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Supplement of

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

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S1. Sampling locations

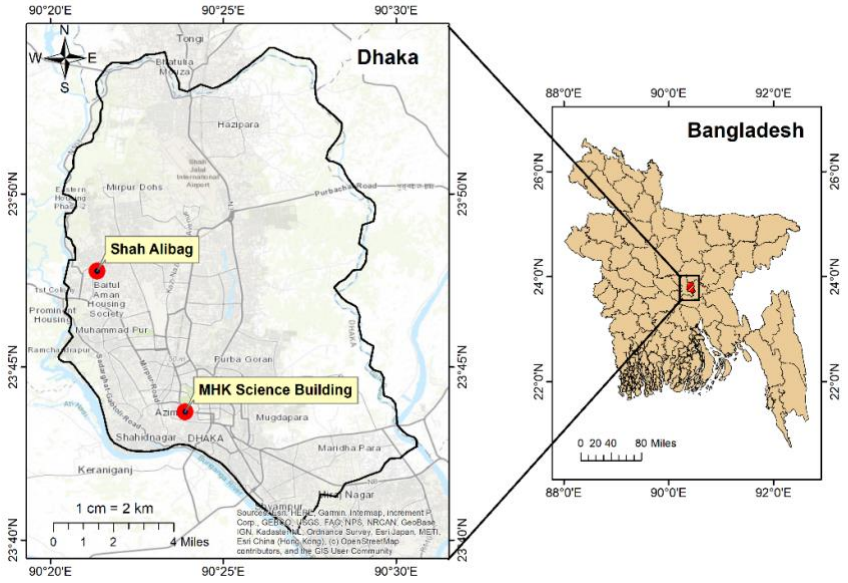
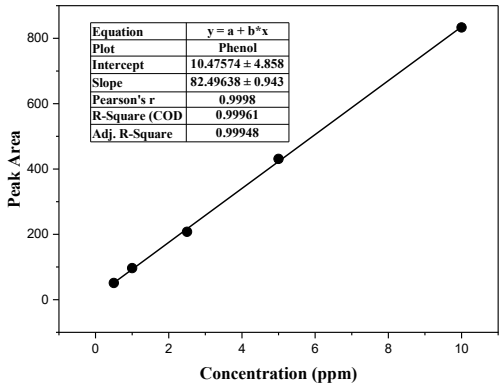


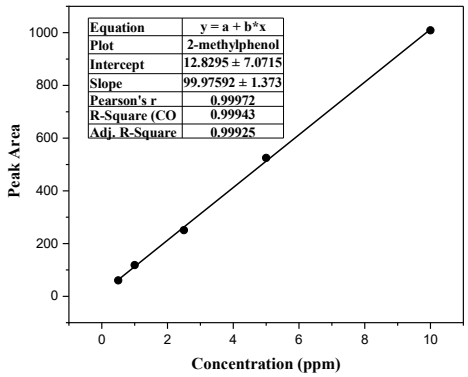
Fig. S1: Map of Bangladesh and Dhaka showing the sampling spots Mokarram Hussain Khundker Bhaban, University of Dhaka and Shah Alibag, Mirpur

S2. Generated a Calibration Curve of Individual Standard Phenolic Compounds

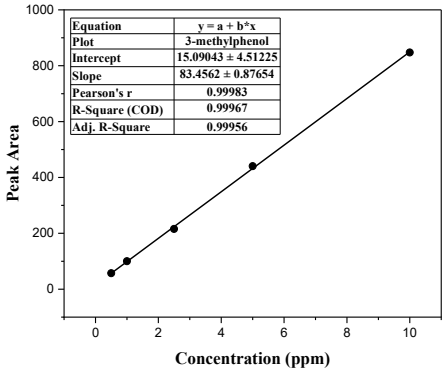
The calibration curve for quantifying the phenolic component was established using the reference standard phenolic solution. A calibration curve was generated by graphing the peak area against the concentration by originPro 2024 software. The individual calibration curves for the desired chemicals are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



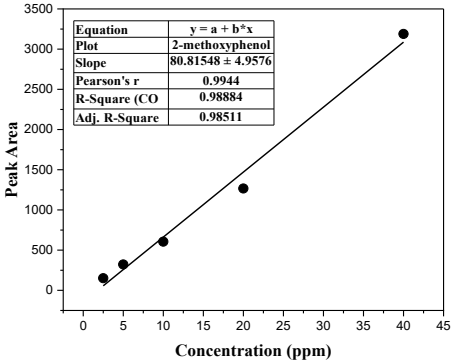
(a) Phenol



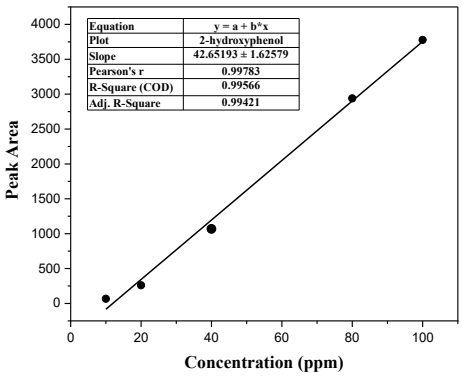
(b) 2-methylphenol



(c) 3-methylphenol



(d) 2-methoxyphenol



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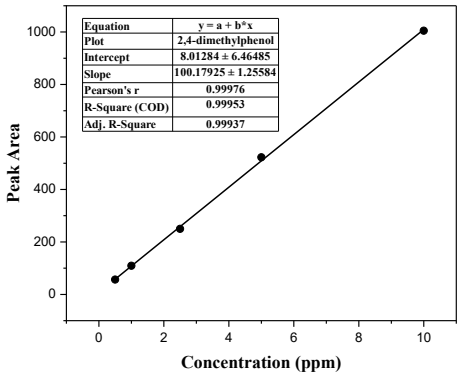
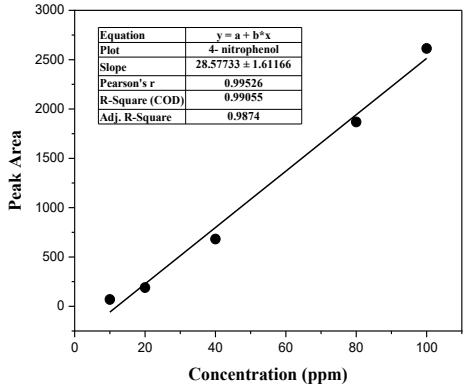
29 **(e) 2-hydroxyphenol**



(f) 2,4-dimethylphenol

30



31 **(g) 4-nitrophenol**

32

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

34

35 **S3. Method validation**

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

37 Quantification), and Recovery rate:

38 **S3.1 LOD & LOQ**

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

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

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

LOQ were determined by injecting serially diluted mixtures of standard solution in GC-FID. For LOD, the peak area of each standard was considered 3 times higher than the baseline noise. In case of LOQ, it was ten times higher. Equations are given as follows

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

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

S3.2 Recovery through sample spiking

In this study to calculate the recovery rate, a known amount of analyte was added (spiked) into the test sample matrix, and its response was measured. The recovery experiment was carried out in three samples by spiking a known amount of standard. 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. According to the following formula, recovery percentages were calculated.

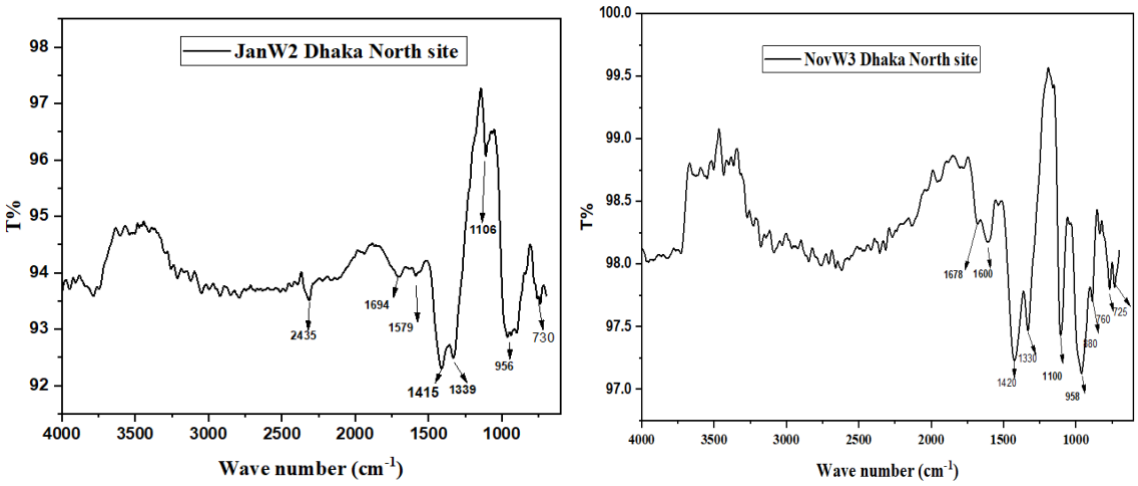
$$\boldsymbol{R = \frac{C_{Spiked} - C_{blank}}{C_{added}} \times 100\ \%}$$

Where R is the recovery (%), $\mathbf{C_{spiked}}$ is the concentration of the phenolic compounds obtained from the chromatogram after spiking, $\mathbf{C_{blank}}$ is the concentration of the compound obtained from the chromatogram of blank samples, $\mathbf{C_{added}}$ is the concentration of the standard added initially in the matrix.

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

S4. ATR-FTIR analysis



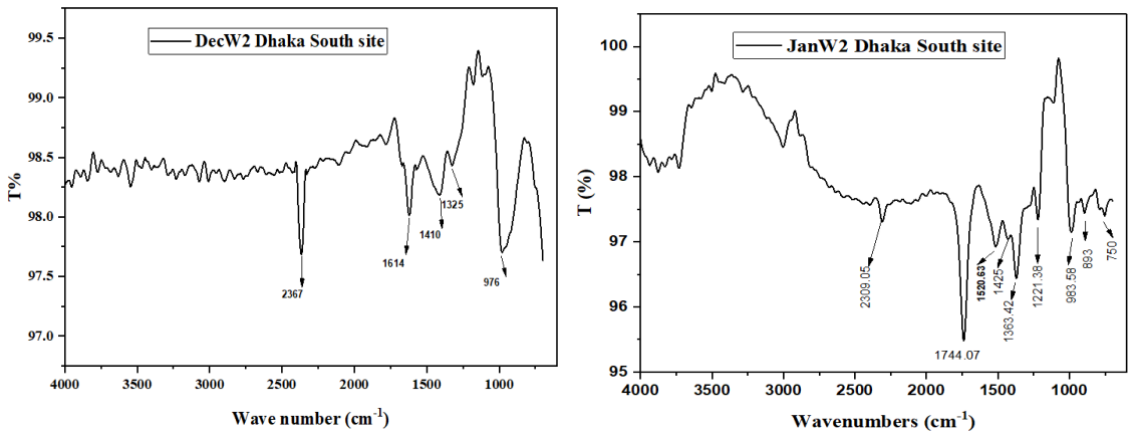


Fig. S3: ATR-FTIR spectrum of particulate matter ($PM_{2.5}$) in the Dhaka city

S5. Chromatogram of GC-FID

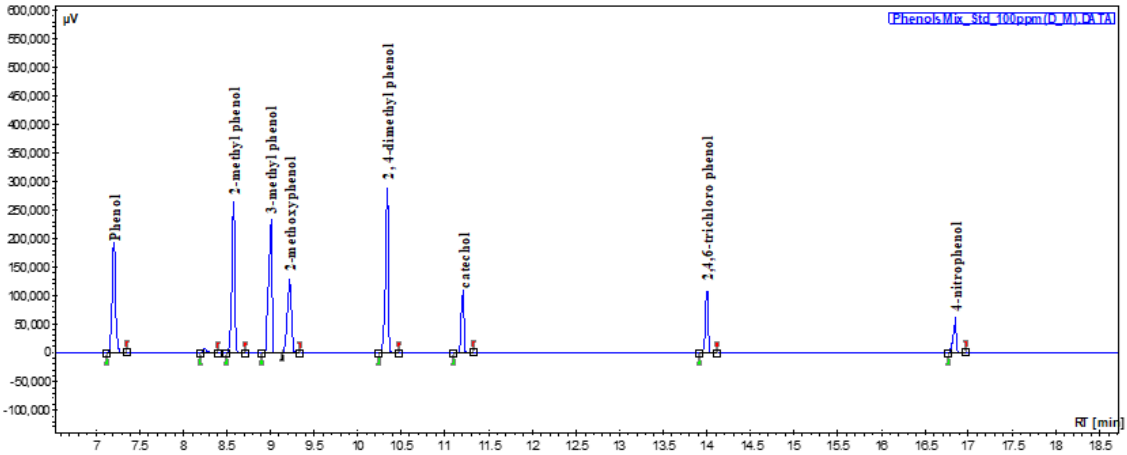


Fig. S4: Chromatogram of standard phenolic compounds

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

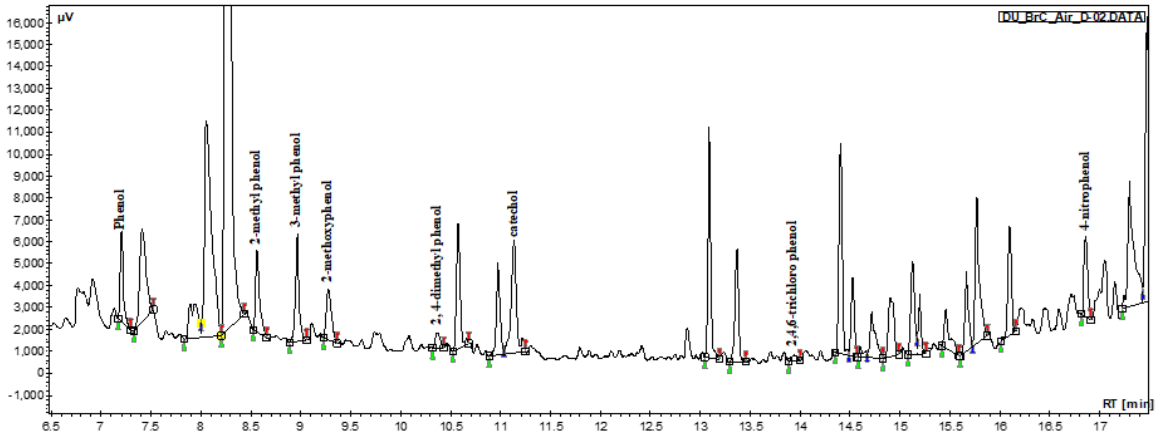


Fig. S5: Chromatogram of the sample D02 (sample at Dhaka South site, August second week)

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 (µg 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**

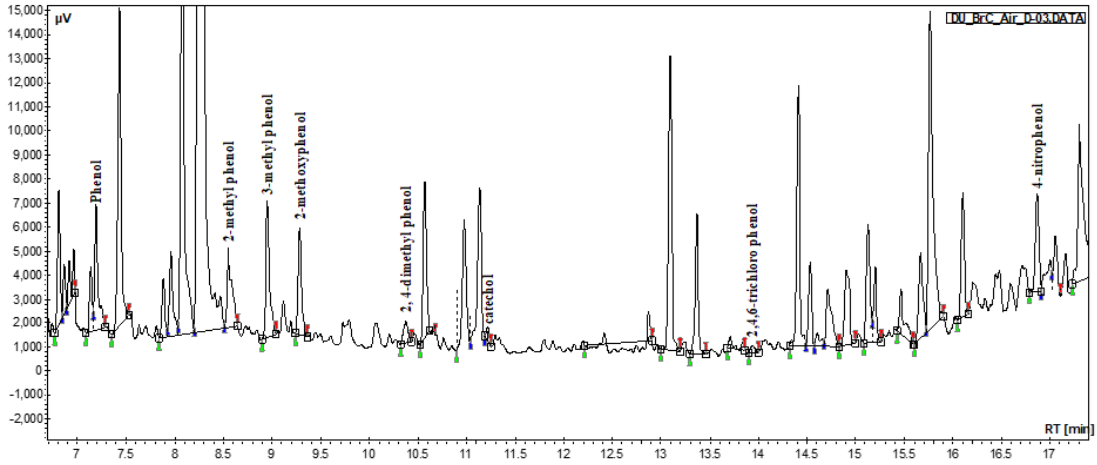


Fig. S6: Chromatogram of sample D-03 (sample at Dhaka South site, September 2nd week)

Table S4: Results of sample D-03

Name of identified compounds	Retention time (min)	Quantity (ppm) from chromatogram	Calculated conc. for total sample (µg 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

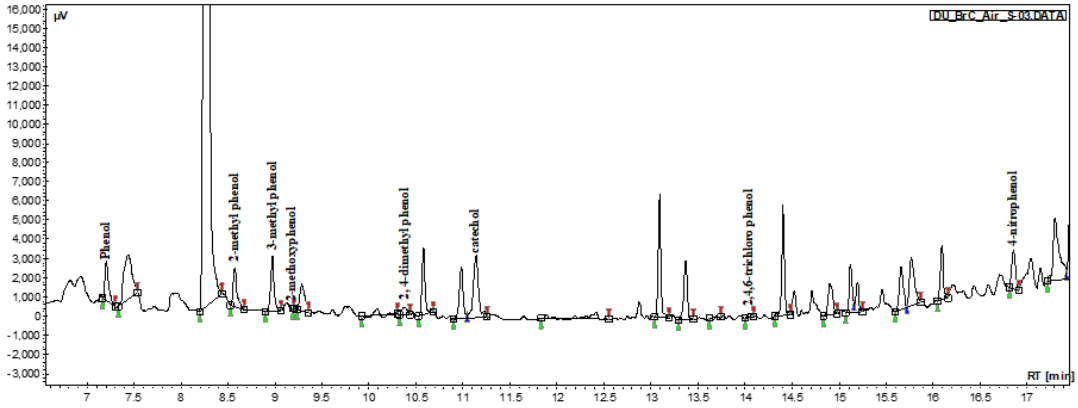


Fig. S7: Chromatogram of the sample M03 (sample at Mirpur, Dhaka North in September 2nd week)

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 (µg 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**

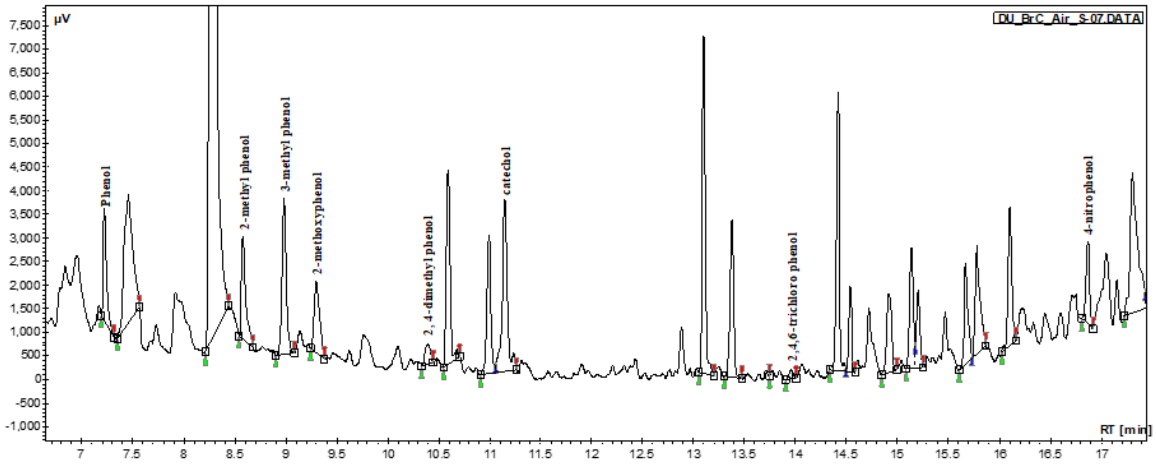


Fig. S8: Chromatogram of the sample S07 (January 2nd week, 2024 at Mirpur, Dhaka South)

Table S6: Results of sample S07

Name of identified compounds	Retention time (min)	Quantity (ppm) from chromatogram	Calculated conc. for total sample (µg 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**

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						
	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

Table S9: 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

S6. 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