Carbonaceous components in airborne nanoparticles ($PM_{0.1}$) during the dry season in the urban area of Phnom Penh City, Cambodia

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Abstract. Airborne particulate matter (PM), typically $PM_{0.1}$, could pose serious health and environmental risks, especially in rapidly growing low- and middle-income countries where environmental control measures and healthcare access are limited. This study investigated the carbon components in $PM_{0.1}$ compared with those in total suspended particulates (TSP) collected from two different locations in Phnom Penh, Cambodia. The diurnal and nocturnal variations were also observed. Aerosol sampling was conducted on a single day of each week, during the high pollution period from January to April 2024. Ambient Nanoparticle Sampler (ANS) and a high-volume sampler (HV) were used to capture PM fractions down to $PM_{0.1}$ and TSP, respectively. The results show a significant increase in the organic carbon (OC) and elemental carbon (EC) during nighttime at both locations. Between locations, ITC indicated the higher OC and EC compared to MoE. However, the total of nanoparticulate OC and EC mainly contributed to those of the TSP in a great portion, up to 25-50%.

1 Introduction

Atmospheric particulate matter (PM) is a critical component of air pollution with well-documented impacts on human health and the ecosystem. PM is composed of a complex mixture of solid particles and liquid droplets suspended in the ambient air environment, and

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is typically categorized by its aerodynamic diameter. It has been summarized that either fine (FPs, $PM_{2.5}$) or ultrafine particles or nanoparticles (UFPs, $PM_{0.1}$) are of particular concern due to their enhanced ability to penetrate deep into alveolar regions of the lungs and translocate into the circulatory system, contributing to a range of adverse health effects, including respiratory, cardiovascular, and neurological disorders [1], [2], [3]. WHO reported a significant number of premature deaths annually due to ambient air pollution exposure, which comprises approximately 7 million people in 2021. However, the air quality guideline (AQG) level for $PM_{0.1}$ has not yet been revealed, while the detailed study of this PM fraction is also limited [1].

Beyond health impacts, PM also plays a significant role in atmospheric chemistry, visibility reduction, and climate forcing through its interactions with solar radiation and cloud formation processes [2]. Several studies have indicated that secondary formation via gas-to-particle conversion processes or photochemical transformation contributes considerably to the concentration of $PM_{0.1}$ [4]. Generally, $PM_{2.5}$ and $PM_{0.1}$ are formed from high-temperature processes and are known to be emitted from various primary sources such as vehicular exhaust, oil and coal combustion, biomass burning, industrial processes, and cooking activities. Hence, traffic has been reported to be an important primary source of $PM_{0.1}$ in urban areas, particularly emissions from on-road vehicles such as motorcycles and automobiles [3]. TSP consists of all PM fractions that could be emitted from diverse sources, including biological material (pollen, mold spores, fungi, bacteria, and other organic detritus) and sea salt. Therefore, the chemical components of particles can be used as an indicator of their emission sources, their behaviours, and consequently their impacts on human health and the environment.

Carbonaceous components have been indicated as the major components in both $PM_{2.5}$ and $PM_{0.1}$ and found to comprise more than 50% and 80%, respectively [3]. Hence, their fraction in PM can be used to infer their emission source; for example, the origin of EC could be from primary combustion, while that of OC could be from primary or secondary sources [5]. In addition, the OC/EC ratio could be used to indicate the source of combustion. Based on [6], OC/EC ratio range from 1.2-1.3 indicates the transportation, 1.6-2.3 for industrial activity, and 3.9-4.2 for biomass burning. Similarly, [7] stated that OC/EC of 1.5 is from motor vehicle emissions, 2.7 from coal burning, and 4.1 from wood burning. A study by [8] shows a higher value of the OC/EC ratio of 6.7, pointing out the emission from crop burning.

Diurnal and nocturnal patterns in PM often reflect variations in anthropogenic activities (e.g., traffic, cooking, and industrial operations), as well as changes in meteorological conditions such as boundary layer height, temperature inversion, and humidity [2], [3], [6]. Dry season is considered the high pollution period due to recognized atmospheric conditions, potential for numerous open burning events such as waste or agricultural residue burning, and wildfires [9]. Agricultural waste burning is still a common practice for farmers to clean their land for the coming crop cycle due to the fast and cheap approach [9], [10], [11]. This activity contributes substantially to haze formation and air quality deterioration. Like many other developing countries, Cambodia has recently faced an environmental challenge due to rapid population growth and economic development. The historical record of $PM_{2.5}$ concentration by the Ministry of Environment of Cambodia (MoE) showed the increase during the dry season, especially in the early year from January to March, available at Acid Deposition Monitoring Network in East Asia (EANET) (https://www.eanet.asia). Yet, the detailed composition of PM, especially $PM_{0.1}$, emission source, and exposure risk, particularly in Cambodia, remains unknown.

To address this limitation, this study examined the variation of carbonaceous components in $PM_{0.1}$ and TSP during diurnal (D) and nocturnal (N) periods in the dry season in the capital city, Phnom Penh, Cambodia. A cascade-type Ambient Nanoparticle Sampler (ANS) equipped with a quartz fibre filter (QFF) was used to collect $PM_{0.1,}$ and a complementary collection of TSP by using a High-volume Sampler (HV). The collection was conducted every 11-12 hours on a single day of each week from January to April 2024. The findings will provide a comprehensive scientific basis for high pollution periods in Phnom Penh and inform evidence for air quality management and mitigation strategies in Cambodia.

2 Methodology

2.1 Study area

Aerosol sampling was carried out at two selected locations in the urban area of Phnom Penh, Cambodia. The first sampling site was located at the Institute of Technology of Cambodia (ITC) on the rooftop of a three-story building, approximately 12 meters above ground level, in the Toul Kork District. ITC is located at the corner of the crossroads of Russian Federation Boulevard and Mohasenapramuk Kim Il Sung Boulevard. This sampling site is surrounded by many universities, offices, restaurants, coffee shops, and popular street food places. It can be considered one of the major educational areas leading to active transportation in local and cross-border areas. The second sampling site was on the top roof of a four-story building at the Ministry of Environment (MoE) of Cambodia near the Tonle Sap River, where there is good ventilation of the natural air. This natural ventilation has the potential to enhance the air quality by dispersing PM. In addition, MoE is located on Samdach Preah Sihanouk Boulevard, which has less traffic congestion compared to the nearby ITC on Russian Federation Boulevard. The sampling locations are illustrated in Figure 1.

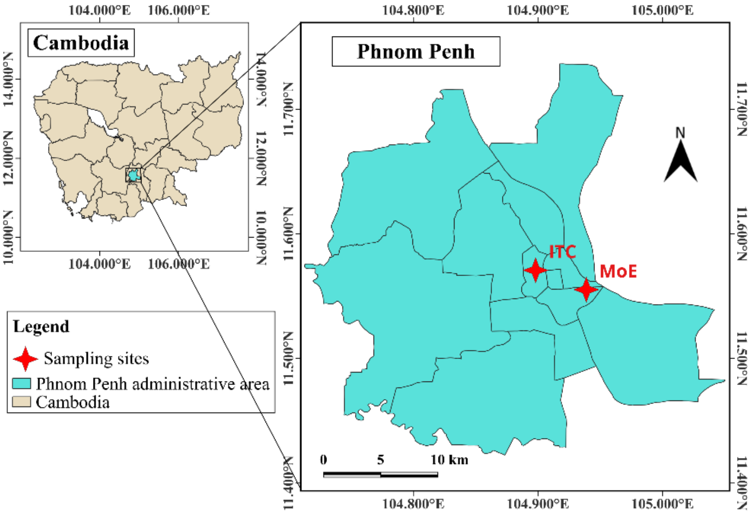

Fig. 1. Sampling locations at the Ministry of Environment (MoE) and the Institute of Technology of Cambodia (ITC) in Phnom Penh City, Cambodia.

2.2 Sampling of $PM_{0.1}$ and TSP

Size-fractionated particle sampling was performed with a filter-based cascade sampler known as ANS with an operating flow rate of 40 L/min. The ANS device consists of 4-impactor stages having aerodynamic diameter (>10, 10-2.5, 2.5-1, 1-0.5 μm) coupled with an inertial filter (IF) consisting of webbed stainless-steel fibers (using SUS304, fiber diameter = 8 μm) plugged in a cartridge nozzle of diameter of 5.25 mm, to classify the particles from

0.5-0.1 µm and a backup filter (BF) to collect the particles smaller than 0.1 µm ($PM_{0.1}$) at the bottom stage. The detailed property of ANS coupled with inertial filters for $PM_{0.1}$ collection was described in previous studies [12]. Two ANS cascade impactors were operated at each site and loaded with a quartz fiber filter (QFF) (diameter of 55 mm; Pallflex, 2500 QAT-UP). HV sampler was operated simultaneously with ANS at ITC to collect the TSP by using the QFF (diameter of 110 mm; Pallflex, 2500 QAT-UP). The ambient samples were sucked in for approximately 11-12 hours, 2 times/day, expected from 6:00 am- 6:00 pm (Day) and 6:00 pm- 6:00 am of the next day (Night). Due to some limitations of the sampling facilitation, the sampling at both MoE and ITC was not performed simultaneously. However, we managed to collect them consecutively within the same week. The detailed information on the sampling is described in Table 1.

Table 1. Sampling information at the Ministry of Environment (MoE) and the Institute of Technology of Cambodia (ITC).

Sites	**Coordinates**	**Date (sample number)**	**Duration**	**Tool**
MoE	11° 33' 18.8"N 104° 56' 19.9"E	January, 2024 (n = 8) February, 2024 (n = 6) March, 2024 (n = 8) April, 2024 (n = 4)	(11– 12 h) x 2 times/day	ANS
ITC	11°34′14.8″N 104°53′53.4″E	January, 2024 (n = 6) February, 2024 (n = 6) March, 2024 (n = 8) April, 2024 (n = 8)	(11– 12 h) x 2 times/day	ANS
ITC	11°34′14.8″N 104°53′53.4″E	January, 2024 (n = 6) February, 2024 (n = 4) March, 2024 (n = 8) April, 2024 (n = 8)	(11– 12 h) x 2 times/day	HV

The samples collected by ANS were used to analyse OC and EC in $PM_{0.1}$ (at the backup impactor). A comparison of OC and EC in TSP collected by HV was also covered. To ensure the reliability of this study, the QFF filters were pre-baked at 350 °C following the protocols established by the Ministry of Environment of Japan [13], thereby removing pre-existing contaminants.

Before sampling, the baked filters were individually wrapped in aluminium foil and stored in a zip-lock plastic bag to prevent potential contaminants, and properly stored to be ready for sampling. Specifically, HV filters were weighed to determine the TSP mass concentration. After sampling, the filters were individually wrapped in their original aluminium foil and immediately placed in the ice box to avoid any evaporation or chemical reaction during delivery to the laboratory of ITC. The samples were then transported to the laboratory of Kanazawa University in Japan for further experiments. In the laboratory, all filters were stored in the freezer at a temperature of -20 °C. To evaluate possible contamination during transportation and from the sampling sites, a set of travel blank filters (n = 3) was also placed alongside the sample filters.

2.3 Carbon analysis

The carbonaceous component was analysed by a thermal/optical carbon analyser (SUNSET Laboratory, OR, USA) following the Interagency Monitoring of Protected Visual Environments-Thermal/Optical Reflectance (IMPROVE-TOR) method. An area of 1.5 cm^2 and 1 cm^2 was punched from a QFF of $PM_{0.1}$ fraction and HV, respectively. The punched filters were then inserted individually into a carbon analyser and began to be heated in pure helium using a heating sequence of 120, 250, 450, and 550 °C set by the instrument program.

Within this process, four organic carbon fractions were separated and quantified as OC_1, OC_2, OC_3, and OC_4. Organic materials in the samples were converted entirely into CO_2. Following that, oxygen was passed through the instrument, providing the oxidizing condition of 2% oxygen and 98% helium. The temperature gradually increased to 550, 700, and 800 °C. This temperature program isolated and evaluated elemental carbon fractions (EC_1, EC_2, and EC_3). However, during this stage, a portion of OC was also carbonized, transformed to pyrolyzed carbon (Pyrol C), and measured. Therefore, total organic and elemental carbon can be calculated following the equation below.

$$OC = OC_1 + OC_2 + OC_3 + OC_4 + \text{Pyrol C} \tag{1}$$

$$EC = EC_1 + EC_2 + EC_3 - \text{Pyrol C} \tag{2}$$

To ensure the repeatability of the analysis, the reference standards, sucrose ($C_{12}H_{22}O_{11}$), obtained from Wako Pure Chemical Industries, Ltd., Japan, were first calibrated and run every time before blank and sample analysis. The subtraction of OC and EC in the blank from the collected samples was also conducted to avoid the potential contamination during transportation or storage. The detailed methodology can be accessed in the protocol of the Ministry of Environment of Japan [13].

3 Results and discussion

3.1 Diurnal and nocturnal concentration variation of OC and EC associated with $PM_{0.1}$

The variation of OC and EC, particularly in $PM_{0.1}$ during distinct daytime (D) and nighttime (N), reveals marked temporal variations and reflects the interplay between anthropogenic activities and boundary layer dynamics. On March 28th at MoE, the highest percentage difference in OC and EC between night and day was 88% and 58%, respectively. Similarly, 70% and 62% difference in OC and EC, respectively, was found at ITC on March 11th. From Figures 2 and 3, OC and EC collected from ITC were higher than those from MoE. This seems to indicate the emission source and geographical effect between the locations. As mentioned in the above section, ITC might be influenced by the traffic activities. At the same time, MoE is located in a less-trafficked area and next to the riverside, which is believed to be dispersed by the natural ventilation. On the other hand, reduced precipitation limits wet deposition processes, allowing for the accumulation of airborne particles, particularly from vehicular emissions, biomass burning, construction, and dust resuspension. Apart from that, transboundary transportation from the agricultural and wildfire areas should not be neglected.

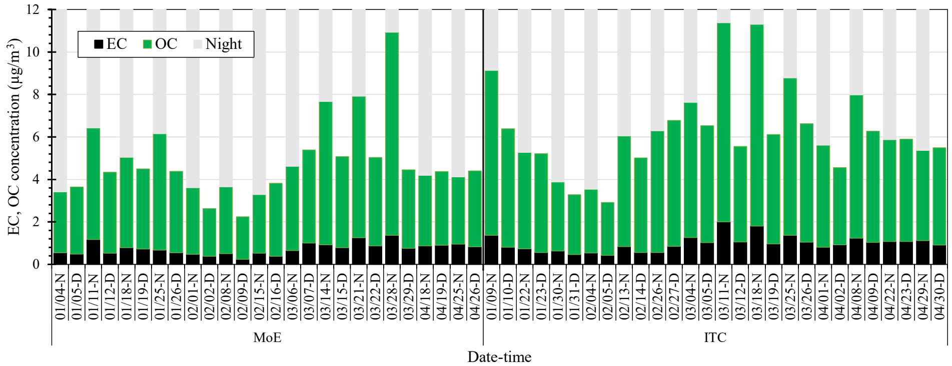

Fig. 2. Diurnal and nocturnal concentration variation of OC and EC associated with $PM_{0.1}$ collected at the Ministry of Environment (MoE) and the Institute of Technology of Cambodia (ITC).

3.2 Monthly average concentration of OC and EC associated with $PM_{0.1}$ and TSP

The comparison of OC and EC in the $PM_{0.1}$ fraction and the TSP is shown in Figure 3. The monthly average OC in both $PM_{0.1}$ and TSP generally shows higher concentration during night-time, except in April, when the OC in TSP at night is lower than during the day. Since OC in TSP might also contribute largely from coarser particles, typically $PM_{2.5}$, which means its various sources of contribution and formation could lead to the variation compared to that of $PM_{0.1}$. On the other hand, OC in the $PM_{0.1}$ fraction should also be one of the contributors that can raise the level of OC of the TSP. Temporal characteristic of OC in $PM_{0.1}$ and TSP was also observed across the period. The highest OC in TSP was significantly found in January at night. The highest OC in $PM_{0.1}$ from both locations was obtained in March at night. This reveals the possible transboundary contribution in January due to the open burning of agricultural residue or forest fire, and resuspension from the ground [14]. Conversely, OC of $PM_{0.1}$, emitted from the local source, might contribute mainly to the OC level in March. Similar to OC, the monthly average of EC also shows an increase during the night, except for those in March and April. The highest EC in $PM_{0.1}$ and TSP was observed to be the same as the OC pattern.

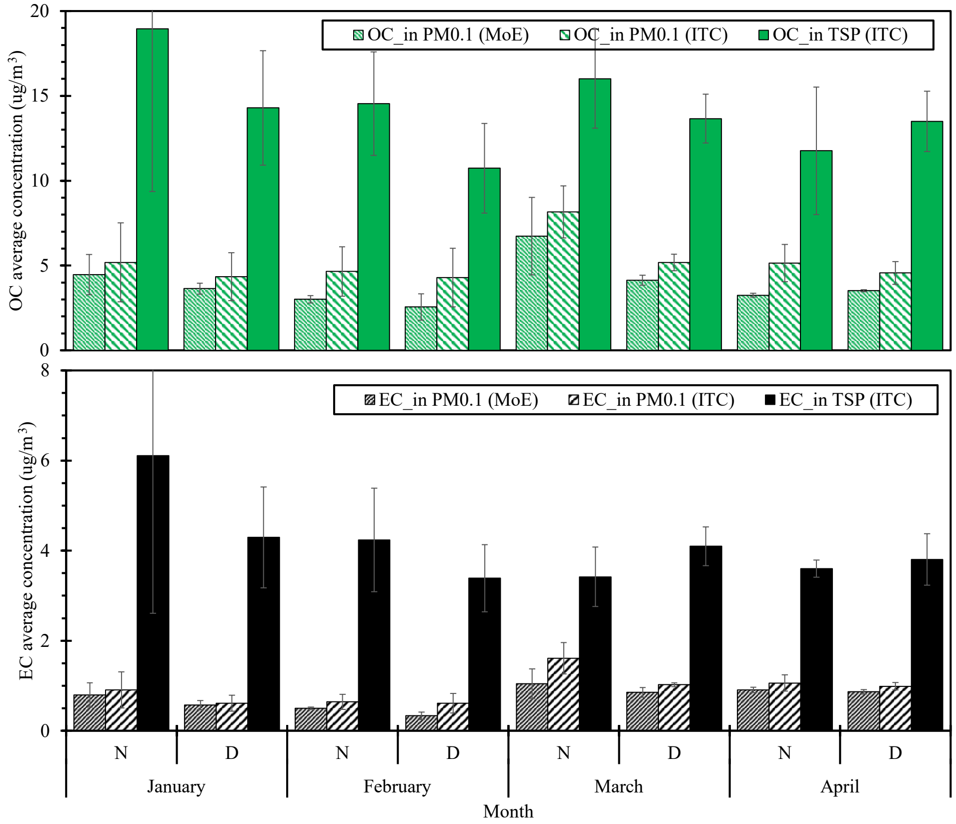

Fig. 3. Monthly average concentration of OC and EC associated with $PM_{0.1}$ and TSP at the Ministry of Environment (MoE) and the Institute of Technology of Cambodia (ITC).

3.3 Comparison of OC, EC, and OC/EC ratio

Table 2 presents the average concentrations of OC, EC, and the OC/EC ratio over the entire period. Based on the results of both locations, OC and EC revealed a higher concentration at nighttime compared to daytime. Conversely, the OC/EC ratio varied slightly over the period, with daytime values higher than nighttime values. The spatial variation of OC and EC concentration was different between the locations, but the OC/EC ratio of PM$_{0.1}$ was obtained similarly. This might indicate a similar emission source, but with different concentrations. Without riverside air ventilation, ITC seems to encounter stagnant air, which could lead to the accumulation of PM. Furthermore, the total carbon (OC+EC) of TSP at ITC contributes around 20% to its PM concentration. While the total carbon in PM$_{0.1}$ over TSP ranged from 5-10%. This means about 25-50% of the total carbon in TSP is comprised by PM$_{0.1}$. As a result, the OC/EC ratio associated with PM$_{0.1}$ from both locations fell within the range of biomass burning [5, 7]. Conversely, OC/EC of TSP was lower than that of PM$_{0.1,}$ suggesting a different emission source, as mentioned in [5, 6], due to its mixed composition of coarser PM.

Table 2. Comparison of average OC, EC, and OC/EC ratio associated with PM$_{0.1}$ and TSP in the whole period.

Sites	**Time**	**PM$_{0.1}$**			**TSP**			
		OC±SD	**EC±SD**	**OC/EC ±SD**	**PM± SD**	**OC±SD**	**EC±SD**	**OC/EC ±SD**
		ug/m^3	**ug/m^3**	**ug/m^3**	**ug/m^3**	**ug/m^3**	**ug/m^3**	**ug/m^3**
MoE	N (n=13)	4.37± 1.70	0.81± 0.23	5.41± 1.27	-	-	-	-
	D (n=13)	3.46± 0.66	0.66± 0.25	5.73± 1.60	-	-	-	-
ITC	N (n=14)	5.78± 1.60	1.06± 0.41	5.71± 1.08	102.28± 21.96	15.32± 2.99	4.34± 1.23	3.62± 0.72
	D (n=14)	4.59± 0.41	0.81± 0.23	5.93± 1.28	144.3± 38.57	13.05± 1.58	3.90± 0.39	3.34± 0.16

Noted: Values are "mean ± standard deviation", N is nighttime, D is daytime, n is sample number, MoE: Ministry of Environment, and ITC: Institute of Technology of Cambodia.

4 Conclusion

Based on the findings, OC and EC increase significantly at all sites during the nighttime. According to MoE data, at least 61% and 85% of sampling days were found to be high in OC and EC at night, respectively. Similarly, those at ITC were found to be high at night on most of the sampling days for about 71% and 78%, respectively. On the other hand, the average OC and EC in PM$_{0.1}$ at ITC were higher than at MoE, which might be due to differences in emission sources and atmospheric conditions. Significantly, the total carbon in PM$_{0.1}$ contributes a large portion to that in the TSP for approximately 25-50%. The confirmation by the OC/EC ratio in PM$_{0.1}$ indicates the influence of open biomass burning emissions. Conversely, the ratio of the OC/EC in TSP suggests that different emission sources. Thus, the detailed study of the composition of PM in various sizes is crucial to understanding its characteristics and sources. This could be a suggestion for further study to analyse more chemical compositions of PM, such as ions, metals, and also carcinogenic compounds, to delve deeply into the primary sources of air pollutants and risk assessment, toward effective mitigation and management.

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