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Composition and Formation Mechanism of Brown Carbon: Identification and Quantification of Phenolic Precursors

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Abstract

Light-absorbing organic aerosols, 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 FESEM-EDX, and functional groups were characterized using 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 role of aqueous-phase reactions and urban sources in BrC formation, offering critical insights for future atmospheric modeling and air quality management strategies in South Asia.

Keywords: Phenolic compounds, functional groups, surface morphology, nitrophenol

1. Introduction

The term "brown carbon" (BrC) describes organic aerosol particles in the atmosphere that absorb light. 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., 2015). 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.

In Bangladesh most of the pollutants are comes from vehicle emissions, solid waste burning, biomass burning, and brick klin emissions (Hossain et al., 2024; Kumar et al., 2021). All these are the major sources of BrC. So studies about BrC composition such as phenolic compounds and its derivatives in Bangladesh is very essential topics. In previous study, Ankhy et al., (2024); Hossen et al., (2023); and Runa et al., (2022) determined the optical properties of BrC emission from biomass burning as well as ambient air in Dhaka Bangladesh. They do not investigate the individual composition of BrC. Yang et al., (2021) investigated that photooxidation of phenolic compounds forms the brown carbon and phenolic compounds are a major class of aromatic compounds which are known as brown carbon precursors. In this study, focused on the surface composition of $PM_{2.5}$, phenolic precursors of BrC in the atmosphere of Dhaka, Bangladesh from July 2023 to January 2024 and the investigation of aqueous nitration of 2-hydroxyphenol (common precursors of BrC) in the laboratory.

2. Methodology

2.1 Sampling sites

$PM_{2.5}$ samples were collected from ambient air at two distinct locations in Dhaka city: Dhaka North (Shah Alibag, Mirpur-1) and Dhaka South (Department of Chemistry, University of Dhaka) (Fig. S1). Both sampling sites were situated approximately 21 meters above the ground level. The Dhaka South site, while located within an educational institution, was adjacent to a busy highway with frequent traffic congestion. Additionally, metro rail construction was ongoing nearby, further contributing to the area's pollution levels. The Dhaka North site, a mixed residential and commercial zone, was surrounded by garment factories, pharmaceutical plants, shopping centers, and restaurants. It was situated about 100 meters from the Mirpur bus station and approximately 4 kilometers from the Taltola solid waste dumping yard.

2.2 Sample Collection

$PM_{2.5}$ samples were collected using a High-Volume Air Sampler equipped with a $PM_{2.5}$ impactor, operating at a flow rate of 16.7 L/min, and $PM_{2.5}$ particulates were captured on Quartz filter paper (Gelman, Membrane Filters, type TISSU Quartz 2500QAT-UP, 47 mm diameter). Before sampling, each Quartz filter was heated at 800°C for 4 hours in a furnace to remove any organic impurities. Sampling was conducted concurrently at both locations (Dhaka South and Dhaka North sites) from July 2023 to January 2024. Each month, four samples were collected from both sites. The sampling period was 24 hours. 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. Flow diagram are given below Fig.1

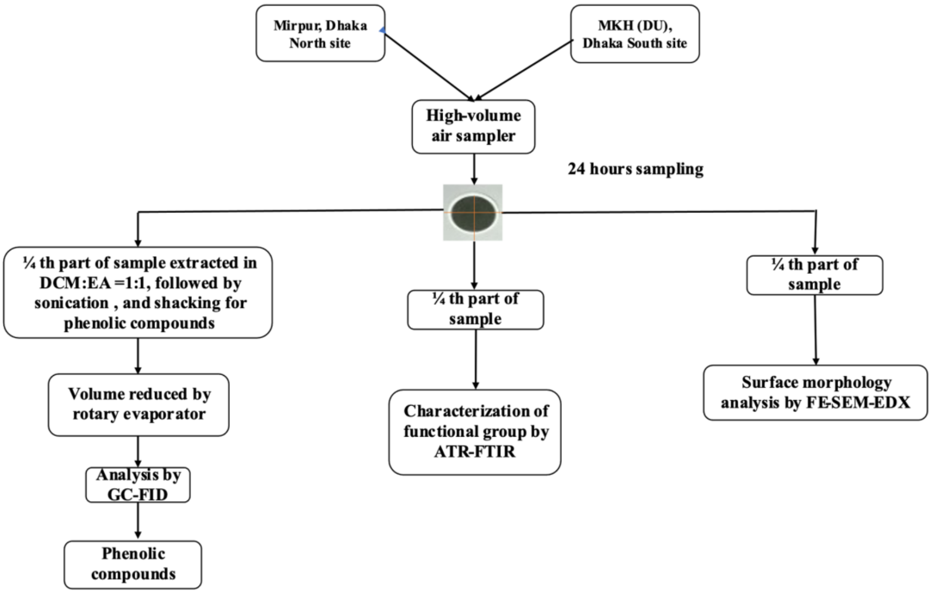

Fig.1: Schematic diagram of overall analysis

2.3 SEM-EDX Analysis

Morphological and chemical analyses of PM$_{2.5}$ were performed by field emission scanning electron microscopy (FE-SEM, Zeiss Sigma 300 VP with 2 Bruker Quantax Xflash 60 mm^2 SDD EDS Detectors). For obtaining a high-resolution SEM image each sample was kept in a desiccator for 1 hour and then freeze-drying 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. The sample surface was subjected to gold sputtering to enhance its conductivity. Due to the presence of non-conducting particles on the surface, the electron beam will collide with the sample, resulting in the accumulation of charge and causing a charging effect that leads to fuzzy pictures which was minimized by gold sputtering. The microscope is controlled entirely by the SmartSEM software suite developed by Zeiss. After gold sputtering under reduced pressure, the sample holder was inserted into the chamber of the SEM-EDX instrument. Air from the chamber was evacuated. When the pressure was reduced below ~ 0.009 Pa extra high tension (EHT) was enabled. SEM image was obtained with an EHT value of 2.0 kV and EDX was performed with an EHT value ranging from 10kV -15kV. The SDD detector was utilized for EDX analysis. For obtaining the EDX report ESPRIT Spectrum software package was used. The images obtained from SEM and EDX were analyzed by the ImageJ software package. For the morphology study, samples collected on filters may introduce positive artifacts and uncertainties due to the fiber structure of the filters. However, SEM-EDX analysis of these filter samples has been widely employed for the morphological and elemental characterization of individual airborne particles (Park et al., 2023).

2.4 ATR-FTIR analysis

An attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometer (Shimadzu, IRPrestige-21, Japan) was utilized to examine the chemical functional group of brown carbon according to Hossen et al., (2023). IR spectra of the samples were obtained within the range of wave number 700–4000 cm^{-1}. Since an ATR probe was utilized in ATR-FTIR, sample preparation was not needed. It is a non-destructive process. During ATR-FTIR analysis, the sample was kept on the crystal (ATR probe), which is composed of high refractive index materials such as AgCl and Si. In this process, infrared (IR) radiation incident on the crystal and interacts with the sample on its surface.

2.5 Sample Extraction and Chemical Analysis

To identification and quantification 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. During the extraction process mouth of the conical flask is completely closed by a cap. The extracted solution was filtered by a syringe filter (PTFE, 0.45 µm). The volume was reduced to approximately 1.0 mL by the rotary evaporator. The final extracted samples were kept in the refrigerator at 4°C until analysis in a gas chromatography-flame ionization detector (GC-FID). The phenolic precursors of BrC in the extracted sample solutions were identified and quantified by gas chromatography coupled with flame ionization detector (GC-FID) (**model**: Varian 450-GC, **column**: VF-5 ms (30m x 0.25mm,ID 0.25µm), **carrier gas**: N_2, Air, H_2, **detector temperature**: 280°C, **Split ratio**: 20, **injection volume**: 1.0µL, **column flow**: 1.2 mL/min, **column temperature**: Initial 60°C (2min hold),180°C (8°C ram/min), 180°C (10°C ram/min,) 4 min hold, **total run time**: 27 min).

Standard solution of seven phenolic compounds such as Phenol (MERCK-Schuchardt), 2-methylphenol (MERCK-Schuchardt), 3-methylphenol (MERCK-Schuchardt), 2-methoxyphenol (MERCK-Schuchardt), 2,4-dimethylphenol (MERCK-Schuchardt), 2-hydroxyphenol (MERCK-Schuchardt), 4-nitrophenol (MERCK-Schuchardt) were prepared using the solvent 1:1 dichloromethane and ethylacetate. Also prepared a mixed standard including these seven standard phenolic compounds. The concentrations of the prepared standard solution were 0.5, 2.5, 5.0, 10.0, 20.0, 40.0, 60.0, 80.0, and 100.0 ppm. At first run the individual standard solution to identify the retention time of target compounds. Then the mixed standard solution was injected into the gas chromatography to separate the individual phenolic compounds. The presence of phenolic compounds in the ambient sample was identified by the presence of a peak at a characteristic retention time in the sample chromatogram compared to that of the chromatogram of the standard solution. On the other hand, the quantitative analysis was conducted by comparing the peak areas of the compounds to those of a standard solution, achieved through the creation of a calibration curve (Fig.S2). Method validation including the limit of detection (LOD), limit of quantification (LOQ), and recovery rate was also carried out for this method of quantification of phenolic

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precursor. The details are described in the supplementary file in section 2. In a brief, the recovery experiment was carried out in three samples by spiking a known amount of standard solution. A blank sample and the two samples that gave very less signal/peak in the chromatogram were used as a sample matrix for the recovery test. A known amount of standard solutions was spiked to the filter sample and allowed the sample to stand for an hour to let the phenolic compound be absorbed into the filter matrix. Then extract this spiked sample by the same process of sample extraction. The average recovery rate of the samples was 85% which is in the acceptable range (Table S1).

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.

Chemical reagent: 1. 1 mM Catechol (1,2 dihydroxy benzene)
2. 1 mM $NaNO_2$
3. 0.1 M H_2SO_4

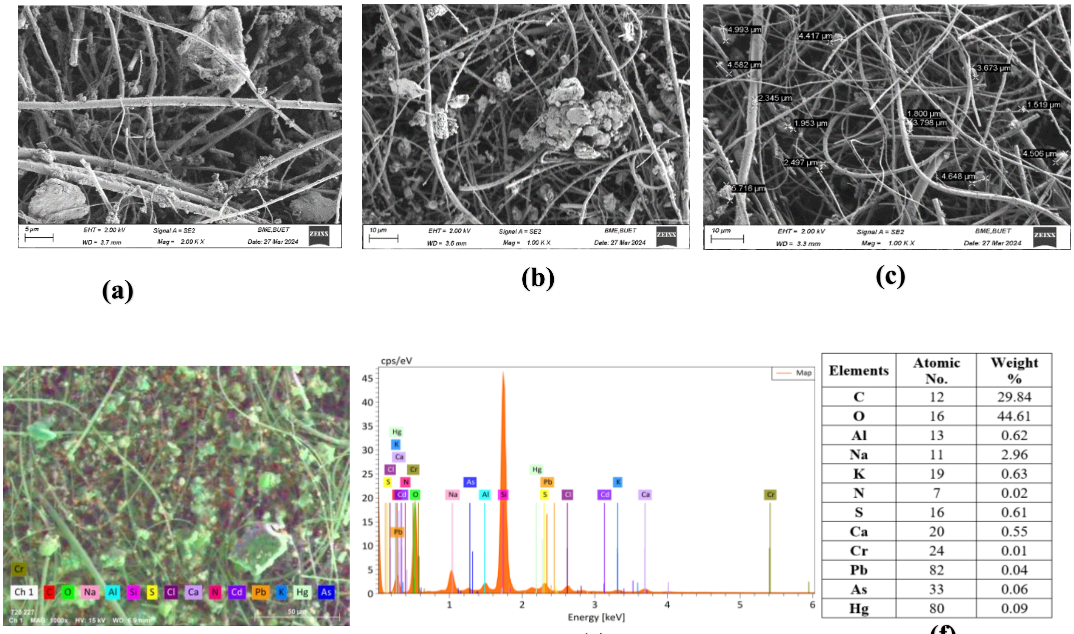
For the nitration reaction, a solution of 1 mM 1,2 dihydroxy benzene and 1 mM $NaNO_2$ is prepared by deionized water in a 50 mL volumetric flask. The 1:1 ratio of catechol and sodium nitrite undergoes a chemical reaction at pH=3-4 (pH adjusted by 0.1 M H_2SO_4 and NaOH) to form nitrated phenol. The 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.

3. Results and Discussion

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.2), which included irregular, aggregate form, and chain-like constituents. Chemical compositions were categorized into carbonaceous, mineral dust, and trace metal. The majority of $PM_{2.5}$ particles have asymmetrical shapes. The SEM image indicates that the size of the particles in $PM_{2.5}$ is approximately 2.5 µm and less than 2.5 µm. However, the aggregate and chain-like particle sizes exceed 2.5 µm (range: 1.88 to 4.99 µm) **(**Fig.2c).



(a) (b) (c)

(d) (e) (f)

Elements	Atomic No.	Weight %
C	12	29.84
O	16	44.61
Al	13	0.62
Na	11	2.96
K	19	0.63
N	7	0.02
S	16	0.61
Ca	20	0.55
Cr	24	0.01
Pb	82	0.04
As	33	0.06
Hg	80	0.09

Fig.2: SEM images of $PM_{2.5}$ loaded filter in (a) Dhaka North site (b) Dhaka, South site and (c) size distribution of particles in $PM_{2.5}$ loaded sample; (d) EDX mapping, (e) Spectra of $PM_{2.5}$ and (f) relative abundance of elements in $PM_{2.5}$

The varying size distributions of surface particles have a direct correlation with the meteorological conditions and emission sources. The aerosol particles in the atmosphere are produced by homogeneous nucleation and heterogeneous condensation (Kulmala et al., 2001). Homogeneous nucleation is the process of creating new particles from gaseous substances without any existing particles present. On the other hand, heterogeneous condensation refers to the transformation of unstable vapors into a solid or liquid phase on the surface of existing seed particles. When the generation process of particles occurs in the environment, the small particles grow due to collision with the surface of the pre-existing particles (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.

3.2 Surface Elements Analysis

According to the EDX data surface chemical compositions were categorized into carbonaceous, mineral dust, and trace metal. Fig.2d,e,f 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). The sequence of carbonaceous elements (C, O, N, and S) in Dhaka North & South sites was O > C > N > S. Their possible emission sources are the combustion of fossil fuels and biomass burning. Sulfur emitted from coal combustion and N mainly comes from agricultural land and fertilizer. The sequence of abundance for minerals is Al > Ca > K > Fe. These minerals originate from mineral dust, biomass burning, and industrial waste. The trace heavy metals were present in meager amounts. Among the five harmful trace metals (Hg, Cr, Pb, Cd, As), lead has the highest abundance of surface elements, while the abundance of Hg was the lowest.

3.3 Characterization of Functional Group

The chemical functional group of brown carbon was examined using an ATR-FTIR spectrophotometer. Initially, we obtain a spectrum for a blank quartz filter paper and subsequently deduct it from the spectrum of the sample. The materials were analyzed using infrared spectroscopy in the wavenumber range of 600 – 4000 cm^{-1}. ATR-FTIR utilized an ATR probe, eliminating the requirement for sample preparation.

The IR spectra (Fig.S3) demonstrates that majority of the material comprises the aromatic ring system because sharp peaks found at ~ 1630-1660 cm^{-1}, and ~1440-1460 cm^{-1}. At this range, conjugated double bond display the IR absorption. Peak obtained at 1600-1690 cm^{-1} which is most probably the characteristic peak of stretching of C-O-C bond. The peak at 1500-1600 cm^{-1} suggested that the stretching of the aromatic ring which is a common peak in all the $PM_{2.5}$ samples (Table-1). So, it's giving an obvious understanding that the particulate matter contains the aromatic ring with a conjugated double bond. Few samples exhibit a peak at 2400-2500 cm^{-1} in this range -C≡N and C≡C undergo stretching vibration. The peak at the wave number 1400-1450 cm^{-1} is the bending of methyl groups and methylene group. Examining the fingerprint region reveals intriguing characteristics. This investigation identified a substantial number of peaks in the fingerprint region, specifically at 1325 and 1340 cm^{-1}, which indicate the existence of organic nitrate aerosol in $PM_{2.5}$.

Table-1: Primary band assignments for ATR-FTIR spectra of PM2.5 particulate matter

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

3.4 Identification and Quantification of Phenolic Compounds (precursor of BrC)

3.4.1 Chromatogram of GC-FID Analysis

The chromatogram generated by GC-FID displayed the retention time, peak area, and identified compound. The identity of the unknown compound is ascertained through a comparison of its chromatogram with that of the standard sample. A calibration curve represents quantitative information regarding the identified compound. The chromatogram was given in the supplementary file in the section 5 (Fig.S4 to S8).

3.4.2 Phenolic Precursor of BrC

The phenolic component serves as the primary precursor of brown carbon. The precursors are initially emitted from the source as primary aerosols. However, in the atmosphere, they transform into secondary aerosols, such as nitrophenol, which is formed from a phenolic compound.

Fig.3 illustrates that the mean concentration of nitrophenol and catechol in $PM_{2.5}$ was comparatively greater than that of other phenolic compounds. The average concentrations of nitrophenol in Dhaka South (DU) during the monsoon, post-monsoon, and winter seasons were 1.52±0.64, 2.50±0.43, and 4.54±2.94 µg m^{-3}, respectively. In contrast, at Mirpur, Dhaka North, the concentrations were 1.34±0.09, 1.65±0.44, and 1.62±0.52 µg m^{-3} during the same seasons. These concentrations were approximately 40-70% lower than the levels observed at the Dhaka South site. 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 levels of phenol and methyl derivatives of phenol were significantly lower compared to nitrophenol. In the Mirpur, Dhaka North, the concentration of 2-hydroxyphenol is higher compared to nitrophenol. This is due to emissions from cooking, burning coal in restaurants, and biomass burning, which directly release 2-hydroxyphenol or catechol. During the winter, the increased combustion of coal and biomass for heating purposes is responsible for the significant rises in phenolic compound concentrations (Wang et al., 2018). After release of 2-hydroxyphenol it undergoes a secondary chemical reaction with NOx or aqueous nitrous acid in the atmosphere to form nitrophenol.

The average concentration of phenol in Dhaka city was 0.15±0.08, 0.17±0.04, and 0.30±0.25 µg m^{-3} in monsoon, post-monsoon, and winter season respectively. The concentration of phenol in winter season was comparatively higher than others seasons because the major emission source of phenol is biomass burning. And most of the biomass burning occurred in the winter seasons. Li (2020) reported that the average concentration of phenol in urban Jinan, China was 16.7±3.7, 7.1±2.6, and 2.6±0.4 ng m^{-3} in winter, spring, and summer respectively. Among the methyl derivatives measured in Dhaka, Bangladesh from July 2023 to January 2024, 2-methoxyphenol exhibited the highest concentration at 0.42±0.29 µg m^{-3},

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while 2,4-dimethylphenol had the lowest concentration, recorded at 0.05±0.04 µg m^{-3}. The high concentration of 2-methoxyphenol, which is directly emitted from biomass burning, likely indicates frequent biomass burning activities occurring near the sampling site in Dhaka, Bangladesh.

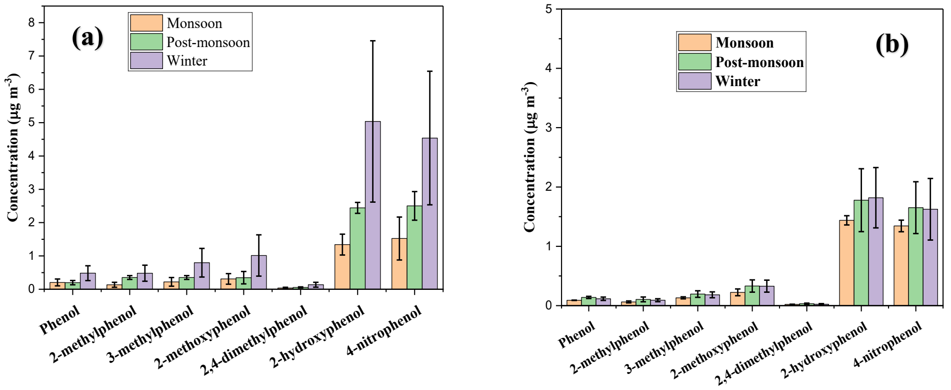


Fig.3: Variation of concentration of phenolic compounds in (a) Dhaka, South and (b) Dhaka North site during monsoon, post-monsoon and winter

In contrast to findings from other research, the mean concentration of nitrated phenols observed in this study is significantly greater than the concentrations reported by Li et al., (2020) in urban Jinan, China during the winter season (0.105 ±0.05 ng m^{-3}) and spring (0.12 ±0.034 ng m^{-3}). Delhomme (2010) quantified the phenolic and nitrated compound in the ambient air and obtained the concentration phenol, m-cresol (3-methylphenol), o-cresol (2-methylphenol) were 10.4, 2.2, and 1.2 ng m^{-3} respectively in urban site.

Fig.4 shows that season and sampling location had an impact on the fractional compositions of phenolic compounds. The most prevalent phenolic compounds in $PM_{2.5}$ during the monsoon, post-monsoon, and winter seasons were 4-nitrophenol and 2-hydroxyphenol, which accounted for 37-40% and 39-41% of the quantified phenolic precursors respectively in Dhaka city from July 2023 to January 2024. 2,4-dimethylphenol lies in the lowest portion among the identified phenolic compounds accounting for 0.8-

1% of the total identified phenolic precursors. The contribution of 3-methylphenol increased by 0.2% from the monsoon to the post-monsoon season and saw a further increase of 0.5% during winter (Fig.4).

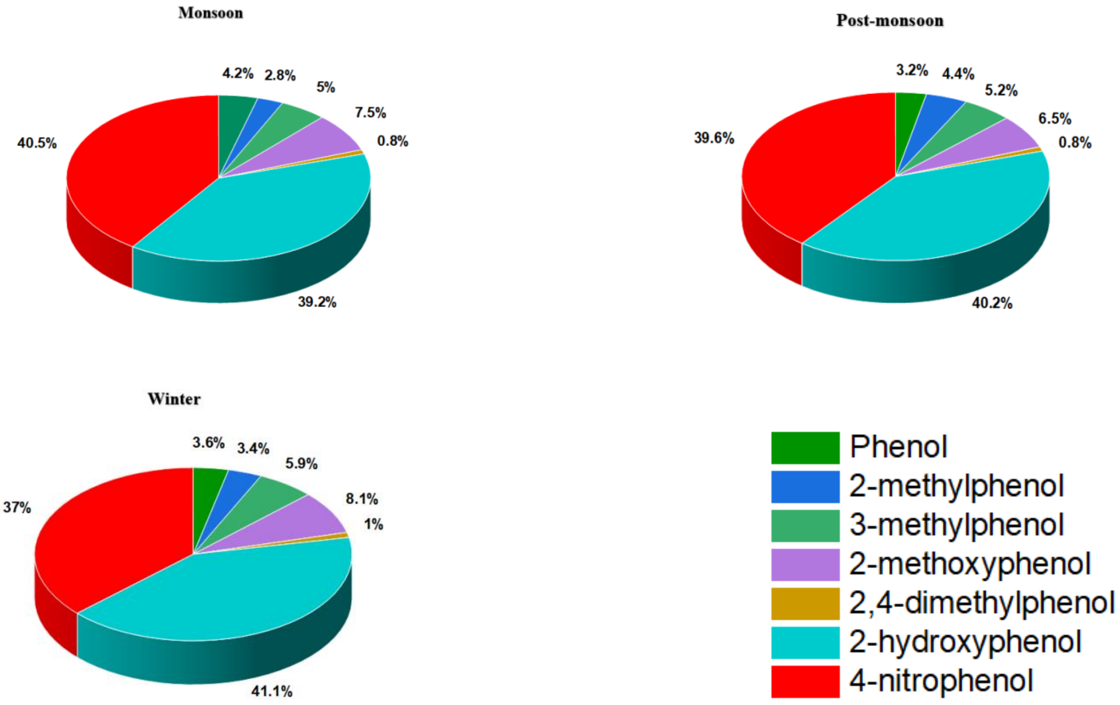


Fig.4: The percentage of distinct phenolic compounds in $PM_{2.5}$ throughout the monsoon, post-monsoon, and winter seasons in Dhaka, Bangladesh

Previous research found that catechols and 4-nitrophenol were the most abundant phenolic compounds detected in Jinan and Beijing, with the highest observed concentrations (Wang et al., 2018**;** Wang et al., 2019)**.** The prevalence of 4-nitrophenol and 2-hydroxyphenol in both Dhaka South and Dhaka North may be attributed to primary emissions, such as combustion activities, as well as the subsequent formation of precursors of BrC. The high value of nitrophenol also indicated that the higher concentration of NO_x in the atmosphere. Liu et al. (2016) reported an enhancement in the light absorption of secondary organic aerosols (SOA) when exposed to elevated NO_x levels and moderate humidity, attributing this primarily to the presence of nitro-aromatic compounds as key chromophores. According to Laskin et al. (2025), the optical characteristics of brown carbon (BrC) can be altered through atmospheric aging, including processes such as photolysis and multiphase reactions that either produce or degrade light-absorbing species.

3.4.3 Correlation analysis of phenolic compounds

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)

Table-2: Correlation analysis of phenolic compounds

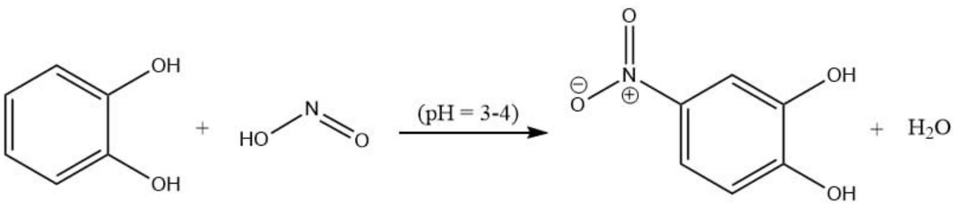
	4-NPh	2-HPh	Ph	2-MPh	3-MPh	2-MOPh	2,4-DMPh
4-NPh	1						
2-HPh	0.974	1					
Ph	0.900	0.889	1				
2-MPh	0.907	0.9199	0.9879	1			
3-MPh	0.957	0.9558	0.9813	0.9898	1		
2-MOPh	0.915	0.9442	0.966	0.9701	0.9723	1	
2,4-DMPh	0.662	0.6809	0.8341	0.8659	0.8077	0.7708	1

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

The correlation analysis (Table-2) shows that most of the compounds exhibit strong correlations with each other (close to 1), indicating that they behave similarly, possibly due to shared structural or chemical properties. This analysis also indicated that most of the phenolic compounds emitted from the same sources most probably it was biomass burning and vehicle emissions. r=0.974 for 4-NPh and 2-HPh and r=0.9879 for Ph and 2-MPh were suggested that extremely strong positive correlation between each pair and behave very similarly. There is a moderate to significant association between 2,4-dimethylphenol (2,4-DMPh) and 2-methoxyphenol (2-MOPh) (r=0.7708). Their relationship is not as strongly connected as some other pairs in Table-2. 4-NPh and 2,4-DMPh show a moderate positive correlation. They may exhibit different behaviors. 2,4-DMPh shows less correlation with others phenolic compounds.

3.5 Formation Pathway of Nitroaromatic Compound

The primary constituent of BrC is the nitroaromatic compounds, which account for around 40-60% of the total BrC composition. Multiple investigations have demonstrated the significant involvement of NOx in the creation of nitroaromatic compounds (Chow et al., 2016). However, this study presents a method for the production of nitro-aromatic compounds by simple aqueous phase nitration of 2-hydroxyphenol (catechol).



Reaction:

This study carried out a simple aqueous phase nitration reaction of catechol (1,2 dihydroxybenzene) with aqueous nitrite $NaNO_2$ in acidic pH=3-4. The 1:1 ratio of catechol and sodium nitrite undergoes a chemical reaction at pH=3-4 (pH adjust by 0.1 M H_2SO_4 and NaOH) to form nitrophenol.

3.5.1 UV-visible light absorption properties of the 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).

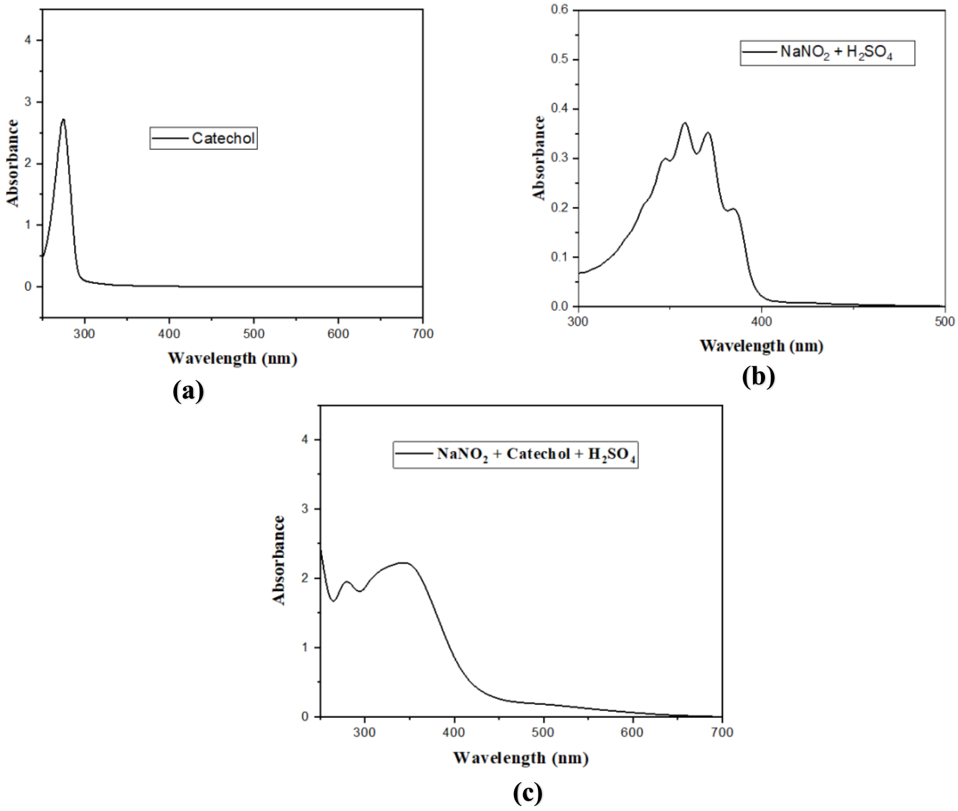
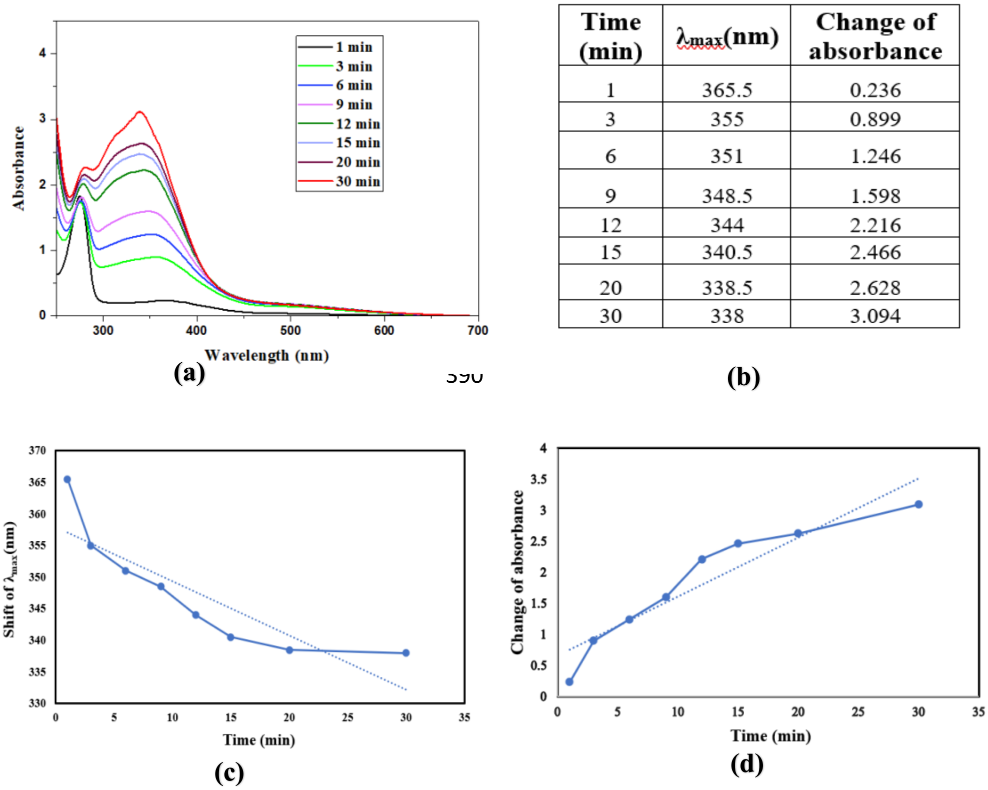


Fig.5: Absorbance of (a) single catechol, λ_{max}=275 nm, (b) $NaNO_2$ + H_2SO_4, and (c) reaction system (catechol-nitrite)

The change of absorbance with time at pH=3.5 of the catechol-nitrite reaction system is represented in Fig.6. At pH=3.0 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

(b)

(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. (b) Data

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for the shift of peak and change of absorbance, (c) Shift of λ_{max} with time, and (d) Change of absorbance with time

The reaction mechanism of nitration of aromatic compounds takes place through the reaction with an aqueous nitrite solution. Esteves et al., (2003) has 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. 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.

4. Conclusions

This study provides comprehensive insights into the compositions, surface elements, and formation mechanism of BrC in the atmosphere of Dhaka, Bangladesh, through the identification and quantification of seven key phenolic precursors and a laboratory-based aqueous-phase nitration experiment.

Summary:

We observed that $PM_{2.5}$ particles predominantly exhibited spherical, irregular, and chain-like morphologies, with carbonaceous (C, O, N, S), mineral (Ca, Fe, K, Al), and trace elements (Pb, Cr, Hg, Cd, As) identified on their surfaces. ATR-FTIR analysis revealed prominent functional groups, including carbonyls, nitro groups ($–NO_2$), and aromatic conjugated systems, suggesting the presence of complex organic structures. Among the phenolic precursors, 4-nitrophenol (2.20±1.21 µg m^{-3}) and 2-hydroxyphenol (2.31 ± 1.39 µg m^{-3}) showed the highest concentrations, especially during winter. A strong seasonal and spatial variation was evident, with higher levels in Dhaka South, indicating the influence of urban emissions and combustion activities. Correlation analysis revealed strong positive relationships among most compounds ($r > 0.9$), suggesting shared emission sources such as biomass and fossil fuel combustion.

These findings suggest that phenolic compounds are not only abundant in the urban air of Dhaka but also highly reactive, forming nitrated derivatives such as 4-nitrophenol that contribute substantially to BrC. The detection of nitrated and hydroxylated phenols further highlights their transformation via atmospheric oxidation processes. The similarity in chemical behavior and high co-occurrence among these phenolic compounds confirms their common origin and potential for secondary aerosol formation.

Compared to other urban regions like Jinan, China, and Strasbourg, France, the concentrations of phenolic and nitrated phenolic compounds in Dhaka are substantially higher, likely due to more intense and unregulated combustion activities (Li et al. 2020, Delhomme et al. 2010). Our findings align with prior studies (e.g., Wang et al., 2018; Li et al., 2020) identifying catechols and nitrophenols as dominant BrC components but extend the understanding by quantifying these compounds across seasons and locations within a South Asian megacity.

While this study presents robust data on $PM_{2.5}$ composition and BrC precursors, limitations include the relatively short sampling period and limited spatial coverage. Additionally, although aqueous-phase nitration experiments were conducted, the ambient contribution of such processes remains to be quantified. Future studies should explore broader geographic regions, perform year-round monitoring, and couple laboratory findings with atmospheric modeling for deeper mechanistic insights. The results underscore the significant contribution of phenolic and nitrated phenolic compounds to atmospheric BrC in Dhaka, with implications for both regional air quality and climate forcing. The demonstrated aqueous-phase nitration pathway of catechol at acidic pH suggests a potentially underappreciated route for BrC formation under humid and polluted conditions. This highlights the importance of regulating combustion-related emissions and considering aqueous-phase chemistry in climate models to accurately assess the radiative effects of organic aerosols.

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Author's contribution

MAH**:** Conceptualization, Sampling, Methodology, Chemical analysis, Writing-original draft, Review & editing

MHS: Chemical Analysis

ARMT: Chemical Analysis, Methodology and Supervision

MFE: Chemical Analysis

AS: Conceptualization, Review & editing, Supervision

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Ethics statement: The research work was done according to the ethical standard of the University of Dhaka, Bangladesh. There is no ethical clearance was required during this research work - because this study did not include any human and animal subjects.

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