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

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1. Sampling locations

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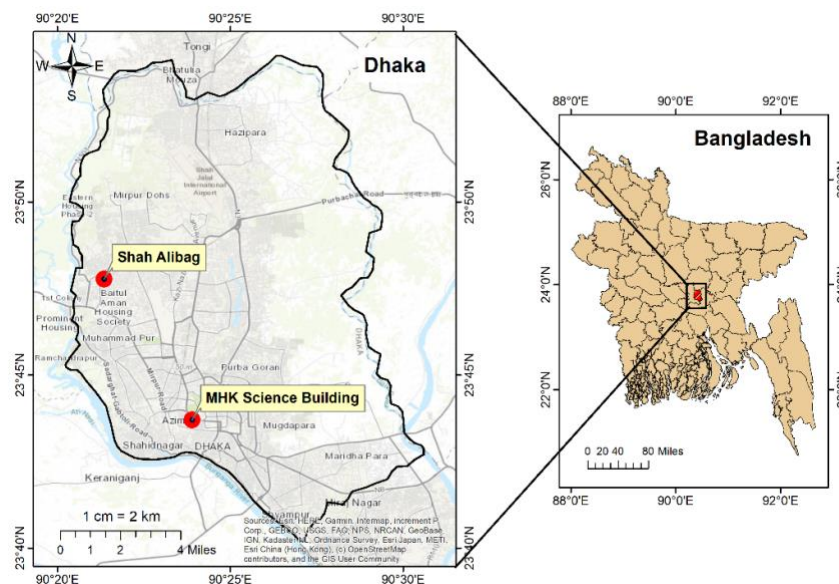
Fig. S1: Map of Bangladesh and Dhaka showing the sampling spots Mokarram Hussain Khundker
Bhaban, University of Dhaka and Shah Alibag, Mirpur

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48 **2. Generated a Calibration Curve of Individual Standard Phenolic Compounds**

49 The calibration curve for quantifying the phenolic component was established using the reference

50 standard phenolic solution. A calibration curve was generated by graphing the peak area against

51 the concentration by originPro 2024 software. The individual calibration curves for the desired

52 chemicals are provided below.

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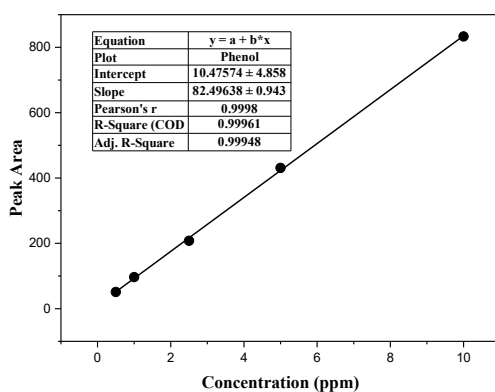
54   **(a) Phenol**   **(b) 2-methylphenol**

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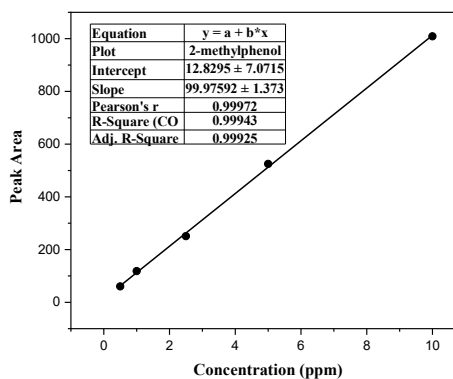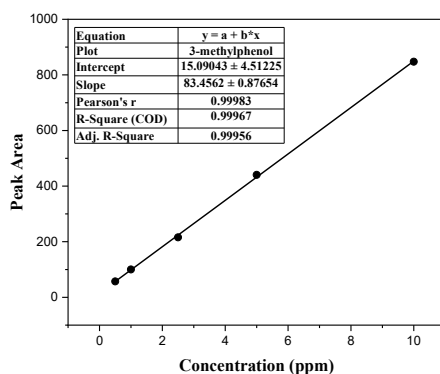
56   **(c) 3-methylphenol**   **(d) 2-methoxyphenol**

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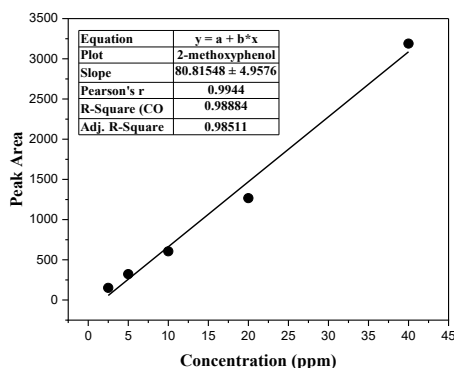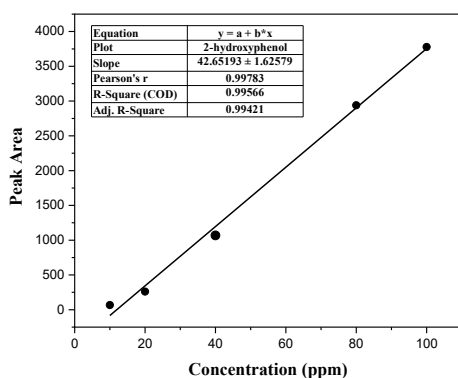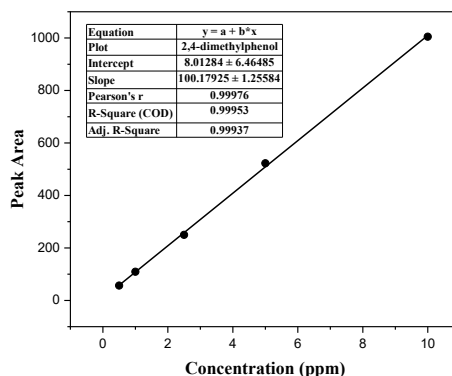
58   **(e) 2-hydroxyphenol**   **(f) 2,4-dimethylphenol**

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60   **(g) 4-nitrophenol**

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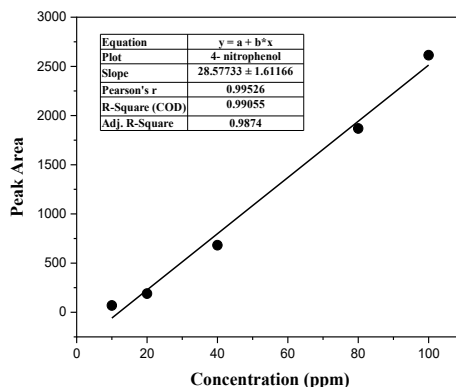
62   **Fig. S2: Calibration curve for seven phenolic compounds**

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3. Method validation

Method validation involves the determination of LOD (Limit of Detection), LOQ (Limit of

Quantification), and Recovery rate:

3.1 LOD & LOQ

LOD refers to the lowest concentration of an analyte sample that can be detected by an analytical

method. On the other hand, LOQ refers to the lowest concentration of an analyte sample that can

be quantified at a specific level of precision and accuracy by an analytical method. Both LOD and

71 LOQ were determined by injecting serially diluted mixtures of standard solution in GC-FID. For

72 LOD, the peak area of each standard was considered 3 times higher than the baseline noise. In case

73 of LOQ, it was ten times higher. Equations are given as follows

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$$LOD = 3.3 \times \frac{\text{Standard Deviation of Intercept}}{\text{Slope of the Calibration Curve}}$$

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$$LOQ = 10 \times \frac{\text{Standard Deviation of Intercept}}{\text{Slope of the Calibration Curve}}$$

76 **3.2 Recovery through sample spiking**

77 In this study to calculate the recovery rate, a known amount of analyte was added (spiked) into the

78 test sample matrix, and its response was measured. The recovery experiment was carried out in

79 three samples by spiking a known amount of standard. A blank sample and the two samples that

80 gave very less signal/peak in the chromatogram were used as a sample matrix for the recovery test.

81 A known amount of standard solutions was spiked to the filter sample and allowed the sample to

82 stand for an hour to let the phenolic compound be absorbed into the filter matrix. Then extract this

83 spiked sample by the same process of sample extraction. According to the following formula,

84 recovery percentages were calculated.

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$$R = \frac{C_{Spiked} - C_{blank}}{C_{added}} \times 100\,\%$$

86 Where R is the recovery (%), C_{spiked} is the concentration of the phenolic compounds obtained from

87 the chromatogram after spiking, C_{blank} is the concentration of the compound obtained from the

88 chromatogram of blank samples, C_{added} is the concentration of the standard added initially in the

89 matrix.

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91   **Table S1: Data for recovery experiment**

Standards	Spiked level (ppm)	Recovery (%)
Phenol	2.5	82
	5	85
2-methylphenol	2.5	83
	5	86
3-methylphenol	2.5	89
	5	84
2-methoxyphenol	2.5	81
	5	87
2,4- dimethylphenol	2.5	83
	5	85
2-hydroxyphenol	2.5	89
	5	91
2,4,6-trichlorophenol	2.5	82
	5	85
4-nitrophenol	2.5	82
	5	87

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93   **4. ATR-FTIR analysis**

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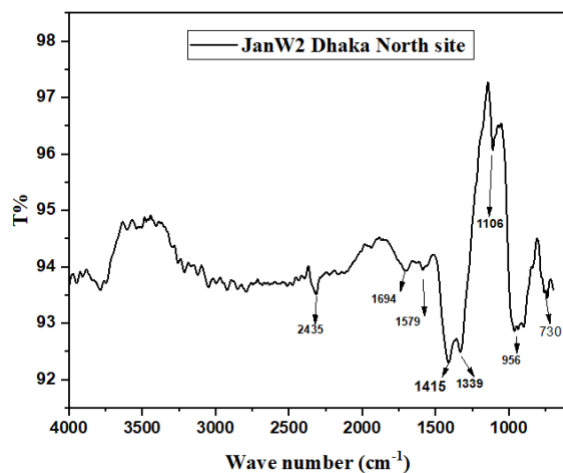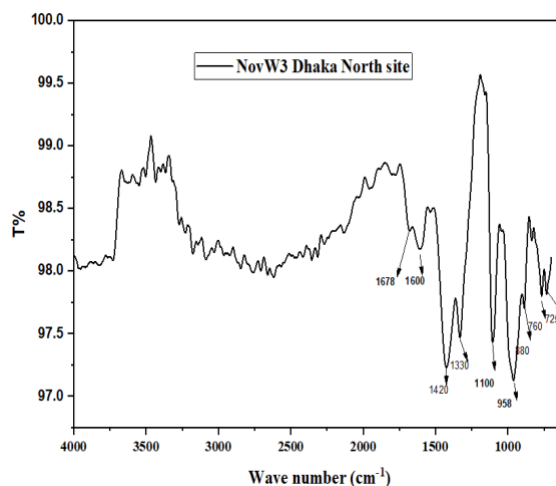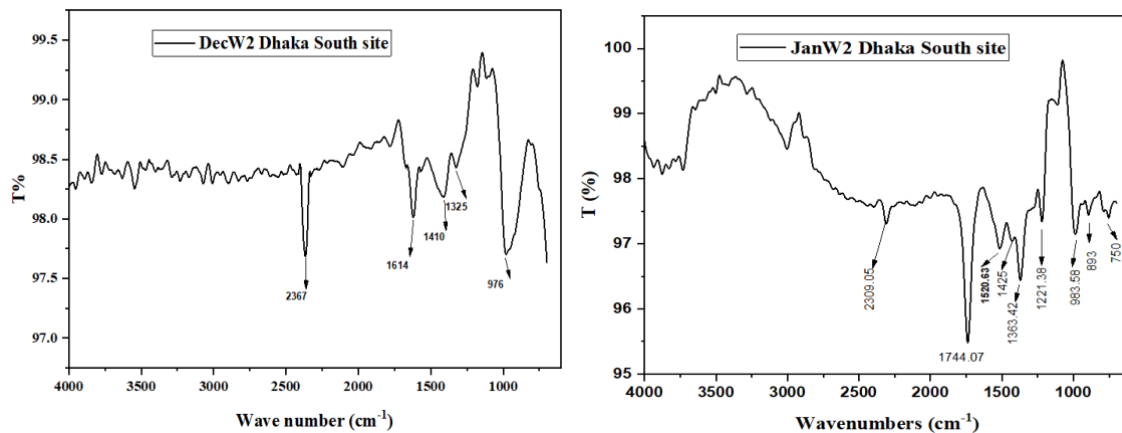
Fig. S3: ATR-FTIR spectrum of particulate matter (PM2.5) in the Dhaka city

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5. Chromatogram of GC-FID

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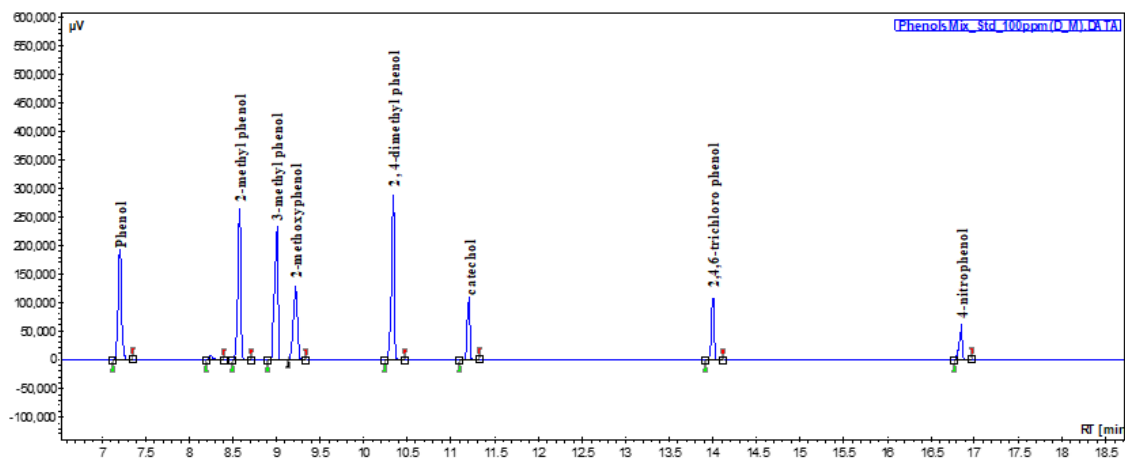
Fig. S4: Chromatogram of standard phenolic compounds

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110   **Table S2: Retention time of the standard phenolic compounds**

Analytical Standards	Retention time (min)
Phenol	7.21
2-methylphenol	8.59
3-methylphenol	9.01
2-methoxyphenol	9.22
2,4-dimethylphenol	10.35
2-hydroxyphenol (catechol)	11.21
2,4,6-trichlorophenol	14.01

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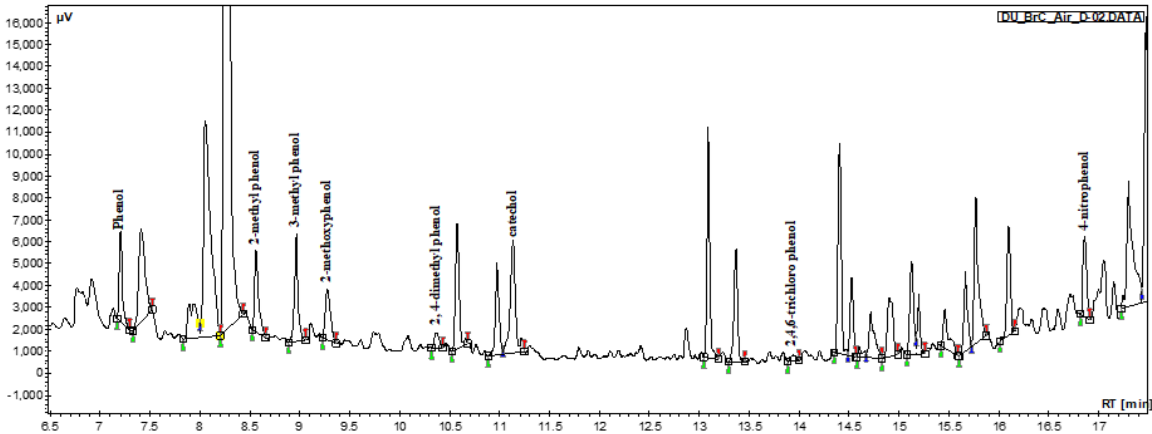
114   **Fig. S5: Chromatogram of the sample D02 (sample at Dhaka South site, August second week)**

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123   **Table S3: Results of the chromatogram for D02 sample**

Name of identified compounds	Retention time (min)	Quantity (ppm) from chromatogram	Calculated data for total sample ($\mu g\ m^{-3}$) involve air volume
Phenol	7.21	1.85	0.16
2-methylphenol	8.59	1.5	0.13
3-methylphenol	9.01	2.59	0.23
2-methoxyphenol	9.22	3.46	0.30
2,4-dimethylphenol	10.35	0.41	0.04
2-hydroxyphenol (catechol)	11.21	19.06	1.69
2,4,6-trichlorophenol	14.01	0.55	0.05
4-nitrophenol	16.85	17.48	1.54

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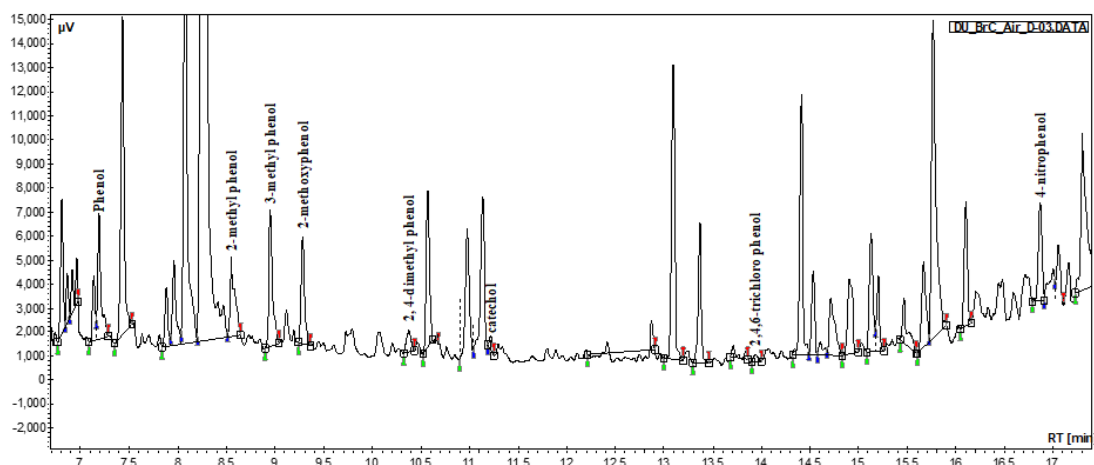
127   **Fig. S6: Chromatogram of sample D-03 (sample at Dhaka South site, September 2nd week)**

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129   **Table S4: Results of sample D-03**

Name of identified compounds	Retention time (min)	Quantity (ppm) from chromatogram	Calculated conc. for total sample ($\mu g\ m^{-3}$) involve air volume
Phenol	7.19	2.44	0.55
2-methylphenol	8.55	1.77	0.40
3-methylphenol	8.96	3.02	0.68

2-methoxyphenol	9.28	3.96	0.90
2,4-dimethylphenol	10.38	0.51	0.12
2-hydroxyphenol (catechol)	11.22	12.39	2.82
2,4,6-trichlorophenol	13.96	0.52	0.12
4-nitrophenol	16.87	17.77	4.04

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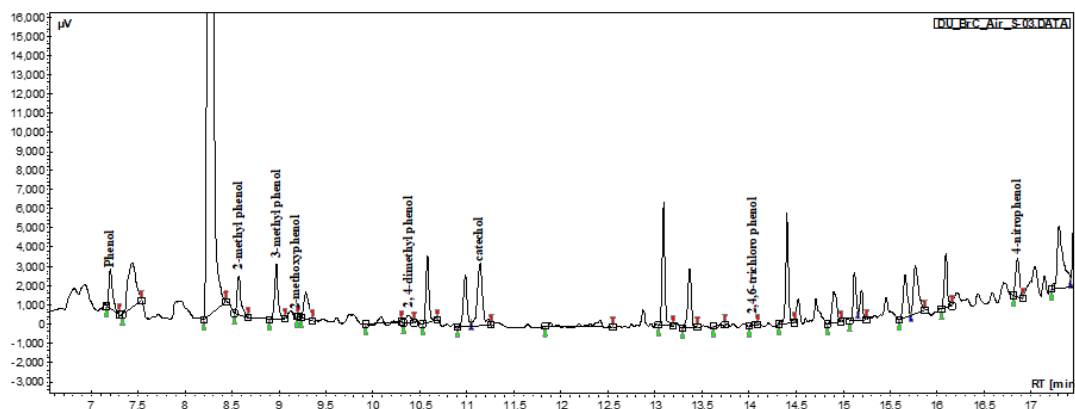
132 **Fig. S7: Chromatogram of the sample M03 (sample at Mirpur, Dhaka North in September**

133 **2nd week)**

134 **Table S5: Results of the M03 sample obtained from the chromatogram**

Name of identified compounds	Retention time (min)	Quantity (ppm) from chromatogram	Calculated conc. for total sample ($\mu g\ m^{-3}$) involve air volume
Phenol	7.21	1.02	0.09
2-methylphenol	8.59	0.82	0.08
3-methylphenol	9.01	1.57	0.15
2-methoxyphenol	9.22	1.8	0.17
2,4-dimethylphenol	10.35	0.26	0.02
2-hydroxyphenol (catechol)	11.21	16.54	1.53
2,4,6-trichlorophenol	14.01	0.4	0.04
4-nitrophenol	16.85	15.04	1.4

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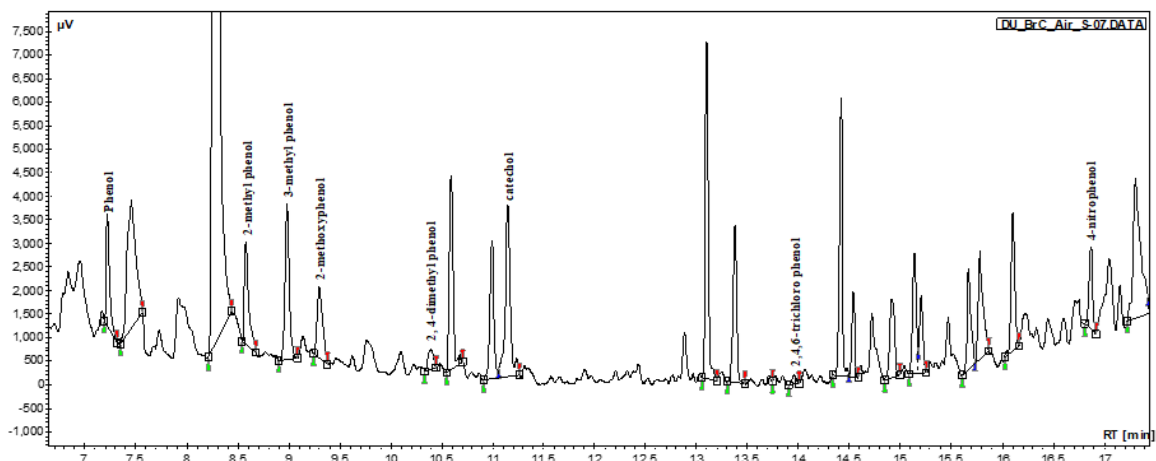
137 **Fig. S8: Chromatogram of the sample S07 (January 2nd week, 2024 at Mirpur, Dhaka South)**

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139 **Table S6: Results of sample S07**

Name of identified compounds	Retention time (min)	Quantity (ppm) from chromatogram	Calculated conc. for total sample ($\mu g\ m^{-3}$) involve air volume
Phenol	**7.21**	**1.13**	**0.13**
2-methylphenol	**8.59**	**0.87**	**0.10**
3-methylphenol	**9.01**	**1.73**	**0.19**
2-methoxyphenol	**9.22**	**3.02**	**0.34**
2,4-dimethylphenol	**10.35**	**0.27**	**0.03**
2-hydroxyphenol (catechol)	**11.21**	**17.15**	**1.92**
2,4,6-trichlorophenol	**14.01**	**0.33**	**0.04**
4-nitrophenol	**16.85**	**14.78**	**1.65**

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Table S7: Concentration of phenolic precursors of BrC in three seasons from July 2023 to January 2024 in Dhaka, Bangladesh

Compositions (µg m^{-3})	Dhaka North site (Mirpur)			Dhaka South site (DU)		
	Monsoon	Post-monsoon	Winter	Monsoon	Post-monsoon	Winter
Phenol	0.09±0.02	0.14±0.02	0.12±0.03	0.20±0.10	0.20±0.06	0.48±0.22
2-methylphenol	0.06±0.02	0.10±0.04	0.09±0.02	0.13±0.07	0.35±0.06	0.48±0.24
3-methylphenol	0.13±0.02	0.19±0.05	0.18±0.05	0.22±0.13	0.35±0.058	0.79±0.43
2-methoxyphenol	0.22±0.06	0.33±0.10	0.33±0.10	0.31±0.16	0.34±0.18	1.01±0.62
2,4-dimethylphenol	0.021±0.002	0.03±0.01	0.024±0.01	0.04±0.02	0.05±0.015	0.13±0.07
2-hydroxyphenol	1.44±0.07	1.78±0.53	1.82±0.51	1.34±0.31	2.44±0.16	5.04±3.42
4-nitrophenol	1.34±0.09	1.65±0.44	1.62±0.52	1.52±0.64	2.50±0.43	4.54±2.94