to calculate the standard deviation is described in the supplementary file (Section 6) as follows:

6. Standard deviation

Standard deviation of the phenolic compounds was calculated by the following formula

$$\sigma = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

Where,
n= Number of observations
x_i= Individual observation
$\bar{x}$= Sample mean or average

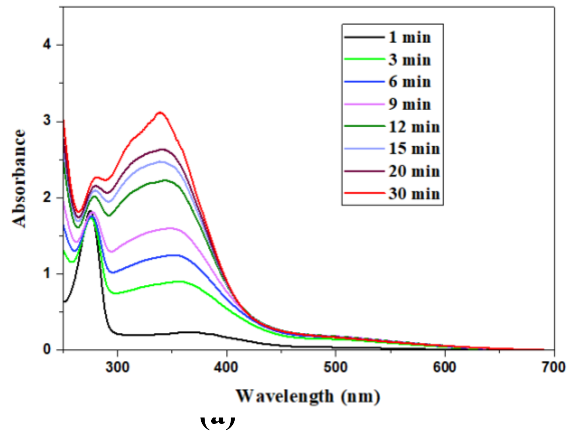
24. Line 300: Please use the same unit for readability throughout the text (ug instead of ng).

Response: Thank you for your suggestion. We have changed the unit ng to µg as follows:

Li (2020) reported that the average concentration of phenol in urban Jinan, China was $(1.67 \pm 0.37) \times 10^{-2}$, $(7.1 \pm 2.6) \times 10^{-3}$, and $(2.6 \pm 0.4) \times 10^{-3}$ µg m^{-3} in winter, spring, and summer, respectively.

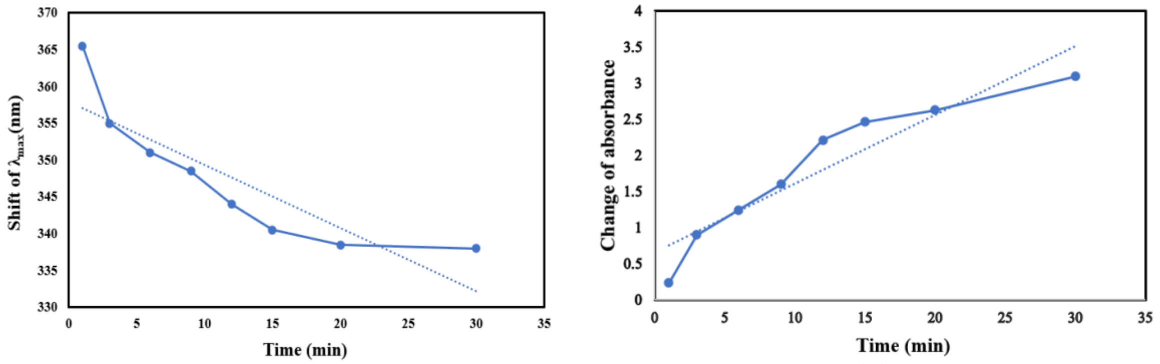
25. Panel b) of Fig. 6 is a Table and not a Figure.

Response: Thank you for pointing it out. We have changed the caption of b) of Fig. 6 to Table as follows:



(a)

Time (min)	λ_{max}(nm)	Change of absorbance
1	365.5	0.236
3	355	0.899
6	351	1.246
9	348.5	1.598
12	344	2.216
15	340.5	2.466
20	338.5	2.628
30	338	3.094



(c) (d)

Fig.6: (a) Change of the absorbance with times of the reaction system containing 1 mM 2-hydroxyphenol and 1 mM $NaNO_2$ at pH=3.0. A distinct color denotes the duration of the sample run in the ultraviolet-visible spectrophotometer. The initial reactant contribution was subtracted from each spectrum. Table b) Data for the shift of peak and change of absorbance, (c) Shift of λ_{max} with time, and (d) Change of absorbance with time

26. Line 398: change ‘has been’ to ‘have been’.

Response: Thank you for your suggestion. We have changed the ‘has been’ to ‘have been’ in Line 398.

Esteves et al., (2003) have been suggested that the exceedingly potent electrophile NO_2^+ facilitated the reaction at a low pH. The NO_2^+ electrophile attacks the benzene ring and forms a C-N bond.

27. Conclusions: Please do not distinguish between ‘Summary’ and ‘Conclusions’, but incorporate it smoothly in the main text of the ‘Conclusions’.

Response: Thank you for your suggestion. We have removed the separate ‘Summary’ section and smoothly incorporated its key points into the main text of the ‘Conclusions’ section in the revised manuscript for better flow and coherence.

Referee 2:

Comment: The manuscript discusses the composition of brown carbon in $PM_{2.5}$ collected from Dhaka, Bangladesh. The manuscript focuses on the composition of phenolic precursors of brown carbon in $PM_{2.5}$. The surface morphology and elemental composition were also analysed in this study. Overall the study is interesting and worth publication since it is important to have information on brown carbon in the South Asian region.

Response: We thank the reviewer for his thorough reading of our manuscript and valuable suggestions. We have addressed each and every comment and made subsequent changes to the manuscript. We believe the manuscript has greatly improved after incorporating the comments.

Detail comment

1. The introduction of the manuscript requires improvement to ensure a better flow of information and proper paragraphing. The first paragraph is too long and should be separated into different paragraphs.

Response: Thank you for your valuable suggestion. We have revised the introduction to improve the logical flow and readability. Specifically, we have divided the first paragraph into shorter, well-structured paragraphs, each focusing on a distinct aspect of the study background. This restructuring ensures a smoother transition between ideas and enhances clarity for the reader. The revised introduction is given below.

1. Introduction

Brown carbon (BrC) is a type of organic carbon that absorbs light at shorter wavelengths, such as 300-400 nm (Laskin et al., 2015). In contrast to black carbon, brown carbon exhibits a wavelength-dependent absorptivity that increases significantly towards the higher energy end of the spectrum (Wang et al., 2023). Similar to black carbon, brown carbon (BrC) also has a positive radiative effect, which lowers the total cooling effect of atmospheric aerosols caused by light scattering (Feng et al., 2013). Because of the complexity and variety of its origins, composition, and atmospheric aging mechanisms, the direct radiative effect of BrC is still unknown despite intensive research (Lee et al., 2014). The two main sources of BrC were automobile emissions and biomass burning. The composition of primary emissions can differ significantly depending on the type of fuel and the conditions under which it burns (Laskin et al., 2015c). There are probably thousands of organic molecules in atmospheric BrC, many of which are unidentified. However, phenolic compounds are a class of components that are commonly discovered (Wang et al., 2018). Phenolic and nitrated phenols are organic substances that contain at least one hydroxyl group and nitro group in the benzene ring. Phenolic derivatives are the major composition of BrC. They originate from diverse processes of production and different emission sources. Large volumes of nitrated phenolic compounds are released into the atmosphere by primary sources such as vehicle exhaust, burning of biomass, and combustion of coal (Li et al., 2020; Wang et al., 2020).The secondary synthesis of these substances from precursors like aromatic hydrocarbons and phenolic compounds via nitration in both gaseous or aqueous phases (Harrison et al., 2005).

According to earlier research, one of the main contributors of brown carbon is nitrated phenolic compounds and R-NO_2 nitroaromatic compound (Hossen et al., 2023; Li et al., 2022). The main reasons for the increased focus on phenolic compounds are their human toxicity (Rahman et al., 2022) and their role in producing secondary organic aerosols (SOAs) (Nakao et al., 2011). According to previous research, phenol and cresols (such as m-cresol, p-cresol, and o-cresol) can oxidize to produce nitrophenol and its derivatives (Harrison et al., 2005). Cresols released during the burning of biomass can undergo photooxidation, producing nitro-catechol and its derivatives (Finewax et al., 2018; Iinuma et al., 2010). Furthermore, studies conducted by Andreozzi et al., (2006) and Hummel et al., (2010) have demonstrated that the primary pathway for the creation of 3-nitrosalicylic acid and 5-nitrosalicylic acid in the aqueous phase is the nitration of salicylic acid. Laboratory investigations have established the importance of aqueous processes as a production mechanism for nitrated phenolic compounds. In particular, when phenol was subjected to aqueous-phase interactions with nitronium ions (NO_2^+), 4-nitrophenol was produced (Heal et al., 2007). The most prevalent nitro-aromatic species were nitrophenols and nitro catechols, which accounted for 31% and 32% of all nitro-aromatic compounds, respectively (Wang et al., 2021). To fully understand the precursor of BrC in the atmosphere, it is crucial to analyze the concentrations, chemical compositions, and sources of their phenolic precursors, along with the derivatives of nitrated and methyl derivatives of phenols. Aerosol surface morphology plays an important role in the light-absorbing properties and reactivity of BrC. Irregular or porous particle surfaces can enhance the adsorption of gaseous precursors, such as phenolic compounds, thereby influencing their heterogeneous oxidation and nitration pathways in the atmosphere. Moreover, morphological features can affect how BrC and its phenolic components interact with cloud or fog droplets, altering aqueous-phase reaction rates and the formation of light-absorbing secondary products.

In Bangladesh, most pollutants originate from vehicle emissions, solid waste burning, biomass burning, and brick kiln emissions (Hossain et al., 2024; Kumar et al., 2021). All these are major sources of BrC. Therefore, studies on BrC composition—such as phenolic compounds and their derivatives—in Bangladesh are essential. In previous studies, Ankhy et al., (2024); Hossen et al., (2023); and Runa et al., (2022) determined the optical properties of BrC emissions from biomass burning as well as ambient air in Dhaka, Bangladesh, but did not investigate the individual composition of BrC. Previous studies have primarily emphasized gas-phase reactions between phenolic VOCs and NOx, followed by photochemical oxidation and subsequent partitioning into the particle phase (Hems et al., 2021; Laskin et al., 2015). Yang et al., (2021) reported that photooxidation of phenolic compounds forms BrC, and phenolic compounds are a major class of aromatic compounds known as BrC precursors. Li et al., (2020) show the formation pathway of nitro aromatic compounds via gas-phase reactions, occurring through $^{*}OH + NO_2$ in daytime and $^{*}NO_3 + NO_2$ at nighttime. Our study reports an alternative pathway for the formation of nitroaromatic compounds in aqueous-phase reactions through electrophilic substitution (mediated by NO_2^+ or HONO) under acidic or alkaline conditions in the absence of sunlight, with demonstrated applicability to biomass samples. The main focus of this work, however, is the quantification of phenolic precursors of BrC. Specifically, we investigate the surface composition of $PM_{2.5}$ and phenolic precursors in the atmosphere of Dhaka, Bangladesh, from July 2023 to January 2024, along with an experiment on the aqueous nitration of 2-hydroxyphenol, a common BrC precursor.

2. There is no information on surface morphology and its relationship with brown carbon and phenolic compounds presented in the introduction.

Response: Thank you for your insightful comment. We have now included text in the introduction discussing the role of aerosol surface morphology in relation to brown carbon and phenolic compounds. Specifically, we explain how particle surface features influence the adsorption of phenolic precursors and affect heterogeneous oxidation and nitration processes, which are important for the formation and optical properties of BrC. The revised introduction already provided in the response of comment 1.

3. The objective of the manuscript presented in the last part of the introduction is considered weak and needs further clarification and improvement.

Response: Thank you for your valuable comment. We have revised the last part of the introduction to clearly and concisely state the main objectives, emphasizing the quantification of phenolic precursors and their role in brown carbon formation in Dhaka's atmosphere. The revised introduction already provided in the response of comment 1.

4. What is the connection between surface morphology and brown carbon presented in the results of this study? I can't see any clear discussion on the relationship between them in the Results and Discussion.

Response: Thank you for your comment. We have added a discussion in section 3.1 explaining that surface morphology influences brown carbon formation by providing reactive sites for phenolic precursors and affecting chemical aging processes that enhance BrC's light absorption. The revised section 3.1 is given below.

3.1 Morphological Study of $PM_{2.5}$

In this research investigated the surface elements that are most prevalent in the Earth's atmosphere. The chemical components of $PM_{2.5}$ were categorized into distinct categories according to their morphology, as indicated by the SEM images (Fig. 2a–c). It shows that $PM_{2.5}$ particles exhibit predominantly irregular, aggregate, and chain-like morphologies. Most individual particles are ≤ 2.5 µm, while aggregates and chain-like structures range from 1.88 µm to 4.99 µm (Fig. 2c). Such coarse aggregates indicate particle growth through coagulation/agglomeration of smaller particles and the condensation of vapours onto pre-existing seed particles, rather than formation by fresh homogeneous nucleation (Lee et al., 2019). Lots of pre-existing particles in the atmosphere are released from the combustion event of biomass in our daily life, fossil fuel, and emissions from vehicles, and other sources. As a result, the gaseous pollutants in the atmosphere (NO_x, SO_x, NH_3, etc) undergo heterogeneous condensation on the surface of the pre-existing particle to form aggregates, chain-like aerosols of sulfate and nitrate. The morphology of the particles in $PM_{2.5}$ including diameter and shape are similar in Dhaka North and Dhaka South sites but the surface chemical compositions are varied with season and sampling locations. The observed surface morphologies of aerosol particles, including irregular, aggregate, and chain-like structures, play a significant role in the formation and optical properties of BrC. These morphologies provide a large reactive surface area that facilitates the heterogeneous adsorption and condensation of gaseous phenolic precursors and other organic compounds onto existing particles. Such interactions promote the chemical aging processes like nitration and oxidation, which enhance the light-absorbing capacity characteristic of BrC (Hossen et al., 2025).

Hossen, M. A. amin, Roy, S., Nahian, S., Zaman, S. U., Selim, A., and Salam, A.: Spectral characteristics of water-soluble Brown carbon and it's radiative impacts on the atmosphere of Dhaka, Bangladesh, Atmos Environ, 351, 121185, https://doi.org/10.1016/J.ATMOSENV.2025.121185, 2025.

5. The authors should include the descriptive data of the phenolic compounds as supplementary material, providing additional important information beyond just the figures in the manuscript.

Response: Thank you for your valuable suggestion. We have already included comprehensive seasonal descriptive data of the phenolic compounds (concentration tables, calibration details, and chromatograms) as supplementary material. In the revised version, we have further added the individual monthly average data with standard deviations to the supplementary file, according to your suggestion as follows:

Table S7: Concentration of phenolic precursors of BrC at Dhaka North site from July 2023 to January 2024

Months	**Concentration of phenolic compounds (µg m^{-3}) at Dhaka North site**						
	Ph	**2-MPh**	**3-MPh**	**2-MOPh**	**2,4-DMPh**	**2-HPh**	**4-NPh**
July	0.093±0.01	0.072±0.023	0.142±0.028	0.242±0.040	0.022±0.008	1.348±0.051	1.248±0.022
August	0.0878±0.015	0.043±0.011	0.112±0.030	0.270±0.037	0.018±0.009	1.493±0.043	1.444±0.06
September	0.0907±0.02	0.073±0.015	0.140±0.041	0.160±0.023	0.023±0.012	1.471±0.036	1.338±0.02
October	0.1254±0.03	0.076±0.020	0.156±0.027	0.258±0.042	0.025±0.01	1.402±0.029	1.343±0.051
November	0.1512±0.023	0.133±0.04	0.234±0.029	0.404±0.035	0.040±0.013	2.153±0.045	1.961±0.034
December	0.1357±0.033	0.109±0.025	0.217±0.051	0.400±0.037	0.025±0.011	2.178±0.056	1.992±0.024
January	0.0962±0.02	0.074±0.013	0.147±0.034	0.257±0.040	0.023±0.015	1.460±0.031	1.258±0.033

Note: 4-NPh= 4-nitrophenol, 2-HPh= 2-hydroxyphenol, Ph= phenol, 2-MPh= 2-methylphenol, 3-MPh= 3- methylphenol, 2-MOPh= 2-methoxyphenol, 2,4-DMPh= 2,4-dimethylphenol

Table S8: Concentration of phenolic precursors of BrC at Dhaka South site from July 2023 to January 2024

Months	Concentration of phenolic compounds (µg m^{-3}) at Dhaka South site						
	Ph	2-MPh	3-MPh	2-MOPh	2,4-DMPh	2-HPh	4-NPh
July	0.220±0.02	0.106±0.03	0.161±0.04	0.265±0.03	0.028±0.034	1.521±0.028	1.496±0.05
August	0.095±0.011	0.077±0.012	0.133±0.023	0.178±0.018	0.021±0.011	0.979±0.025	0.893±0.025
September	0.299±0.034	0.217±0.015	0.371±0.045	0.486±0.045	0.063±0.015	1.521±0.045	2.181±0.035
October	0.245±0.021	0.232±0.05	0.394±0.05	0.480±0.03	0.066±0.01	2.496±0.061	2.199±0.045
November	0.154±0.023	0.141±0.011	0.312±0.06	0.216±0.031	0.045±0.012	2.264±0.065	2.807±0.040
December	0.326±0.045	0.311±0.02	0.493±0.051	0.575±0.043	0.084±0.02	2.619±0.05	2.456±0.043
January	0.64±0.05	0.651±0.022	1.101±0.035	1.451±0.05	0.187±0.06	7.455±0.052	6.621±0.023

Note: 4-NPh= 4-nitrophenol, 2-HPh= 2-hydroxyphenol, Ph= phenol, 2-MPh= 2-methylphenol, 3-MPh= 3- methylphenol, 2-MOPh= 2-methoxyphenol, 2,4-DMPh= 2,4-dimethylphenol

6. Section 3.5: Should the methodology of this section and the formula of the interaction be included in the Methodology Section?

Response: Thank you for your suggestion. We have added this to the methodology section 2.6 as follows:

2.6 Nitration Experiment of Catechol to Formation of Light-Absorbing Product

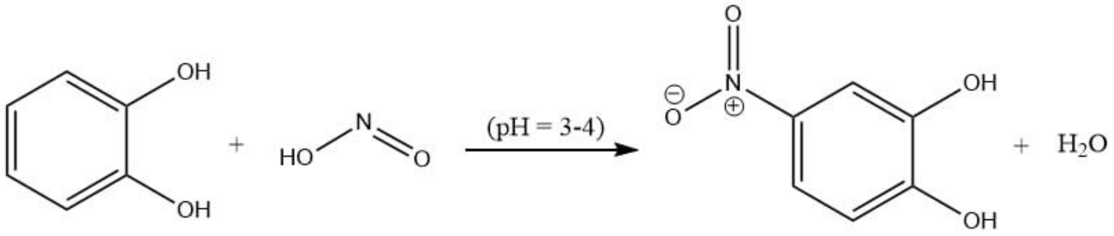
Nitrophenols are the major component of light-absorbing atmospheric organic aerosol, commonly referred as brown carbon. Most of the nitrophenol formation pathways involve the reactions of phenolic compounds with NO_3, and NO_2 in the gas phase in ambient atmosphere (Wang et al., 2023). Aqueous phase nitration of 1,2 dihydroxy phenol (catechol) forms a major component of brown carbon such as 4-nitrocatechol. Catechol is produced from biomass burning and vehicle emissions. This catechol reacts with nitrous acid in the aqueous phase to form secondary aerosol nitrophenol which is the major light-absorbing component of organic aerosol.

Table-1: List of required reagents for the laboratory experiments to study the formation of nitro-aromatic compounds.

S/N	**Reagents**	**Required Concentration**
1.	Catechol (1,2-dihydroxybenzene), $C_6H_4(OH)_2$	1 mM
2.	Sodium Nitrite, $NaNO_2$	1 mM
3.	Sulfuric Acid, H_2SO_4	0.1 M
4.	Ammonia Buffer (pH~8) & 6% H_2O_2	Used for alkaline conditions
5.	Hydrogen Peroxide, H_2O_2	6%

For the nitration reaction, a solution of 1 mM 1,2 dihydroxy benzene and 1 mM $NaNO_2$ is prepared by deionized water in a 50 mL volumetric flask. The 1:1 ratio of catechol and sodium nitrite undergoes a chemical reaction both in acidic (pH=3-4, pH adjusted by 0.1 M H_2SO_4 and NaOH) and alkaline medium (used ammonia buffer to maintain pH=8-9, and H_2O_2, which facilitates more NO_2^+) to form nitrated phenol. The pH of the solution was measured by a pH meter (model L-510, voltage DC 5V, S/N PK51028202310104). During the reaction continuously measured the absorbance at different times and observed the change of absorbance with time.

Reaction:



Comments of CC1:

Comment: This research focuses on brown carbon (BrC) phenolic precursors in the South Asian megacity of Dhaka, filling a gap in the region's understanding of $PM_{2.5}$ in the quantification of phenolic compounds and the study of formation mechanisms, which is of great value in understanding atmospheric pollution and climate change in tropical cities. Combining various techniques such as GC-FID, FESEM-EDX, and ATR-FTIR, we systematically analyzed the chemical composition, surface morphology, and functional groups of $PM_{2.5.}$ The chemical composition, surface morphology and functional groups of PM_5 were systematically analyzed, and the aqueous-phase nitrification experiments also provided evidence for a new mechanism of BrC formation. The research design is reasonable, the data are detailed, the logic is clear, and the conclusions are reliable and of publication value. I suggest a slight revision for publication in this journal.

Response: We thank the reviewer for his thorough reading of our manuscript and valuable suggestions. We have addressed each and every comment and made subsequent changes to the manuscript. We believe the manuscript has greatly improved after incorporating the comments.

1. It is recommended to further emphasize the comparison with other cities around the globe in the introduction section to highlight the uniqueness of Dhaka's high pollution characteristics and enhance the regional representativeness of the study.

Response: Thank you for your suggestion. We have added comparisons with other cities worldwide in the introduction to better highlight Dhaka’s unique pollution characteristics. The revised introduction is given below.

1. Introduction

Brown carbon (BrC) is a type of organic carbon that absorbs light at shorter wavelengths, such as 300-400 nm (Laskin et al., 2015). In contrast to black carbon, brown carbon exhibits a wavelength-dependent absorptivity that increases significantly towards the higher energy end of the spectrum (Wang et al., 2023). Similar to black carbon, brown carbon (BrC) also has a positive radiative effect, which lowers the total cooling effect of atmospheric aerosols caused by light scattering (Feng et al., 2013). Because of the complexity and variety of its origins, composition, and atmospheric aging mechanisms, the direct radiative effect of BrC is still unknown despite intensive research (Lee et al., 2014). The two main sources of BrC were automobile emissions and biomass burning. The composition of primary emissions can differ significantly depending on the type of fuel and the conditions under which it burns (Laskin et al., 2015c). There are probably thousands of organic molecules in atmospheric BrC, many of which are unidentified. However, phenolic compounds are a class of components that are commonly discovered (Wang et al., 2018). Phenolic and nitrated phenols are organic substances that contain at least one hydroxyl group and nitro group in the benzene ring. Phenolic derivatives are the major composition of BrC. They originate from diverse processes of production and different emission sources. Large volumes of nitrated phenolic compounds are released into the atmosphere by primary sources such as vehicle exhaust, burning of biomass, and combustion of coal (Li et al., 2020; Wang et al., 2020).The secondary synthesis of these substances from precursors like aromatic hydrocarbons and phenolic compounds via nitration in both gaseous or aqueous phases (Harrison et al., 2005).

According to earlier research, one of the main contributors of brown carbon is nitrated phenolic compounds and R-NO_2 nitroaromatic compound (Hossen et al., 2023; Li et al., 2022). The main reasons for the increased focus on phenolic compounds are their human toxicity (Rahman et al., 2022) and their role in producing secondary organic aerosols (SOAs) (Nakao et al., 2011). According to previous research Harrison et al., (2005), phenol and cresols (such as m-cresol, p-cresol, and o-cresol) can oxidize to produce nitrophenol and its derivatives. Cresols released during the burning of biomass can undergo photooxidation, producing nitro-catechol and its derivatives (Finewax et al., 2018; Iinuma et al., 2010). Furthermore, a study conducted by Andreozzi et al., (2006) and Hummel et al., (2010) have demonstrated that the primary pathway for the creation of 3-nitrosalicylic acid and 5-nitrosalicylic acid in the aqueous phase is the nitration of salicylic acid. Laboratory investigations have established the importance of aqueous processes as a production mechanism for nitrated phenolic compounds. In particular, when phenol was subjected to aqueous-phase interactions with nitronium ions (NO_2^{+}), 4-nitrophenol was produced (Heal et al., 2007). The most prevalent nitro-aromatic species were nitrophenols and nitro catechols, which accounted for 31% and 32% of all nitro-aromatic compounds, respectively (Wang et al., 2021). To fully understand the precursor of BrC in the atmosphere, it is crucial to analyze the concentrations, chemical compositions, and sources of their phenolic precursors, along with the derivatives of nitrated and methyl derivatives of phenols. Aerosol surface morphology plays an important role in the light-absorbing properties and reactivity of BrC. Irregular or porous particle surfaces can enhance the adsorption of gaseous precursors, such as phenolic compounds, thereby influencing their heterogeneous oxidation and nitration pathways in the atmosphere. Moreover, morphological features can affect how BrC and its phenolic components interact with cloud or fog droplets, altering aqueous-phase reaction rates and the formation of light-absorbing secondary products.

In Bangladesh, most pollutants originate from vehicle emissions, solid waste burning, biomass burning, and brick kiln emissions (Hossain et al., 2024; Kumar et al., 2021). All these are major sources of BrC. Therefore, studies on BrC composition—such as phenolic compounds and their derivatives—in Bangladesh are essential. In previous studies, Ankhy et al., (2024); Hossen et al., (2023); and Runa et al., (2022) determined the optical properties of BrC emissions from biomass burning as well as ambient air in Dhaka, Bangladesh, but did not investigate the individual composition of BrC. Previous studies have primarily emphasized gas-phase reactions between phenolic VOCs and NOx, followed by photochemical oxidation and subsequent partitioning into the particle phase (Hems et al., 2021; Laskin et al., 2015). Yang et al., (2021) reported that photooxidation of phenolic compounds forms BrC, and phenolic compounds are a major class of aromatic compounds known as BrC precursors. Li et al., (2020) show the formation pathway of nitro aromatic compounds via gas-phase reactions, occurring through $^{*}OH + NO_2$ in daytime and $^{*}NO_3 + NO_2$ at nighttime. Our study reports an alternative pathway for the formation of nitroaromatic compounds in aqueous-phase reactions through electrophilic substitution (mediated by NO_2^{+} or HONO) under acidic or alkaline conditions in the absence of sunlight, with demonstrated applicability to biomass samples. The main focus of this work, however, is the quantification of phenolic precursors of BrC. Specifically, we investigate the surface composition of $PM_{2.5}$ and phenolic precursors in the atmosphere of Dhaka, Bangladesh, from July 2023 to January 2024, along with an experiment on the aqueous nitration of 2-hydroxyphenol, a common BrC precursor.

2. The experiments were conducted under acidic conditions, while the actual pH range of the atmosphere is much wider, and it is recommended that the effect of different pH conditions on the nitrification reaction be discussed, or that additional comparisons of atmospheric droplet pH data in the field be made.

Response: Thank you for your valuable comment. We agree with your observation. Aqueous-phase nitration is generally favored under acidic conditions (pH ~3–4). However, we also conducted experiments under alkaline conditions (pH ~8) using an ammonium buffer, followed by H_2O_2 addition, which facilitated greater NO_2^+ formation. These details have been added to the revised manuscript.

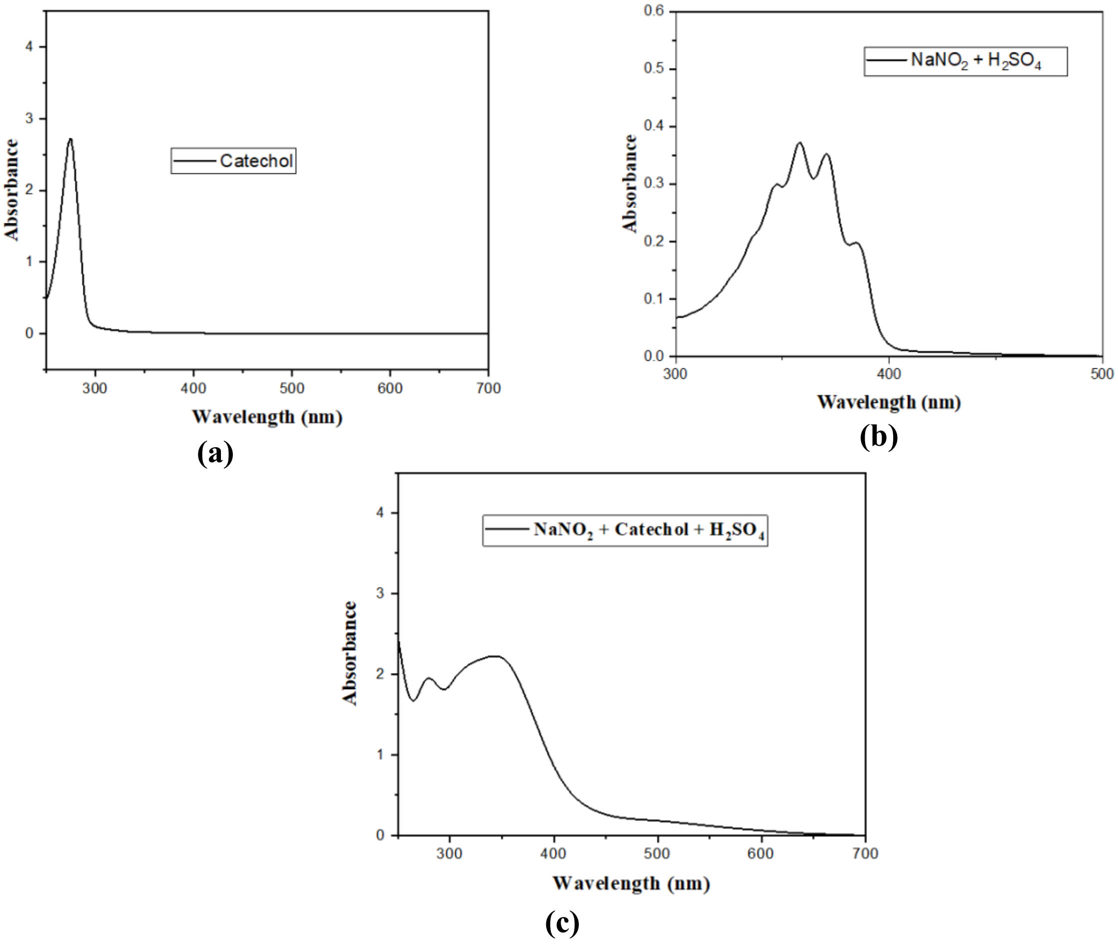
3.5 Formation of light-absorbing nitro-aromatic compounds

In our study, we quantified several common brown carbon (BrC) precursors in the ambient atmosphere. Among them, 2-hydroxyphenol and 4-nitrophenol were found in the highest amount in our sampling area, both of which are well-known products of biomass burning. To gain a better understanding of the possible formation processes of nitroaromatic compounds under atmospheric conditions, we conducted controlled aqueous-phase nitration experiments in the laboratory.

In these experiments, catechol (2-hydroxyphenol), selected because it was the most abundant precursor detected in our samples, was reacted with sodium nitrite under both acidic conditions (pH adjusted using H_2SO_4 and NaOH) and basic conditions (pH adjusted using ammonia buffer, with H_2O_2 added to enhance NO_2^- production) to form light absorbing nitro aromatic compound.

3.5.1. UV-visible light absorption properties of the catechol-nitrite reaction system

The catechol (2-hydroxyphenol) absorbs the UV-visible light at 280 nm (peak at 280 nm) (Scalzone et al., 2020). When it reacted with the sodium nitrite in the presence of H_2SO_4, the peak (λ_{max}) was shifted to a longer wavelength. This shift of λ_{max} indicated that there was an interaction between 2-hydroxyphenol and the nitrite ions in the reaction system (Fig.5).



(a)

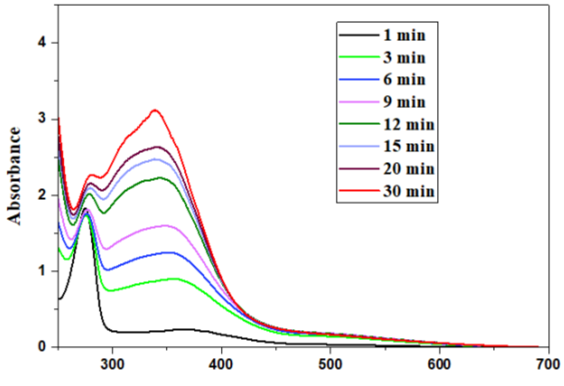
(b)

(c)

Fig.5: Absorbance of (a) single catechol, λ_{max}=275 nm, (b) $NaNO_2 + H_2SO_4$, and (c) reaction system (catechol-nitrite)

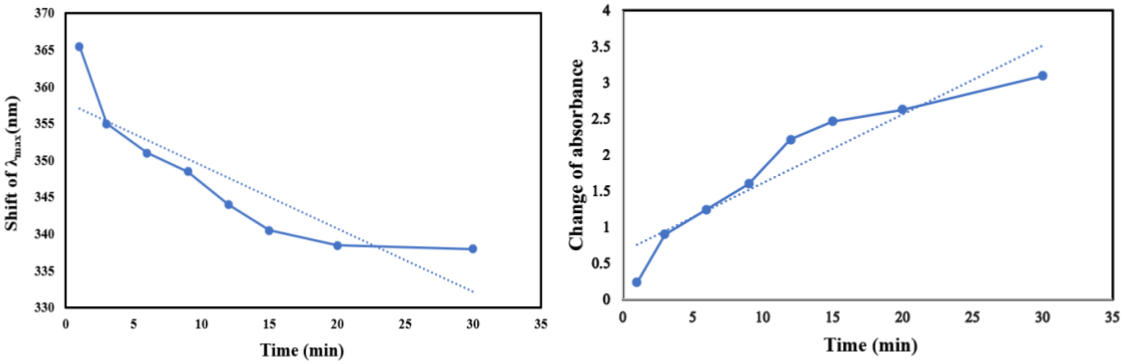
The change of absorbance with time at pH=3.5 of the catechol-nitrite reaction system is represented in Fig.6. At pH=3.5 the absorbance gradually increases with time in the wavelength range from 300 – 700 nm and the λ_{max} shifted to a shorter wavelength with time increase.

Initially, at 1 min the λ_{max} obtained at 355 nm then as time increased the absorbance increased gradually and the λ_{max} shifted to a shorter wavelength such as 338 nm after half an hour and no change further increase in time (Fig.6a). It is clear from this change that the nitro group has been added to the aromatic ring, leading to an increase in absorption and a shift in the position of the peak.



(a)

Time (min)	λ_{max}(nm)	Change of absorbance
1	365.5	0.236
3	355	0.899
6	351	1.246
9	348.5	1.598
12	344	2.216
15	340.5	2.466
20	338.5	2.628
30	338	3.094



(c) (d)

Fig.6: (a) Change of the absorbance with times of the reaction system containing 1 mM 2-hydroxyphenol and 1 mM $NaNO_2$ at pH=3.0. A distinct color denotes the duration of the sample run in the ultraviolet-visible spectrophotometer. The initial reactant contribution was subtracted from each spectrum. Table (b) Data for the shift of peak and change of absorbance, (c) Shift of λ_{max} with time, and (d) Change of absorbance with time

Fig. 6 shows the UV–Vis spectrum of the $NaNO_2$ and 2-hydroxyphenol reaction system in acidic medium shows a clear time-dependent evolution in absorbance over the 1–30 min period, indicating progressive formation of new light-absorbing species. At the early stage (1 min), the spectrum is dominated by the characteristic π→π* transition of the aromatic ring near 270–280 nm with relatively low intensity in the higher wavelength region. As the reaction proceeds, both the main aromatic band and a second band in the 300–350 nm region gradually increase in intensity, with the latter showing a slight bathochromic shift. This hyperchromic effect and modest red-shift are consistent with the formation of nitro-substituted aromatic compounds such as o- or p-nitrophenol. The strong electron-withdrawing nature of the nitro group extends conjugation and enhances n→π* and charge-transfer transitions, leading to stronger and slightly longer wavelength absorption than the parent phenol. The continuous increase in absorbance with time, without any later decline, confirms the accumulation of these nitro-aromatic products in solution. This spectral change therefore provides strong evidence that the reaction proceeds through electrophilic aromatic substitution of 2-hydroxyphenol by nitronium ions generated from $NaNO_2$ in the acidic medium, yielding stable nitro-phenol derivatives with enhanced UV absorption.

Reaction in alkaline medium

At high pH, nitrite remains primarily in the form of NO_2^-, and the formation of electrophiles such as HONO, NO_2^+, or N_2O_3 is strongly suppressed. Although phenolates are highly activating toward substitution, the lack of these electrophilic species makes aromatic nitration largely ineffective. However, the presence of peroxide facilitates the formation of NO_2^+.

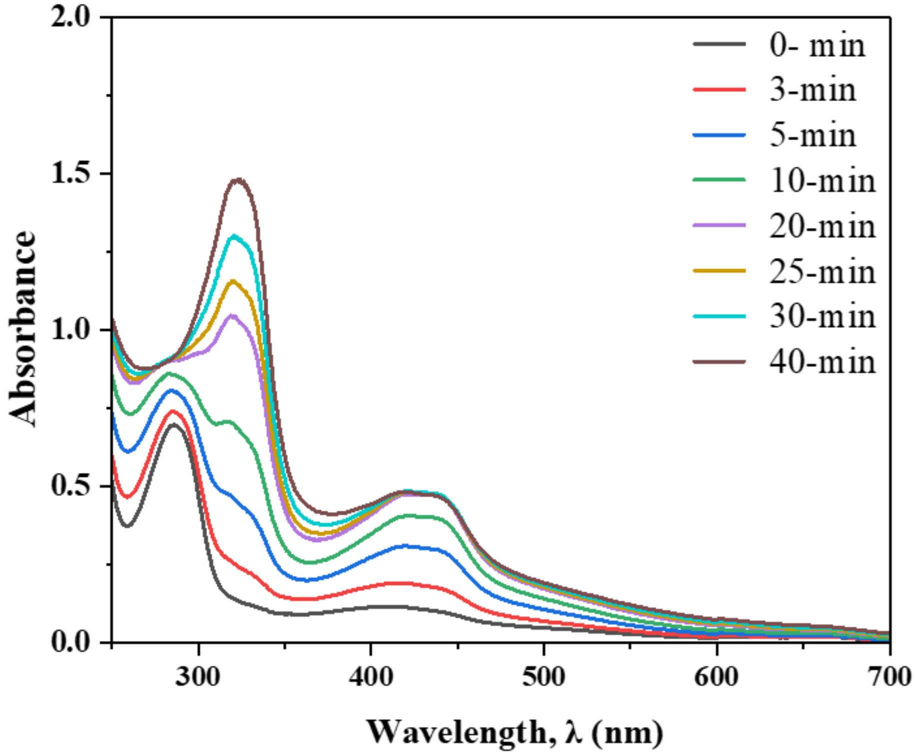


Fig. 8: UV-visible absorption spectra of the nitrite-catechol reaction system in alkaline medium pH~7-8 to form a light-absorbing nitro aromatic compound

Fig. 8, the UV–Vis spectra of the $NaNO_2$–2-hydroxyphenol system in alkaline medium with H_2O_2 show a time-dependent evolution of absorption features, indicating the formation of light-absorbing products. Initially, the spectrum is dominated by the characteristic UV absorption of phenolate anions (~280–300 nm), but with reaction time (0–15 min) the peak intensity increases and a broad shoulder emerges and intensifies in the 350–450 nm region. This bathochromic shift and visible-range growth reflect the formation of conjugated nitroaromatic and quinone-like species with extended π-systems, likely via oxidation of phenolate by HO_2^-/oxidants and subsequent nitration by reactive nitrogen species from nitrite. The progressive increase in visible absorption is consistent with the generation of chromophoric, brown carbon-type products with potential atmospheric light-absorbing properties. These spectral changes strongly suggest nitro-substituted aromatic and quinone-type chromophores are forming in the system.

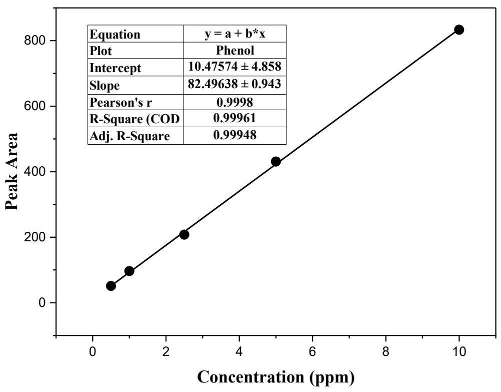
Under acidic conditions, nitrite generates the potent electrophile NO_2^+ (via HNO_2/HNO_2^+) and N_2O_3/NO^+ equilibria). The activated aromatic ring of phenol or catechol then undergoes rate-determining electrophilic attack by NO_2^+ to form the Wheland (σ) intermediate, directed ortho/para by the OH group(s). Subsequent deprotonation restores aromaticity, yielding the nitroaromatic product. The reaction mechanism of the nitration of aromatic compounds takes place through the reaction with an aqueous nitrite solution. Esteves et al., (2003) have also suggested that the exceedingly potent electrophile NO_2^+ facilitated the reaction at a low pH. The NO_2^+ electrophile attacks the benzene ring and forms a C-N bond. According to Wang et al., (2023) HONO acts as an electrophile in the aqueous nitration of catechol (2-hydroxybenzene). This explains the accelerated nitration rate in acidic environments, as HONO, being a stronger electrophile than NO_2^-, is more readily formed at lower pH levels.

3. The GC-FID quantification section mentions method validation but does not show the linear correlation coefficient (R^2) of the standard curve, and it is recommended that this be added to the supplementary material.

Response: Thank you for your comment. The calibration curves, including their linear correlation coefficients (R^2), were already provided in the supplementary material (section 2. Generated a Calibration Curve of Individual Standard Phenolic Compounds). The section is given below.

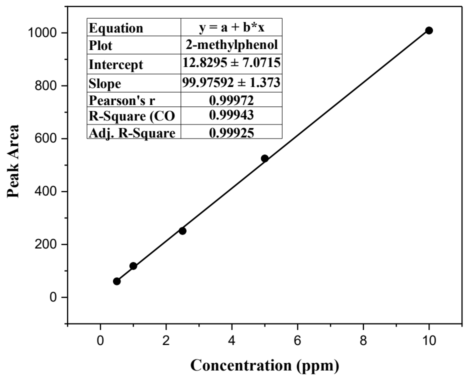
2. Generated a Calibration Curve of Individual Standard Phenolic Compounds

The calibration curve for quantifying the phenolic component was established using the reference standard phenolic solution. A calibration curve was generated by graphing the peak area against the concentration by originPro 2024 software. The individual calibration curves for the desired chemicals are provided below.



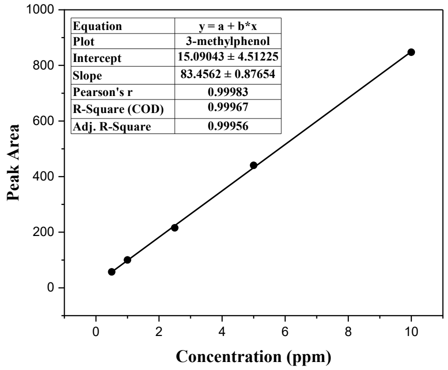
Equation	y = a + b*x
Plot	Phenol
Intercept	10.47574 ± 4.858
Slope	82.49638 ± 0.943
Pearson's r	0.9998
R-Square (COD	0.99961
Adj. R-Square	0.99948

(a) Phenol



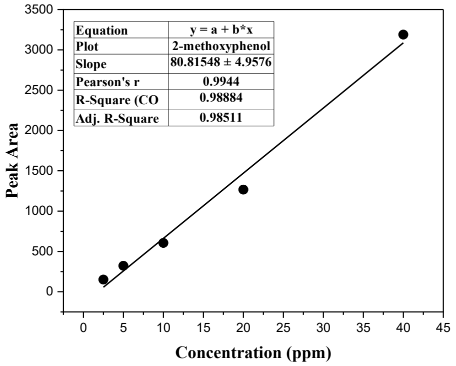
Equation	y = a + b*x
Plot	2-methylphenol
Intercept	12.8295 ± 7.0715
Slope	99.97592 ± 1.373
Pearson's r	0.99972
R-Square (CO	0.99943
Adj. R-Square	0.99925

(b) 2-methylphenol



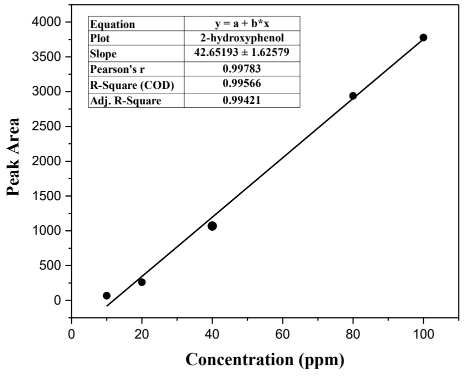
Equation	y = a + b*x
Plot	3-methylphenol
Intercept	15.09043 ± 4.51225
Slope	83.4562 ± 0.87654
Pearson's r	0.99983
R-Square (COD)	0.99967
Adj. R-Square	0.99956

(c) 3-methylphenol



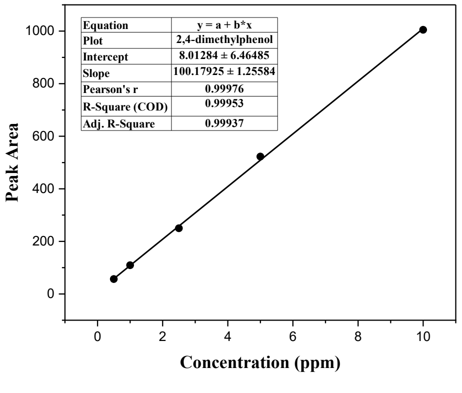
Equation	y = a + b*x
Plot	2-methoxyphenol
Slope	80.81548 ± 4.9576
Pearson's r	0.9944
R-Square (CO	0.98884
Adj. R-Square	0.98511

(d) 2-methoxyphenol



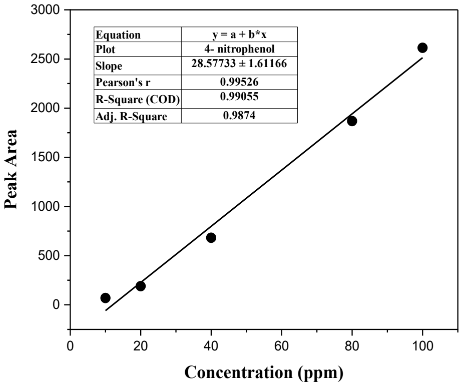
Equation	y = a + b*x
Plot	2-hydroxyphenol
Slope	42.65193 ± 1.62579
Pearson's r	0.99783
R-Square (COD)	0.99566
Adj. R-Square	0.99421

(e) 2-hydroxyphenol



Equation	y = a + b*x
Plot	2,4-dimethylphenol
Intercept	8.01284 ± 6.46485
Slope	100.17925 ± 1.25584
Pearson's r	0.99976
R-Square (COD)	0.99953
Adj. R-Square	0.99937

(f) 2,4-dimethylphenol



(g) 4-nitrophenol

Fig. S2: Calibration curve for seven phenolic compounds

4. Some of the tables do not show all compound associations in full, and the data in the abstracts need to be formatted consistently with the body presentation to improve readability.

Response: Thank you for your comment. We have revised the tables to include all compound associations in full and reformatted the data in the abstract to be consistent with the presentation in the main text, improving overall readability.