CHARACTERISTICS OF ELEMENTAL AND ORGANIC CARBON IN ATMOSPHERIC NANOPARTICLES AT DIFFERENT SAMPLING LOCATIONS IN VIETNAM

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ABSTRACT

Atmospheric ultrafine particles (NPs or PM0.1) were investigated at a roadside of Nguyen Van Cu road (Vinacomin) and at a mixed site in the Hanoi University of Science and Technology (HUST) in Hanoi, Vietnam. The sampling was conducted during a rainy reason and a dry season to determine the characteristics of atmospheric elemental and organic carbon in the nanoparticles. The relative contributions of organic carbon (OC) and elemental carbon (EC) to total carbon (TC) at HUST were 83.7 – 85.0 % and 15.0–16.3 %, respectively; whereas those at Vinacomin’s sampling site accounted for 78.6 – 81.5 % and 18.5 – 21.4 %, respectively. The study provides an interesting observation that particulate OC and EC have spatial and temporal variations dependent on sampling sites and weather conditions. In contrast, consistent OC/EC ratios were also found at both seasons of each location, in which the ratios were from 3.68 to 5.68. The correlations of OC and EC were found in the rainy season with the slopes ranging from 0.21–0.34; however, these correlations were not observed in the dry season. The relationships between OC and EC, char – EC and soot – EC can be used in primarily determining the sources of NPs in the atmosphere.

Keywords: nanoparticles, EC, OC, char-EC, soot-EC.
1. INTRODUCTION

Recently, substantial attention has been paid to atmospheric particulate matter, which is believed to be strongly associated with adverse health effects [1 - 4] and environments [5]. In the past decade, it has been found that the smaller, respirable particles (PM$_{2.5}$ or, especially, ultrafine particles) pose a higher risk to human health [6, 7]. Due to intensive research, there is emerging evidence that exposure to nanoparticles (NPs) may adversely affect human health [8 - 11]. These particles could also influence the visibility and global climate [12, 13]. Such adverse effects of NPs could be attributed to their small size, and high number concentration, as well as bounded elemental/organic carbon, sulfate, elements and PAHs (polycyclic aromatic hydrocarbons). Therefore, it is important to gain the best understanding about the species’ concentrations of NPs to assess these effects. Carbonaceous matter is a major component of the ambient atmospheric nanoparticles [14 - 19]. These carbonaceous aerosols are mainly divided into two fractions: elemental carbon (EC), often called BC or soot, and organic carbon (OC). BC is one of the key components of atmospheric aerosols that warm the atmosphere by absorbing sunlight, while aerosols containing OC cool the atmosphere by increasing the Earth’s reflectivity [21]. More significantly, while EC originates from the burning of carbonaceous matter, OC may be emitted directly in the particulate phase or formed from a gas-to-particle conversion process in the atmosphere [22]. Therefore, particulate OC and EC have large spatial and temporal variations dependent on sampling sites and weather conditions. In contrast, consistent OC/EC ratios are more often found corresponding to a certain location and season [23]. Hence, information of EC and OC plays a vital role in not only evaluating the impacts of NPs but also understanding the source type and strength. EC can also be subdivided into two classes: char – EC (EC1 – POC) and soot – EC (EC2 + EC3) [24 - 25]. Char consists of the solid residues of combustion and retains some original properties of the source materials. Soot, on the other hand, is formed through high-temperature condensation of hot gases emanating from solid and liquid fuels during combustion; soot retains very few of the physical and chemical properties of the source materials [26].

However, data on carbonaceous components in NPs are still scarce in developing countries including Vietnam. To the best of our knowledge, only few research studies on NPs in Vietnam [27, 28]. Our previous studies only stated data on OC and EC fractions, they have not shown the relationship between OC and EC as well as the char – EC and soot – EC ratios. This study is, therefore, aimed at the determination of the characteristics of atmospheric EC and OC in NPs in Vietnam in which, the relationships between OC and EC, char – EC and soot – EC ratios will be analyzed deeply. These relationships would be valuable to examine the possible emission sources of NPs in the atmosphere.

2. MATERIALS AND METHODS

2.1. Study area

Hanoi is the capital of Vietnam and the second largest city in the country. Hanoi is located in the north of the country so it has monsoon and tropic climate with the cold and dry winter and hot and rainy summer. A number of activities such as transportation, industry, construction, and domestic cooking can be considered to be the main local sources of NPs emission into the air of Hanoi. Two sites, located at Gia Lam district (Vinacomin) and Hanoi University of Science and Technology (HUST), were selected to be sampling sites. Summary information of the sampling sites is presented in Figure 1 and Table 1.
The first sampling site is located on the 5th floor of Vinacomin building, at a roadside of Nguyen Van Cu road; it is near an intersection of two main roads, Gia Lam bus station, and Gia Lam railway station. Gia Lam district is also one of places that have strong biomass burning activities. The other sampling site is located on the 3rd floor of the Center of Foreign Languages, HUST, which is surrounded by trees, a lake and lecture halls. This sampling site can be considered as a mixed site with a lot of activities such as transportation, construction, and domestic cooking... that can contribute to the compositions of NPs.

**Figure 1.** Location of sampling sites in Hanoi.

<table>
<thead>
<tr>
<th>Site name</th>
<th>Coordinates</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>HUST</td>
<td>21°00.17 N and 105°50.37 E</td>
<td>3rd floor of Center of Foreign Languages, HUST (8 m)</td>
</tr>
<tr>
<td>Vinacomin</td>
<td>21°03.01 N and 105°53.04 E</td>
<td>5th floor of Vinacomin building, Nguyen Van Cu road (18 m)</td>
</tr>
</tbody>
</table>

Sampling was conducted during the wet season and the dry season for both sites. These sampling periods were selected so that the influence of seasonal reversing winds with temperature and relative humidity characteristics corresponding to the seasons in Hanoi, Vietnam, could be observed.

### 2.2. Sampling collection and analytical method

An inertial fibrous filter (INF) sampler (the newest version KU – TSC 26A57C1, Kanazawa University) with a design airflow of 40.0 l min⁻¹ was used to collect NPs. The INF sampler consists of four impaction stages that collect particles with diameters of 10, 2.5, 1.0, and 0.5 µm. The system also has one inertial filtration stage composed of unwoven stainless steel fibers for collecting particles larger than 0.1 µm after the four impaction stages. NPs are collected uniform on to a 55 mm quartz fiber filter (2500 QAT – UP, Pallflex, CT, USA).

The 24-h sampling duration was conducted in August (rainy season) and from October to December (dry season) of 2015. Seven samples were taken for each season at Vinacomin. At HUST, seventeen samples were collected for the rainy season and twenty-eight samples were taken for the dry season. Six blank samples (three samples/season) and ten blank samples (three samples/rainy season, seven samples/dry season) were taken for Vinacomin and HUST, respectively. Flow rates of the samplers and meteorological parameters, including wind direction and velocity, temperature and humidity, were measured every hour during sampling. Some meteorological data are shown in Table 2.

Quartz fiber filters were pre-baked at 900 °C for four hours to remove any possible contamination [29, 30]. After sampling, each quartz filter was put in a Petri dish and kept in a
The samples were analyzed for OC and EC by using a thermal/optical carbon analyzer (DRI Model 2001, Atmoslytic, Inc., Calabasas, CA, USA), which is based on the IMPROVE (Interagency Monitoring of Protected Visual Environments) method [30, 31]. A $0.503\, \text{cm}^2$ punch-out from the quartz fiber filter was analyzed for eight carbon fractions stepwise at temperatures of 120 (OC1), 250 (OC2), 450 (OC3), 550 °C (OC4) in a non-oxidizing helium atmosphere and at 550 (EC1), 700 (EC2), and 800 °C (EC3) in an oxidizing atmosphere of 2 % $\text{O}_2$, with the balance being helium. A portion of the volatilizable carbon chars in the absence of oxygen, and this is monitored by the reflected laser light as the filter darkens. After $\text{O}_2$ is added, the original EC and pyrolyzed char evolves and the filter lightens as detected by increasing reflectance. The carbon that evolves in the oxidizing atmosphere until the reflected light achieves its initial value is termed pyrolyzed organic carbon (POC). POC was continuously monitored by reflectance or transmittance of laser signal. OC is operationally defined as OC1 + OC2 + OC3 + OC4 + POC, and EC is defined as EC1 + EC2 + EC3 – POC. The EC fraction was divided into char-EC and soot-EC [24 - 25]. Char-EC is defined as EC1 minus POC, and the soot–EC is defined as the sum of EC2 and EC3 [32, 33].

3. RESULTS AND DISCUSSION

3.1. Concentrations of carbonaceous components

Average concentrations of carbonaceous components of NPs, collected at the both sites in the two seasons, are shown in Table 3.

Table 3. Average carbonaceous concentrations and their ratios at both sites.

<table>
<thead>
<tr>
<th>Component</th>
<th>Roadside site (Vinacomin)</th>
<th>Mixed site (HUST)</th>
<th>Mixed site /Roadside site ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration (25°C, 1atm, µg/m$^3$)</td>
<td>Mass/mass</td>
<td></td>
</tr>
<tr>
<td>OC</td>
<td>2.31 ± 0.51</td>
<td>4.29 ± 0.77</td>
<td>2.04 ± 0.67</td>
</tr>
<tr>
<td>EC</td>
<td>0.53 ± 0.20</td>
<td>1.17 ± 0.32</td>
<td>0.67 ± 0.17</td>
</tr>
<tr>
<td>TC</td>
<td>2.84 ± 0.72</td>
<td>5.46 ± 1.09</td>
<td>2.48 ± 0.86</td>
</tr>
</tbody>
</table>
Concentrations at the roadside

Generally, the measured amount of OC accounted for 78.6% to 81.5% of TC in NPs. The average concentrations of carbonaceous components in the dry season is higher than those in the rainy season. The higher concentrations of the dry season samples might be related to increased energy (fuel) consumption and biomass burning activities around the sampling site. Gia Lam district is a place that has strong biomass burning activities in October. This period was also the time when the collection of NPs in the dry season was conducted.

The results of carbonaceous components of NPs in this study can be compared with those in the roadside environment of other studies as shown in Table 4.

Table 4. OC and EC concentrations of NPs at the roadside of different locations

<table>
<thead>
<tr>
<th>Carbonaceous components</th>
<th>Rainy season (µg/m³)</th>
<th>Dry season (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Study [33, 34]</td>
<td>Japan [23]</td>
</tr>
<tr>
<td></td>
<td>[23] Germany</td>
<td>This study [33, 34]</td>
</tr>
<tr>
<td></td>
<td>Japan USD</td>
<td>[35]</td>
</tr>
<tr>
<td>OC</td>
<td>2.31 ± 0.51</td>
<td>1.12 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>1.01 ± 0.16</td>
<td>1.21 ± 0.43</td>
</tr>
<tr>
<td></td>
<td>4.29 ± 0.77</td>
<td>1.12 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>1.10 ± 0.30</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>0.53 ± 0.20</td>
<td>0.19 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.08 ± 0.05</td>
<td>0.14 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>1.17 ± 0.32</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.50 ± 0.10</td>
<td></td>
</tr>
</tbody>
</table>

Generally, the carbonaceous components in this study are higher than those of other studies. These results support the likelihood of site-specific differences such as sampling period, location, and sampler. It may be needed to know the concentrations of nanoparticles at different time periods under various environmental conditions to get better understanding about the level of nanoparticles in the atmosphere. These data will make a significant contribution to push up further studies of NPs in Vietnam.

Concentrations at the mixed site.

In contrast with the roadside site, carbonaceous concentrations of NPs in the rainy season were slightly higher than those in the dry season. These results might be explained by the different number of rainy days in the two sampling periods as shown in Table 3.

Generally, the OC fractions at this site were higher than those at the roadside site (83.7% - 85.0%). To evaluate the different levels of carbonaceous components in NPs at the two sites, the mass ratios between the mixed site and roadside site (M/R ratios) are calculated and also presented in Table 3. The M/R ratios in NPs were 0.88 (OC), 1.26 (EC), and 0.87 (TC) in the rainy season; whereas the M/R ratios in dry season were 0.43 (OC), 0.27 (EC), and 0.39 (TC). These results support the probability of the impact of the biomass burning activities or increased energy (fuel) consumption in the dry season at the Vinacomin site.

3.2. Seasonal variation OC/EC ratios

EC originates from primary anthropogenic sources (e.g., biomass and fossil fuels) and is not formed by reactions involving gaseous hydrocarbon precursors in the atmosphere. However, OC is emitted from primary emission sources and can also be derived from the chemical reactions of gaseous organic precursors in the atmosphere. Secondary OC is also formed by condensation of low vapor pressure products during photo-oxidation of hydrocarbons. The ratios between OC and EC concentrations have been used to study the emissions and transformation characteristics of carbonaceous aerosols.
The OC/EC ratios at Vinacomin’s site were 3.68 and 4.39 in the rainy season and the dry season, respectively; whereas these ratios at HUST had values of 5.14 and 5.68 in the rainy season and the dry season, respectively. These ratios can be considered to be consistent at each location.

The correlation between OC (x–axis) and EC (y–axis) in NPs at Vinacomin and HUST is shown in Figure 2, (a) and (b) respectively; these plots show the relative contributions of OC and EC fractions to the composition of the particles during the sampling period in each season. They showed strong correlations in the rainy season ($R^2 = 0.74$ at Vinacomin and $R^2 = 0.72$ at HUST). Generally, slopes ranged from 0.21–0.34. The slopes in this study can be considered to be in the same range with those of other studies [32, 34] although the concentrations of carbonaceous components in the former were higher than those of the later. The particulate OC and EC have large spatial and temporal variations dependent on sampling sites and weather conditions. In contrast, the consistent OC/EC ratios are more often found corresponding to a certain location and season. However, the relationships between OC and EC was not found in the dry season. Therefore, in order to use the relationships between OC and EC to determine the sources of NPs, it is necessary to conduct deeper and longer studies to have the comprehensive knowledge about them.

### 3.3. Char EC/ Soot EC ratios

EC is not a single chemical compound. It can be subdivided into two classes based on our analytical methods: char – EC and soot – EC. Char – EC was defined as a carbonaceous material obtained by heating organics. It is formed directly from pyrolysis or as an impure form of graphitic carbon obtained as a residue when carbonaceous material is partially burned or heated with a limited supply of air. Soot was defined as only those carbon particles that form at high temperature via gaseous phase processes [35]. Char – EC is emitted largely from biomass and coal combustion while soot – EC is emitted largely from motor vehicle emissions and forest fires. The soot – EC/char – EC ratio depends upon the mixing function of the different sources: motor vehicle emissions and possibly grass burning result in higher soot – EC/char – EC ratios, while wood combustion, particularly biomass burning by smoldering at low temperature, produces lower soot EC/char – EC ratios [36, 37]. Therefore, char – EC/soot – EC ratios can
also be used as an indicator of the emission sources, and the char-EC/soot – EC ratio of motor vehicle emissions tends to be lower than that of biomass or coal combustion.

The average concentrations of char – EC and soot – EC in the two seasons at two sampling sites and the char – EC/soot – EC ratios is shown in Table 5.

The average concentrations of char – EC and soot – EC for the two seasons were 0.55 ± 0.24 and 0.29 ± 0.07 µg/m³ at Vinacomin site, and 0.18 ± 0.10 and 0.18 ± 0.05 µg/m³ at HUST, respectively. The char – EC/soot – EC in the NPs ranged from 0.81 to 2.79 (Table 5). The char – EC/soot – EC ratio at Vinacomin tended to be high in the dry season samples reflecting the contribution of the biomass burning during the sampling period. These results can be considered to be in the same range with those of other studies (0.73 - 3.04) although the concentration of char – EC/soot – EC of NPs in this study is higher than those of other studies [33, 34]. Once again, these results support the theory that consistent char – EC/soot – EC ratios can be found corresponding to a certain location and season.

**Table 5. Average concentrations of char-EC and soot-EC and their ratios.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Roadside site (Vinacomin)</th>
<th>Mixed site (HUST)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rainy season</td>
<td>Dry season</td>
</tr>
<tr>
<td>Char-EC (µg/m³)</td>
<td>0.26 ± 0.13</td>
<td>0.84 ± 0.34</td>
</tr>
<tr>
<td>Soot - EC(µg/m³)</td>
<td>0.26 ± 0.08</td>
<td>0.32 ± 0.06</td>
</tr>
<tr>
<td>Char-EC/Soot EC ratios</td>
<td>0.96 ± 0.27</td>
<td>2.79 ± 1.47</td>
</tr>
</tbody>
</table>

The observed correlations of char – EC and soot – EC with EC in NPs in each season at the two sites are plotted all together to show the relationships. As shown in Figure 3, both char – EC and soot – EC in the NPs had a strong positive correlation with EC, except for the dry season at Vinacomin (soot – EC with EC). This exception of correlations of EC and soot – EC in the dry season may be influenced by biomass burning activities at the sampling site. In addition, these relationships between EC, char – EC, and soot – EC concentrations can be found in other studies but they have the lower slopes [33, 34]. This result implies that the char – EC/soot – EC ratio may be a useful indicator for source identification. However, it is also important to note that the char EC/soot – EC ratio can be varied depending on the characteristics of the study area.

**Figure 3. Correlations of EC with char-EC and soot-EC.**

a) Vinacomin  
b) HUST
4. CONCLUSION

The atmospheric carbonaceous components, particularly OC, EC, char – EC and soot – EC in the NPs, were measured in a rainy season and a dry season (August to December) at the two locations in Hanoi, Vietnam. It was found that OC accounts for 78.6 – 81.5 % of TC in the NPs at the Vinacomin site, and 83.7 – 85.0 % of TC in the NPs at HUST site. The relationships between OC and EC were also found at both sites in the rainy season with the slopes ranging from 0.21–0.34. The char –EC/soot – EC ratio distribution indicated their association with source profiles. Char – EC/soot – EC rations varied from 0.81–2.79. Both char – EC and soot – EC in NPs had a strong positive correlation with EC in both sites in the two seasons, except for the dry season at Vinacomin (soot – EC with EC). The relationships between OC, EC, char – EC and soot – EC provide an opportunity for better understanding of carbonaceous aerosols. These results are a significant contribution to Vietnam’s database of carbonaceous components in the NPs.

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Characteristics of elemental and organic carbon in atmospheric nanoparticles…
