CHARACTERISTICS OF ORGANIC AND ELEMENTAL CARBON IN PARTICULATE MATTER ON THE US EAST COAST: A CASE STUDY AT METROPOLITAN NEWARK IN NEW JERSEY

By

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ABSTRACT OF THE THESIS

Characteristics of organic and elemental carbon in particulate matter on the us east coast:

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Abstract

To investigate the day- and night-time variability of carbonaceous aerosols in the ambient air in metropolitan Newark in New Jersey on the US east coast, particulate air samples of PM_{2.5} (particles with diameter \leq 2.5 µm) and PM_{2.5-10} (particles with diameter 2.5-10 µm) were collected from downtown Newark. Air samples were analyzed by thermal-optical analysis methods for elemental carbon (EC) and organic carbon (OC). The results show that the total carbonaceous particulate matter (PM) in the air was dominated by coarse-mode particles. The OC/EC ratios varied from 5.3 to 50.9, with an average of 19.2 ± 11.7 for PM_{2.5}, and from 5.1 to 13.7, averaging 7.5 ± 2.1 for PM_{2.5-10}. Higher concentrations of OC in PM_{2.5} particles occurred at night with a moderate correlation with Relative Humidity (RH) (R²=0.52), suggesting the possible formation of secondary organic aerosols (SOC) via aqueous-phase oxidation of low volatility organic

compounds. Fine-mode OC had moderate correlations with PM_{2.5} sodium (R²=0.59) and PM_{2.5-10} sodium (R²=0.37), suggesting a mixed influence of anthropogenic and marine sources. Fine mode EC had a strong relationship with PM_{2.5} nitrate (R² = 0.75), suggesting an anthropogenic source for PM_{2.5} EC, as nitrate is a secondary aerosol formed from nitrogen oxides (NO_x) emitted mainly by traffic sources. The concentrations of coarse-mode EC (PM_{2.5-10}) were higher during the daytime than at night, suggesting a major contribution from mobile sources. The PM₁₀/PM_{2.5} ratios observed during this study were 4.6 for OC and 8.0 for EC, higher than those from selected previous studies. The highest concentrations of carbonaceous aerosols were associated with east-southeast winds; busy highways were also in that direction, while the concentrations of them were the lowest under west winds. This suggests that winds played an important role in the variations of carbonaceous aerosols in the air in this region.

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1. Introduction

Particulate matter (PM) is a mixture of solid particles and liquid droplets composed of various organic and inorganic compounds in the air. PM is often categorized by size fractions: fine-mode fraction (PM_{2.5}) with an aerodynamic diameter of $\leq 2.5 \mu m$ and coarse-mode fraction (PM_{2.5-10}) with 2.5 - 10µm (Choi et al., 2004). Carbonaceous particles are important constituents of the fine fraction of PM, especially in highly industrialized and urbanized areas (Cao et al., 2004). They are often divided into two categories: elemental carbon (EC) and organic carbon (OC). OC may be composed of several organic compounds that can be classified as aromatic, aliphatic compounds, and others.(Molnár et al., 1999). Total carbon (TC), the sum of EC and OC, is an additional parameter used to analyze some processes involving their formation, concentration variation and source strength, although TC does not provide complete or comprehensive information on the emission sources and formation processes. TC provides only mixed signals from different sources and processes, whereas, those of individual compounds are not likely to provide original information of their source because of modification by photo-oxidation processes in the atmosphere (Huang et al., 2006).

Atmospheric aerosols with diameters less than 10 micrometers, derived from natural and anthropogenic sources, containing OC and EC can influence snow coverage by warming the atmosphere, reducing surface-incident solar energy and snow reflectance after deposition (Flanner et al., 2009). They play an important role in controlling a number of atmospheric processes, such as the deposition, and optical properties of different compounds. In addition, the surface of EC particles contains numerous adsorption sites which are capable of enhancing catalytic processes (Molnár et al., 1999). These particles greatly affect air-quality, atmospheric chemistry, visibility, and Earth's radiation budget (Fuzzi et al., 2015, Han et al., 2011). High concentrations of PM with significant carbonaceous aerosols content, negatively affect human health, primarily respiratory problems (Valavanidis et al., 2008, McClellan, 1996). Other effects include visibility reduction (Larson et al., 1989, Zhou et al., 2012) and climatic impacts on a regional scale (Kupiainen and Klimont, 2007).

Black carbon plays an important and unique role in the Earth's climate system because it absorbs and reflect solar radiation, intervening in the radiative balance, influences cloud formation processes, and significantly alters the melting process of snow (Jacobson, 2001a, Conant et al., 2002). BC is defined as a strong absorber of visible light and some studies estimate that it may be the second largest contributor to global warming after greenhouse gases. On the other hand, black carbon can also reflect sunlight (the socalled "albedo") and has an average residence time in the atmosphere between 1 and 2 weeks, so the measures to reduce the emissions of these aerosols can be much more efficient to slow down the loss of glaciers in a short term than in the case of greenhouse gases (Chung and Seinfeld, 2005). Finally, hygroscopic nuclei (Buseck et al., 2014, Chughtai et al., 1999), due to adherence to particles of water present in the atmosphere, along with acidic pollutants, such as sulfides, can cause acid rain (Gray et al., 1986, Dockery et al., 1993).

Elemental carbon is a product of the incomplete combustion of fossil fuels, especially diesel, and biomass (Figure 1) (Kim et al., 2011, Briggs and Long, 2016). EC particles are formed in the first stage of the pyrolysis process, from small molecular aggregates. When gas phase polymerization reactions produce compounds of higher molecular weight, they lead to the formation of particles (Lahaye and Ehrburger-Dolle, 1994). This particle formation is closely related to the chemical composition of fuel, temperature of combustion and quantity of oxygen. According to the dynamics of their formation, these particles are mixed with other particles of different composition through absorption, on the surface of vapors from organic species and inorganic gases including SO_x, O_x, and moisture (Rajput et al., 2014). Particle size is related to formation mechanism and corresponds to the range of accumulation, between 0.1 and 1 μ m. Most emitted EC particles are smaller than 0.2 μ m, but sometimes larger due to coagulation (Ogren and Charlson, 1983). EC concentrations decrease rapidly with emission reduction, as it is rapidly removed from the atmosphere by dry or wet deposition. Thus, EC emission reduction is an important mitigation strategy that could reduce global climate forcing in the short term (Bond et al., 2013). EC is the most important visible light absorber in the atmosphere (Bond et al., 2013), and it has been suggested that, after carbon dioxide, it may have the highest positive radiative forcing (Jacobson, 2001b). European studies have shown that between 11 and 17% of PM_{10} is composed of EC, and emission exacerbates global warming, visibility, and health problems. It decreases visibility and irradiation, influences cloud processes, and alters the melting of snow and ice cover (Flanner et al., 2007, Qian et al., 2015). EC is also relevant because it is a carrier of gases such as oxides of sulfur and nitrogen which, together with atmospheric humidity, generate the acidity of particulate material (Chang et al., 1982).



Figure 1. The mechanisms/pathways and sources for EC, OC, primary organic aerosol (POA), volatile organic carbon (VOC), SOA, water-soluble organic carbon (WSOC), and water-insoluble organic carbon (WIOC) in the atmosphere (The dashed arrows represent the pathways for two different types of OC).

Organic carbon is an aggregate of hundreds of individual components with a range of chemical and thermodynamic properties, formed by various processes (Figure 1) (Alves et al., 2001, Abas and Simoneit, 1996). The compounds identified in atmospheric aerosols can be classified into alkanes, alkenes, alkynes, alkanoic acids, aliphatic dicarboxylic acids, diterpenoid acids, aromatic polycarboxylic acids, and many others. The sources of primary OC include combustion processes such as biomass burning, oil and petroleum residues and the combustion of fossil fuels, cooking, dust from paved roads, cigarette smoke, pesticides, vegetation emissions, etc. OC is also composed of volatile organic compounds (VOCs), associated with the chemistry of the atmosphere

(Huang et al., 2020, Kwon et al., 2016). OC aerosols also include SOC, which originates in greater quantity in the presence of gaseous precursors (compounds aliphatic or polycyclic) and warm temperatures (Alves et al., 2001). SOC is formed in the atmosphere by mass transfer from gas to aerosol phase, due to low volatility compounds resulting from the successive oxidation of volatile and semi-volatile organic compounds (Odum et al., 1994). The aerodynamic diameter of these particles is in the range of 0.1 to 10 μ m. Usually, OC variability is substantially larger than EC variability, indicative of the more complex nature of OC secondary aerosols (Gaffney et al., 1984). OC can cause mild respiratory conditions and chronic diseases of pulmonary obstruction (Kim et al., 2012). Although some climate models treat OC as purely scattering (Myhre et al., 2007), absorption by OC can occur at shorter visible and UV wavelengths (Kirchstetter and Thatcher, 2012, Lack and Cappa, 2010, Barnard et al., 2008), commonly known to as brown carbon (BrC). Light absorption by BrC could be comparable with black carbon in the spectral range of near-ultraviolet light (300-400 nm) and BrC related with anthropogenic sources, tends to be more light-absorbing than those related with biogenic emissions (Cheng et al., 2016).

Newark, Jersey, on the US east coast is a metropolitan city highly impacted by air pollution, including marine sources. Although there are many reports on atmospheric carbonaceous aerosols over urban areas, few studies have been conducted in coastal areas affected by air pollution. Previous OC and EC concentration measurements for Newark indicate that the highest levels originate from local sources around the city of Newark (Gaffney et al., 1984). Newark International Airport and Port Newark are located south southeast of the city. There are several chemical manufacturing facilities, lacquer and pigment manufacturers, metal fabricators, smelters, plating, auto body shops in the city. Major local and interstate highways, notably the New Jersey Turnpike, Garden State Parkway, Route I-95 and Route 1-9, all serve as the sources of motor vehicle traffic emissions (Lioy, 2017).

In this paper, we report and discuss the results of atmospheric EC and OC observed over downtown Newark. The major objectives of this study are to: (1) investigate the daily, diurnal and nocturnal temporal variation of this carbonaceous particles in fine- and coarse-modes in Newark; (2) explore their relationship with major ionic species in this area (nitrate, sulfate, sodium, and potassium); and (3) to investigate the weather factors that may impact the temporal variation of these aerosols. Our results will fill the data gap in urban carbonaceous aerosols impacted by air pollution (including marine influences) in Newark, for a better understanding of their formation processes.

2. Methods

2.1 Study Site

Ambient $PM_{2.5}$ and $PM_{2.5-10}$ samples were collected on the roof of a building (~20 m height above the ground), at the Newark campus of Rutgers University, located downtown Newark (40.74 N, 74.18 W), New Jersey, on the US east coast. It is about 14 km west of Manhattan and 20 km northwest of the Atlantic Ocean (Figure 2). This sampling site, located in a densely populated area of Newark (~285,000), is impacted by major highways and industrial facilities. Newark International Airport is ~ 4 km to the south and Port Newark is ~ 5 km to the south southeast of this site. A survey of the surrounding area showed that some major emissions, such as large chemical and petrochemical complexes are located close to the site, as well as a number of small truck,

auto body repair and painting shops (Lioy, 2017). There are also chemical plants, metal processing, smelters, finishing operations, a paint pigment manufacturing facility, and other industries in close proximity to the site.



Figure 2. Main sources of air pollution in the Newark metropolitan area (Source: http://jaxmit.github.io/2016/advancedGIS/adv_gis_final.html#).

2.2 Field sampling

The sampling was done with a Partisol 2000i-D Dichotomous Air Sampler (Thermo Scientific, MA, USA). The instrument was placed on a platform on the roof of Bradley Hall, from April 19 – 27, 2019, to collect both PM _{2.5} and PM_{2.5-10} (Table 1). The sampler consists of two sample flows directed through two 47 mm filters, a high flow (15 L min⁻¹) for PM_{2.5}, and a low flow (1.67 L min⁻¹) for PM_{2.5-10}. The sampling duration was 11:30 h (except for two samples that were only 9:45 h due to technical issues) for each sample, collected in the daytime and night-time. Two Whatman Quartz Filters (Grade QM-A, 47 mm), with the same lot number, were used for sampling. The filters were placed in aluminum foil liners and baked in a furnace at 550 °C in air for 24 h before use (Park et al., 2007). The filter area with particle loading was 17.35 cm², corresponding to a face velocity of 14.41 and 1.60 cm s⁻¹ for high flow (PM_{2.5}) and low flow (PM_{2.5-10}), respectively. After sample collection, the filters were placed, using metal tweezers, in petri dishes that had been pre-cleaned three times with deionized water and then wrapped in aluminum foil, sealed in zipper bags and stored in a freezer at -20°C, until they were analyzed.

| _ | Vol (r | n ³) | | | |
|-------------|--------|------------------|--------|------------|-------------------------|
| Date, Time | PM2.5 | PM2.5-10 | RH (%) | Air T (°C) | WS (m s ⁻¹) |
| 4/20, 6:30 | 10.3 | 1.15 | 90 | 19.9 | 5.1 |
| 4/20, 18:30 | 8.9 | 0.99 | 92 | 16.9 | 1.6 |
| 4/21, 6:30 | 10.6 | 1.18 | 87 | 13.0 | 0.9 |
| 4/21, 18:30 | 8.9 | 1.00 | 69 | 16.4 | 1.6 |
| 4/22, 6:30 | 10.7 | 1.19 | 74 | 13.6 | 1.7 |
| 4/22, 18:30 | 10.6 | 1.18 | 37 | 16.4 | 2.4 |
| 4/23, 6:30 | 10.6 | 1.18 | 88 | 15.1 | 0.9 |
| 4/23, 18:30 | 10.4 | 1.15 | 49 | 21.4 | 1.3 |
| 4/24, 6:30 | 10.4 | 1.15 | 62 | 19.2 | 1.9 |
| 4/24, 18:30 | 10.4 | 1.15 | 38 | 19.5 | 2.6 |
| 4/25, 6:30 | 10.6 | 1.18 | 53 | 13.9 | 2.0 |
| 4/25, 18:30 | 10.6 | 1.18 | 53 | 14.5 | 2.0 |
| 4/26, 6:30 | 10.7 | 1.19 | 84 | 12.1 | 1.1 |
| 4/26, 18:30 | 10.5 | 1.17 | 95 | 12.9 | 2.1 |
| 4/27, 6:30 | 10.5 | 1.17 | 82 | 12.8 | 2.3 |
| 4/27, 18:30 | 10.5 | 1.17 | 35 | 13.9 | 2.9 |

Table 1. Sampling information.

2.3 Analytical methods

2.3.1 EC/OC analysis

For EC/OC analysis, the laboratory-based thermal-optical analyzer (Sunset Laboratory) was used, following the NIOSH 5040 protocol (Birch, 2002). A 1.45 cm²

punch of the quartz fiber filter was heated in an oxygen-free ultra-high purity helium atmosphere (Bae et al., 2004), gradually increasing the chamber temperature step by step, until it reached 870°C. The detached carbon was converted to CO₂ as it passed through a catalyst, thermally reabsorbing the organic components and products of the pyrolysis, inside a chamber of oxidation of manganese dioxide (MnO₂). The CO₂ was swept from the oxidation chamber by a stream of helium, mixed with nitrogen and flowed through a heated nickel catalyst, where it was quantitatively converted to methane. The methane was subsequently measured using a Flame Ionization Detector (FID). Once the initial temperature rise ramp of the measuring chamber was completed, it cooled to 600 °C and the flow of entrained gas exchanged for a mixture of helium/oxygen. Subsequently, a second temperature ramp commenced for the oxidation of the EC to be quantified in the same way as OC.

A small amount of the pyrolyzed OC can be translated into a high measure of EC if it is not corrected. The Thermo/Optical method of Sunset Laboratory uses the characteristics of high light absorption of EC to correct it. This was done by incorporating a He-Ne red light laser or a tuned laser diode focused on the camera, whose beam passes through the filter. The transmittance of the modulated laser beam was recorded. Similarly, as the process of the temperature increase ramp was recorded, the transmittance of the laser was continuously recorded by the instrument's data acquisition system. Any pyrolyzed carbon from the OC manifested itself in a decrease in transmittance of the laser. After the initial temperature ramped, when the Helium was changed by the He/O₂ mixture, all the elemental carbon was oxidized, and transmittance of the laser returned to base level. Any EC detected before this point was said to have

been formed pyrolytically from OC. Any carbon measured before the split was assigned as thermal OC, and any carbon measured after the split was assigned as thermal EC (Bauer et al., 2009, Bae et al., 2004).

The detection limit (DL) for our sample was 0.10 μ g cm⁻². The precision for the range of concentration of TC and OC in our samples (1-9 μ g cm⁻²) has been estimated around 5%, and for EC samples, with a range of 0.1-0.7 μ g cm⁻², the precision was estimated around 10% and 25% for optical and thermal EC, respectively. The low EC concentration, close to the DL (or below in two of the samples, 0.037 and 0.068 μ g cm⁻²), contributed to the poor precision of EC (Bauer et al., 2009).

2.3.2 Ionic species analysis

Four water soluble ions: anions (nitrate and sulfate) and cations (sodium and potassium) were determined in aqueous extracts (Milli-Q DI ultrapure water) of the filters. The selected water-soluble ion species in samples were analyzed in the Atmospheric Chemistry Lab of Rutgers University, Newark campus. Anion analysis was completed by a Dionex Integration High Pressure Ion Chromatography (HPIC) and cations analysis, by a Dionex Ion Chromatography System-2000 (ICS). All anion species were analyzed with an AS11 analytical column, KOH eluent generator cartridge and 25 µL sample loop, while all cations were analyzed with a CS12A analytical column, MSA generator cartridge and 25 µL sample loop.



Figure 3. Standard calibration curves for selected ions.

Operation procedures occurred in the following sequence: ¹/₄ of each exposed quartz fiber filter was placed in a vial with 10 mL Milli-Q DI water, in an ultrasonic bath for 20 minutes at room temperature. The solutions were filtered, using a syringe and a 0.2 μ m pore size Teflon (PTFE) syringe filter; 650 μ l of the filtered samples were transferred to vials and in the IC autosampler in ranks. Finally, 25 μ l of each sample was injected into the IC column for analysis, with a flow rate of 0.40 μ l min⁻¹ for cations and 0.36 μ l min⁻¹ for anions. The detection limit for sulfate and nitrate is <9 μ g L⁻¹. Based on seven duplicate spike samples, the precision of the analytical procedures is ~1% (Zhao and Gao, 2008). After the analysis, the peak area of each ion was calculated by Chromeleon 7 software. Based on the peak area, the calibration curve was generated (Figure 3), and the concentration of each ion was calculated.

2.4 Weather Data and Analysis

Meteorological data was collected from Rutgers Weather Station, which is operated by the Department of Earth & Environmental Science and is located at the top of Bradley Hall adjacent to the collector used in this study. Concurrent meteorological data including, precipitation intensity, wind direction, wind speed, air temperature and relative humidity were recorded (Table 1).

3. Results and discussion

3.1 Daily Average Concentrations of carbonaceous aerosols

The total concentrations of OC (PM₁₀) (sum of OC PM_{2.5} and PM_{2.5-10}, in the 24hour samples) varied from 23.5 to 42.9 μ g m⁻³, with an average of 32.0 ± 7.0 μ g m⁻³ (Figure 4). The daily concentrations of OC in PM_{2.5} varied from 3.7 to 13.4 μ g m⁻³ (average: 7.0 ± 2.9 μ g m⁻³) whereas it varied from 19.9 to 37.8 μ g m⁻³ (average: 25.0 ± 7.0 μ g m⁻³) in PM_{2.5-10} (Figure 5a). The total concentrations of EC (PM₁₀), that is, the sum of EC PM_{2.5} and PM_{2.5-10}, in the 24-hour samples, varied from 3.1 to 5.1 μ g m⁻³, with an average of 3.9 ± 0.7 μ g m⁻³ (Figure 4). The daily concentrations of EC in PM_{2.5} varied from 0.2 to 1.0 μ g m⁻³ (average: 0.5 ± 0.2 μ g m⁻³), whereas it varied from 2.7 to 4.7 μ g m⁻³ (average: 3.4 ± 0.8 μ g m⁻³) in PM_{2.5-10} (Figure 5b). For total TC (PM₁₀), that is, the sum of TC PM_{2.5} and PM_{2.5-10}, the daily concentrations varied from 27.2 to 47.7 μ g m⁻³, with an average of 35.9 ± 7.5 μ g m⁻³ (Figure 4). The daily concentrations of TC in PM_{2.5} varied from 4.3 to 14.0 μ g m⁻³ (average: 7.4 ± 3.0 μ g m⁻³) whereas it varied from 22.1 to 42.2 μ g m⁻³ (average: 28.4 ± 7.6 μ g m⁻³) in PM_{2.5-10} (Figure 5c).



Figure 4. Average concentrations and standard deviations of particulate carbonaceous aerosols in in the ambient air at Newark, NJ.



Figure 5. Temporal variations of particulate (a) OC, (b) EC, and (c) TC in the ambient air at Newark, NJ.

Table 2. Daily average concentrations of fine- and coarse-modes carbonaceous aerosols in this and other studies ($\mu g m^{-3}$).

| Cites | Period | | PM ₂ | | | \mathbf{PM}_{10} | | Reference |
|---------------|-----------|------|-----------------|-------|-------|--------------------|-------|-----------------------|
| | | OC | EC | ТС | OC | EC | TC | |
| Newark | 1981, | | | | 6.8 | 2.9 | 9.7 | (Daisey et al., 1984) |
| (40°N, 74°W) | July-Aug. | | | | | | | |
| Hong Kong | 2002, | 5.3 | 3.2 | 8.5 | 6.3 | 3.9 | 10.2 | (Cao et al., 2004) |
| (22°N, 114°E) | June-July | | | | | | | |
| Shenzhen | 2002, | 7.6 | 4.2 | 11.8 | 10.4 | 5.0 | 15.4 | (Cao et al., 2004) |
| (22°N, 114°E) | June-July | | | | | | | |
| Budapest | 2002, | 13.7 | 6.6 | 20.3 | 22.0 | 6.9 | 28.9 | (Salma et al., 2004) |
| (47°N, 19°E) | April-May | | | | | | | |
| Kanpur | 2010, | 91.6 | 16.4 | 108.0 | 120.6 | 21.2 | 141.8 | (Ram and Sarin, 2011) |
| (26°N, 80°E) | October | | | | | | | |
| San Francisco | 2011-2012 | | | | 4.81 | 0.94 | 5.75 | (Yoon et al., 2018) |
| (38°N, 122°W) | NovOct. | | | | | | | |
| Los Angeles | 2012-2013 | 4.51 | 1.40 | 5.91 | | | | (Soleimanian et al., |
| (34°N, 118°W) | Jul-June | | | | | | | 2019) |
| Athens | 2013, | 7.63 | 2.44 | 10.07 | | | | (Kaskaoutis et al., |
| (38°N, 24°E) | JanFeb. | | | | | | | 2020) |
| Sao Paulo | 2013, | 3.24 | 2.25 | 5.49 | | | | (dos Santos et al., |
| (24°S, 47°W) | SepNov. | | | | | | | 2016) |
| Nagoya | 2013-2016 | 4.6 | 1.9 | 6.5 | | | | (Yamagami et al., |
| (35°N,136°E) | Spring | | | | | | | 2019) |
| Newark | 2019, | 7.0 | 0.5 | 7.4 | 32.0 | 3.9 | 35.9 | This study |
| (40°N, 74°W) | April | | | | | | | |

The statistics for OC and EC concentrations for this and other ten sampling sites are shown in Table 2. Among these sites, average OC and EC at Kanpur with the highest concentrations, are attributable to high level of biomass (from burning wood-fuel and agricultural waste) emissions during the night, and formation of secondary organic aerosol (SOA) during the day (Ram and Sarin, 2011).

The PM₁₀/PM_{2.5} ratio for TC was 4.8. For both, OC and EC, the PM₁₀/PM_{2.5} ratio was higher in our study. The ratio for OC in our study was 4.6, while at other sites, the highest ratio is 1.6, notably the Budapest sample. The PM₁₀/PM_{2.5} ratio for EC in our study was 8.0, while the highest ratio among other sites is 1.3 for the Kanpur samples, 6 times lower than our sample. Notably, the lowest fine-mode EC concentration among those sites is 1.4, in Los Angeles, which is higher than our sample. This lower fine mode EC concentrations in our study could be the main cause of the higher $PM_{10}/PM_{2.5}$ ratios in comparison with the rest of the studies. The EC fraction of the PM is emitted mostly by mobile sources, since Newark is highly impacted by traffic from major highways, and Newark International Airport is less than 5 km from the study site. Despite these factors, levels of EC were significantly lower in our study. This unusual low EC concentration could be one cause of the high OC/EC ratios. There was a major difference between the concentration of PM₁₀ carbonaceous aerosols in the 1981 study in Newark and our study. The increase in EC PM_{10} was 34%, while for PM_{10} OC was 371%. Coarse-mode TC increased by 270%. In their study, Daisey et al. (1984) found EC/OC ratios for PM₁₀ aerosols between 0.36 and 0.52 in Newark during the summer season.

3.2 Day-night variation of carbonaceous aerosols

Organic carbon had an average nocturnal total concentration of $33.7 \pm 14.5 \ \mu g \ m^{-3}$, varying from 16.5 to 55.7 $\mu g \ m^{-3}$. The concentration levels of nighttime OC in PM_{2.5} samples varied from 2.9 to 13.1 $\mu g \ m^{-3}$ (average: $7.1 \pm 2.9 \ \mu g \ m^{-3}$), and from 13.6 to 48.7 $\mu g \ m^{-3}$ (average: $26.6 \pm 13.8 \ \mu g \ m^{-3}$) in PM_{2.5-10}. Organic carbon had an average diurnal total concentration of $30.2 \pm 4.5 \ \mu g \ m^{-3}$, varying from 24.1 to 37.8 $\mu g \ m^{-3}$. The concentration levels of OC daytime samples in PM_{2.5} varied from 3.2 to 13.7 $\mu g \ m^{-3}$ (average: $6.8 \pm 3.5 \ \mu g \ m^{-3}$), and from 18.9 to 29.8 $\mu g \ m^{-3}$ (average: $23.5 \pm 3.8 \ \mu g \ m^{-3}$) in PM_{2.5-10} (Figures 6a and 7a).





Figure 6. Average concentrations and standard deviations of the carbonaceous aerosols (a) OC, (b) EC, and (c) TC during day and night, observed at Newark, NJ.



Figure 7. Day and night temporal variations in (a) OC, (b) EC and (c) TC concentrations in their fine- and coarse-modes during the sampling period.

For OC, concentrations in both modes were higher during the night; however, there were two nighttime samples in the coarse-mode with very high concentrations (samples 2 and 5, Figure 7a). Although these two peaks had a relationship with wind direction, their high concentrations did not correlate with other weather parameters or ionic species; rather, they seem to be related to source strength. Thus, without consideration of these two extreme concentrations, OC in its coarse-mode was higher during the day than at night (22.9 and 19.3, respectively). Higher concentrations of finemode OC at night could suggest the formation SOC via aqueous-phase oxidation of low volatility organic compounds through dissolution of hydrophilic organic precursors in the bulk of the pre-existing water droplets and subsequent heterogeneous oxidation reactions in the liquid phase (Figure 9) (Saffari et al., 2016, McNeill, 2015, Ervens et al., 2011).



Figure 8. Schematic of aaSOA and aqSOA formation pathways in the aqueous phase of the atmosphere.



Figure 9. Bulk aqueous chemical processes involved in aqSOA formation. The same chemical mechanism applies for cloud droplets and aerosol water, however the dominant reactions differ due to differences in the chemical environment such as pH, inorganic, and organic concentrations (McNeill, 2015).

Kawamura and Ikushima (1993) suggested that dicarboxylic acid, a short-chain organic compound with polar functional group, may be a major contributor of SOC in its fine-mode. Short-chain dicarboxylic acids in the atmosphere are thought to be generally produced through photochemical oxidation of various precursors, principally of cyclic olefins and other hydrocarbons. Engine exhaust is an important source of these compounds in urban atmosphere (Kawamura and Kaplan, 1987). They are abundantly present in PM_{2.5}, contributing to the SOC fraction. Higher concentrations of fine-mode OC during the night, rather than the daytime when cloud processes are enhanced, could support this suggestion (Figure 6a). Unlike photochemical secondary organic aerosol (SOA) formation, the aqueous-phase SOA formation is strongly dependent on preexisting low volatility organic compounds, produced through photochemical oxidation of various precursors (Saffari et al., 2016). $PM_{2.5-10}$, however, contains organic compounds with high molecular weight, that are not water-soluble (Mkoma et al., 2013). This could be the reason why there is no correlation between coarse-mode OC and RH, restraining the formation of secondary coarse-mode OC via aqueous-phase oxidation.

The average nocturnal total concentration for EC was $3.7 \pm 1.5 \ \mu g \ m^{-3}$, varying from 1.9 to 6.1 $\mu g \ m^{-3}$. The concentration levels of EC during nighttime samples in PM_{2.5} varied from 0.3 to 0.9 $\mu g \ m^{-3}$ (average: $0.5 \pm 0.2 \ \mu g \ m^{-3}$) whereas it varied from 1.6 to 5.7 $\mu g \ m^{-3}$ (average: $3.2 \pm 1.5 \ \mu g \ m^{-3}$) in PM_{2.5-10} (Figures 6b and 7b). Elemental carbon had an average diurnal total concentration of $4.1 \pm 0.6 \ \mu g \ m^{-3}$, varying from 3.4 to 5.2 $\mu g \ m^{-3}$. The concentration levels of EC during daytime samples in PM_{2.5} varied from 0.1 to 1.2 $\mu g \ m^{-3}$ (average: $0.5 \pm 0.4 \ \mu g \ m^{-3}$) whereas it varied from 2.8 to 4.4 $\mu g \ m^{-3}$ (average: $3.6 \pm 0.5 \ \mu g \ m^{-3}$) in PM_{2.5-10}.

Elemental carbon concentrations were higher during daytime than during nighttime, in both modes, even taking into account the extremely high concentrations of coarse-mode EC in samples 2 and 5 during the night (Figure 7b) which, as in the case of the peaks of OC discussed above, seem to be related to source strength. These concentrations are in concordance with major consumption of fossil fuel during the day, mainly from mobile sources.

The average nocturnal TC total concentration was $37.4 \pm 15.9 \ \mu g \ m^{-3}$, varying from 18.7 to 61.5 $\mu g \ m^{-3}$. In nighttime samples of PM_{2.5}, the concentration levels of TC varied from 3.2 to 13.6 $\mu g \ m^{-3}$ (average: $7.6 \pm 2.9 \ \mu g \ m^{-3}$), and from 15.6 to 53.7 $\mu g \ m^{-3}$

(average: $29.8 \pm 15.2 \ \mu g \ m^{-3}$) in PM_{2.5-10} (Figures 6c and 7c). The average diurnal concentration of total TC was $34.3 \pm 4.6 \ \mu g \ m^{-3}$, varying from 28.0 to 42.1 $\mu g \ m^{-3}$. In daytime samples of PM_{2.5}, the concentration levels of TC varied from 3.3 to 14.4 $\mu g \ m^{-3}$ (average: $7.3 \pm 3.8 \ \mu g \ m^{-3}$), and from 22.6 to 33.6 $\mu g \ m^{-3}$ (average: $27.1 \pm 4.0 \ \mu g \ m^{-3}$) in PM_{2.5-10}.

When compared, OC and EC concentrations during day and night times for this and other two sampling sites, the highest levels were at Kanpur (Tables 3 and 4). Such high concentrations are attributable, as stated above, to high level of emissions from biomass burning at night and the formation of SOA during the day (Ram and Sarin, 2011). Kanpur is more populated (~3 millions) than Budapest (~1.8 millions) and Newark (~300 000); however, OC and EC concentrations in Budapest and Newark are very similar, except for fine-mode EC, which was very low in our study. The OC concentration in Newark is higher than in the Budapest study, mainly in its coarse-mode fraction, which was more than twice as large. Budapest has around 6 time the population of Newark and is more than three times larger in area than Newark; however, Newark is surrounded by other large cities, including NYC, in addition to the other major local mobile and stationary sources mentioned above.

| Site | Period | | PM _{2.5} PM ₁₀ | | | Reference | | |
|----------|-----------------|------|------------------------------------|------|------|-----------|------|-----------------------|
| | | OC | EC | TC | OC | EC | TC | |
| Budapest | 2002, April-May | 6.8 | 3.4 | 10.2 | 11.0 | 3.6 | 14.6 | (Salma et al., 2004) |
| Kanpur | 2010, October | 36.6 | 6.2 | 42.8 | 49.3 | 7.5 | 56.8 | (Ram and Sarin, 2011) |
| Newark | 2019, April | 6.8 | 0.5 | 7.3 | 30.3 | 4.1 | 34.4 | This study |

Table 3. Comparison of diurnal concentrations of fine and coarse-modes

carbonaceous aerosols at different sampling sites ($\mu g m^{-3}$).

Table 4. Comparison of nocturnal concentrations of fine- and coarse-modes

| carbonaceous aerosols at different s | sampling sites (| (µg m ⁻³) | |
|--------------------------------------|------------------|-----------------------|--|
|--------------------------------------|------------------|-----------------------|--|

| Site | Period | | PM _{2.5} | | PM ₁₀ | | | Reference |
|----------|-----------------|------|-------------------|------|-------------------------|------|------|-----------------------|
| | | OC | EC | TC | OC | EC | TC | |
| Budapest | 2002, April-May | 6.9 | 3.2 | 10.1 | 11.0 | 3.3 | 14.3 | (Salma et al., 2004) |
| Kanpur | 2010, October | 55.0 | 10.2 | 65.2 | 71.3 | 13.7 | 85.0 | (Ram and Sarin, 2011) |
| Newark | 2019, April | 7.1 | 0.5 | 7.6 | 33.7 | 3.7 | 37.4 | This study |

3.3 OC/EC relationship

The OC/EC ratios for PM_{2.5} varied from 5.3 to 50.9, with an average of 19.2 ± 11.7 . PM_{2.5-10} ratios varied from 5.1 to 13.7, with an average of 7.5 ± 2.1 (Figure 10). One possible cause of these high ratios could be that they are usually higher in the method (NIOSH), used in this study than other methods, such as IMPROVE (Khan et al., 2012). However, the higher ratios usually obtained by NIOSH do not adequately explain the high ratios in our study. These high ratios could be due to high concentrations of OC

containing non-polar aliphatic, aromatic and polycyclic aromatic hydrocarbons, directly emitted from combustion sources (Daisey et al., 1984), or by the formation of SOC (Yu et al., 2004, Daisey et al., 1984). This SOC could originated from some gaseous hydrocarbon precursors at a large number of small industries such as auto body shops, tanneries and chemical and paint industries present in the area. It is noteworthy; however, that these ratios are consistent with rural rather than urban areas (Khan et al., 2012). The increase in the ratio values of samples in the fine-mode: 10, 15, and 16 (Figure 10), is due to the very low concentrations of EC in these samples (Figure 5b).



Figure 10. OC/EC ratios in fine- and coarse-mode particles.

3.4 Carbonaceous aerosols and relationship with weather

Although fine-mode OC showed a strong relationship with wind direction, like other carbonaceous aerosols, it also showed a moderate correlation with RH ($R^2=0.52$). This correlation could suggest, as stated above, the formation of SOC via aqueous-phase oxidation of low volatility organic compounds through dissolution of hydrophilic organic precursors in the bulk of the pre-existing water droplets and subsequent heterogeneous oxidation reactions in the liquid phase. Thus, some of the causes of fine-mode OC variations could be the formation of SOC via aqueous-phase and wind direction.

The weak correlation between fine- and coarse-modes OC aerosol ($R^2=0.0032$) and between coarse-mode OC and all the inorganic ionic species could suggest that PM_{2.5-10} OC was released by primary sources instead of secondary processes. On the other hand, coarse-mode OC had a strong correlation with coarse-mode EC ($R^2=0.68$) but there was no apparent relationship between these two aerosols in the fine-mode, the ionic species, temperature, or relative humidity. Thus, this correlation seems to be due to physical processes driving the loading of coarse-mode carbonaceous aerosols in the area, rather than by real interaction between these two aerosols. Samples with average winds from the east-southeast, such as samples 3, 9, and 12 (Figure 11), where the greatest concentrations of roads and highways are present, (Figure 2) had the highest PM_{2.5-10} OC concentrations (peaks in Figure 5a). It is significant that, when the wind was also blowing from east-southeast the days before, such as in sample 3, high humidity and rain episodes provoked an increase in PM_{2.5-10} OC concentration because the air was already loaded with these aerosols. On the other hand, with predominant westerly winds, such as in samples 7 and 11 (combined with the same wind direction days before, and high RH or rain), the PM_{2.5-10} OC concentrations were the lowest. Thus, the variations of coarsemode OC concentrations seem to be caused, as for the rest of the carbonaceous aerosols, mainly by meteorological conditions, instead of source strength or secondary processes.

As previously explained, the minimal variation in night/day fine-mode EC concentrations and weekday/weekend PM_{2.5} EC concentrations, suggest that source

strength was not the main cause for variation in fine-mode EC. This low variability was most likely caused by increased atmospheric mixing depths and concomitant dispersion (Gaffney et al., 1984). PM_{2.5} EC concentrations increased when the wind blew from east or southeast (Figure 11), where the main mobile and stationary sources are located (Figure 2). There were three exceptions; however, in samples 3, 4, and 15, where the wind blew from these locations, but their low concentrations could be attributed to rain, which may had aided in deposition of aerosols from the atmosphere, including carbonaceous aerosols. It was consistent with the increase in concentrations of the preceding samples (Figure 12), including sample 14, with the highest concentration, even when the wind originated from the northwest. In addition, during the collection of sample 14, haze was present, which could be an important factor in the increase of aerosol concentrations (Ram and Sarin, 2011). Thus, the variations in fine-mode EC concentrations seem to be caused mainly by meteorological conditions, such as wind direction and intensity, rain, etc.



Figure 11. Wind roses for some samples. Samples 2, 9, and 12 show winds blowing from east or southeast and fine-mode EC peaks of higher concentrations. When the wind originated from other directions, such as west (sample 6) or southwest (sample 10), fine- mode EC concentrations decreased, except for samples 3, 4, and 15, where the wind blew mainly from east-southeast, and the concentrations decreased. This could be attributed to rain, which may have removed some aerosols from the atmosphere. The other exception was sample 14, where northwest winds carried the highest concentration, than all the samples, probably caused by heavy rain, high RH, a fog event, and other meteorological conditions not related to source strength.



Figure 12. Temporal variations in the concentration of fine-mode EC and rain (24 hrs. avg.).

Coarse-mode EC can be produced by primary sources, such as traffic-induced non-exhaust emissions such as tire wear, or it can be formed by secondary processes, such as $PM_{2.5}$ coated with organic and/or inorganic substances (Zhang et al., 2013). The poor correlation between fine- and coarse-modes EC aerosol ($R^2=0.01$) could suggest that $PM_{2.5-10}$ EC was released by primary, instead of secondary processes. There was also a weak relationship between coarse-mode EC and all the inorganic ionic species. As in other aerosols, wind direction, more than source strength, seems to play the main role in coarse-mode EC concentration. Samples 3, 9, and 12, associated with average winds from the east-southeast, where the greatest concentrations of roads and highways are present (Figure 2), had the highest $PM_{2.5-10}$ EC concentrations. It is noteworthy, that when the wind was blowing from east-southeast on previous days, high humidity and rain episodes provoked an increase in $PM_{2.5-10}$ EC concentration (such as in sample 3), because the air

was already loaded with these aerosols. On the other hand, when average winds originated from the west, combined with high RH or rain and winds from the same direction the days before, PM_{2.5-10} EC concentrations were the lowest. Thus, the variations in coarse-mode EC concentrations seem to be caused, as for fine-mode EC, mainly by meteorological conditions, instead of source strength or secondary processes. *3.5 Carbonaceous aerosols and relationships with inorganic ions*

3.5.1 Sodium

Sodium had the highest total concentration among all inorganic species, with an average of $5.85 \pm 8.03 \ \mu g \ m^{-3}$ (Figure 13). The concentration levels of sodium in PM_{2.5} varied from 0.02 to 1.09 $\ \mu g \ m^{-3}$ (average: $0.27 \pm 0.33 \ \mu g \ m^{-3}$) whereas it varied from 0 (under detection limits) to 25.78 $\ \mu g \ m^{-3}$ (average: $5.57 \pm 7.73 \ \mu g \ m^{-3}$) in PM_{2.5-10}.



Figure 13. Average concentrations and standard deviations of the inorganic species.



Figure 14. Potassium/sodium ratios for PM_{2.5} aerosols.

Fine-mode OC had a moderate correlation with PM_{2.5} sodium (R²=0.59) and PM_{2.5-10} sodium (R²=0.37). Refuse incinerators are considered to be the most significant anthropogenic source of fine-mode sodium and potassium in the urban air (Ooki et al., 2002). A moderate correlation (R²=0.46) between sodium and potassium in fine-mode may suggest waste incineration as a major source for them in the area; a major waste incinerator facility, Covanta Essex, is located 3 miles east to the sampling site. However, according to (Ooki et al., 2002) the potassium/sodium ratios in the urban air for fine particles are between 1-5, the potassium/sodium ratios in the marine air are below of 0.5. In this study the potassium/sodium ratios for PM_{2.5} (Figure 14) are from 0.02 to 0.18 (average: 0.07 ± 0.04) suggesting the influence of sea-salt. The correlation (R²) with sodium and potassium ions and fine-mode OC was higher during daytime than during the night (0.77-0.41 for PM_{2.5} sodium and 0.56-0.35 for PM_{2.5} potassium respectively). Winds blow from sea to land during the day, or either from east or southeast, where the waste incinerator facility, major stationary and mobile sources of carbonaceous aerosols are

located. Thus, the correlation between fine-mode OC and fine-mode sodium (and with fine-mode potassium ($R^2=0.47$)) could be mainly due to the fact that their main sources are in the same location, rather than by another relationship. The correlation (R^2) between fine mode OC and coarse-mode sodium was higher during daytime than during the night (0.71-0.31 respectively). The main source of coarse-mode sodium in coastal zones are sea-salt aerosols. This relationship, as in the case of fine-mode ionic aerosols, could be mainly because its main sources are in the same location (east and southeast), rather than any other possible relationship. There was no correlation between elemental carbon and sodium in any of their modes.

3.5.2 Sulfate

Sulfate had the second highest total concentration among all inorganic species, with an average of $3.17 \pm 1.99 \ \mu g \ m^{-3}$ (Figure 13). The concentration levels of sulfate in PM_{2.5} varied from 0.41 to 1.26 $\mu g \ m^{-3}$ (average: $0.71 \pm 0.25 \ \mu g \ m^{-3}$) whereas it varied from 0.66 to 6.83 $\mu g \ m^{-3}$ (average: $2.46 \pm 1.88 \ \mu g \ m^{-3}$) in PM_{2.5-10}. No weekly or daynight concentration differences were found for sulfate.

No correlation was found between fine-mode sulfate and the carbonaceous aerosols. In the coarse-mode, sulfate can be generated by primary and secondary sources. Primary PM_{2.5-10} sulfate is usually from natural sources. A main source of primary coarse-mode sulfate in this area is sea salt (Zhao and Gao, 2008). PM_{2.5-10} sodium and sulfate show a strong correlation in this study (R^2 =0.92), suggesting a sea-salt origin of PM_{2.5-10} sulfate. Furthermore, coarse-mode sulfate and potassium also show a strong correlation (R^2 =0.75), reinforcing this suggestion. However, in these kinds of areas, influenced by both continental and oceanic air, the ratio of sulfate-sodium in sea water is 0.59, which is higher than the sulfate-sodium in sea water (0.123) (Zhao and Gao, 2008). The ratios in this study are between 0.26 and 7.55 (average: 1.33), suggesting that sea-salt is not the main source of coarse-mode sulfate in this area.

Secondary coarse-mode sulfate can by produced by reactions of SO₂ on the surface of sodium and calcium-containing particles. This kind of reaction occurs under wet condition. A moderate correlation between fine-mode OC-RH (Figure 15) and fine-mode OC-coarse-mode sulfate (R^2 =0.44), could suggest this process as the main pathway for secondary PM_{2.5-10} sulfate formation. However, the correlation between fine-mode OC and coarse-mode sulfate was higher during daytime than during the night (R^2 =0.81- R^2 =0.43 respectively), contradicting the interactions between fine-mode OC-coarse-mode sulfate through wet processes. Thus, this relationship, as in the case of fine mode ionic aerosols, could be mainly because its main sources are in the same location (east and southeast), rather than any other possible relationship. The weak correlation between EC and sulfate in fine-mode particles (Figure 16) is expected, as sulfur is principally emitted from stationary sources and EC from mobile sources (Gaffney et al., 1984).



Figure 15. Relationships between RH and fine-mode OC and coarse-mode sulfate particles.



Figure 16. Relationship between EC and sulfate and nitrate in fine-modes.

3.5.3 Nitrate

Nitrate had an average total concentration of $0.47 \pm 0.30 \ \mu g \ m^{-3}$ (Figure 13). The concentration levels of nitrate in PM_{2.5} varied from 0.01 to 0.18 $\mu g \ m^{-3}$ (average: 0.07 ±

0.05 μg m^-3) whereas it varied from 0.03 to 0.89 μg m^-3 (average: 0.40 \pm 0.25 μg m^-3) in PM_{2.5-10}.

Nitrate in fine-mode particles does not show any correlation with the rest of the ionic inorganic species. However, nitrate has a strong relationship with $PM_{2.5}$ EC (R² = 0.75) (Figure 16). Nitrate is usually a secondary aerosol formed from nitrogen oxides (NO_x), emitted mainly by traffic sources, but also by stationary sources (Butler et al., 2011). This relationship suggests that anthropogenic emissions were the main sources of PM_{2.5} EC.

No weekdays-weekends or day-night variation in concentrations were found for PM_{2.5} EC and PM_{2.5} nitrate, thus, source strength is not the main factor for fine-mode EC and nitrate concentration. However, there is a possible relationship between wind direction and speed with the concentration of these two aerosols. When the wind was blowing south, east, or between PM_{2.5} EC and PM_{2.5} nitrate show their higher concentrations, with picks in samples 3, 9 and 12, and when the wind was blowing from the west, they exhibited their lower concentrations, in samples 7 and 11. Maybe the only exception was sample 14 for $PM_{2.5}$ nitrate, which shows a high concentration with western winds. However, strong components from the northwest, where there is the presence of many highways, combined with a weak negative correlation with temperature $(R^2 = 0.11)$ and a weak positive correlation with relative humidity $(R^2 = 0.18)$, suggest that fine-mode nitrate aerosol could be produced through the condensation of its precursors onto pre-existing particles. High humidity favors the reactions of precursors species with the particles. High humidity during sampling 14 (there was also a fog event during this period), combined with a relatively high concentration of sodium and others

ionic particles, could explain the peak of $PM_{2.5}$ nitrate concentration in this sample. Also, the average temperature during sample 14 was below 15 °C and, according to (Zhao and Gao, 2008), nitrate moves its major fraction from coarse to fine-mode particles when the average temperature is lower than 17 °C.

Nitrate in the coarse-mode shows a weak correlation with the carbonaceous aerosols ($R^2 < 0.3$), suggesting that the strength of the sources is not a dominant cause for an increase in the PM_{2.5-10} nitrate mass during this period. On the other hand, coarse-mode nitrate had a moderate relationship with the rest of the ionic inorganic species in their coarse-modes (Figure 17).



Figure 17. Relationship between nitrate and (a) sodium, (b) sulfate, and (c) potassium in their coarse-modes.

This relationship, in addition with the fact that $PM_{2.5-10}$ nitrate concentration was anti-correlated with the air temperature and positively correlated with relative humidity (although in both cases the correlation was very weak, $R^2 = 0.02$ and $R^2 = 0.2$, respectively), may suggest that aerosol formation and hygroscopic growth was the dominant cause for the concentration variation of nitrate.

3.5.4 Potassium

Potassium had the lowest total concentration among all inorganic species, with an average of $0.20 \pm 0.18 \ \mu g \ m^{-3}$ (Figure 13). The concentration levels of potassium in PM_{2.5} varied from 0.002 to 0.03 $\ \mu g \ m^{-3}$ (average: $0.01 \pm 0.008 \ \mu g \ m^{-3}$) whereas it varied from 0.03 to 0.61 $\ \mu g \ m^{-3}$ (average: $0.19 \pm 0.18 \ \mu g \ m^{-3}$) in PM_{2.5-10}.

Potassium has been used as a conventional biomass/fossil fuel-burning tracer (Emami et al., 2018), however, its contribution from sea-salt and soil aerosol may be an important source (Mkoma et al., 2013).

As stated above, fine-mode OC had a moderate correlation with $PM_{2.5}$ potassium and refuse incinerators are considered to be the most significant anthropogenic source of fine-mode potassium in the urban air but, as explained before, this relationship could be mainly due to the fact that their main sources are in the same location, rather than by another relationship. The potassium/OC ratio has usually a range between 0.04 and 0.13 for biomass burning (Ram and Sarin, 2011). The potassium/OC ratios in fine-mode particles in this study varied from 0.0006 to 0.003 (average: 0.0017 ±0.0008), much lower than the expected values for biomass burning, suggesting that $PM_{2.5}$ potassium is from fossil fuel combustion.

PM_{2.5} potassium shows a relatively good correlation with fine-mode EC aerosol $(R^2=0.32)$, however, this correlation changes dramatically if compared daytime-nighttime potassium-EC correlation. Potassium and EC in their fine-mode have a very strong correlation during daytime ($R^2=0.75$). On the other hand, at night PM_{2.5} potassium concentration had a weak anti-correlation with PM_{2.5} EC concentration (R²=0.01). But this negative correlation at night was only during the weekends because during weekdays their correlations at night was very strong ($R^2=0.96$). During the weekends $PM_{2.5}$ EC concentration suffered a decline, while potassium showed a pronounced increase. This decrease of fine-mode EC concentrations on weekends in could be attributed to the decreased traffic density due to the official days-off of government institutions, schools, colleges, etc. (Khoder and Hassan, 2008), although these concentrations also depend of weather conditions (mainly precipitations, as explained above), variability of stationary sources emissions, and others. The increases of PM2.5 potassium during weekends could be associated with recreational activities such as bonfires (wood burning), barbeques (meat cooking) (Emami et al., 2018). Potassium in fine-mode particles are commonly from biomass/fossil fuel-burning. The potassium/EC ratios in biomass burning aerosols are usually between 0.20 and 0.69. On the other hand, fossil-fuel emissions have lower potassium/EC ratios (Ram and Sarin, 2011). The low potassium/EC ratios in our study, from 0.009 to 0.068 (average: 0.029 ± 0.018), which were lower than expected from biomass burning, suggest that PM_{2.5} EC was mainly from fossil fuel combustion, as expected in an urban, highly industrialized region. Coarse-mode potassium exhibited a strong correlation with coarse-mode sodium (0.88), suggesting that sea-salt could be the main source of PM_{2.5-10} potassium. Furthermore, the highest concentrations of potassium,

as well as for sodium, were when the average winds were blowing from east or southeast, that is, from the sea (Figure 11).

4. Conclusions

This research showed that the carbonaceous aerosol concentrations observed at metropolitan Newark in New Jersey were dominated by coarse-mode particles and OC/EC ratio depicted significant temporal variability. Higher concentrations of finemode OC at night and a strong correlation with RH suggested the formation of SOC via aqueous-phase oxidation of low volatility organic compounds. Coarse-mode EC concentration was higher during the day than at night which was consistent with major consumption of fossil fuel during the day, mainly from mobile sources. Observed temporal variability of PM2.5 and PM2.5-10 carbonaceous aerosols at this location suggested that their concentrations were governed by wind direction, more than source strength, secondary formation processes or any other weather factors. Fine-mode OC had moderate correlations with $PM_{2.5}$ sodium ($R^2=0.59$) and $PM_{2.5-10}$ sodium ($R^2=0.37$), suggesting a mixed influence of anthropogenic and marine sources. Fine-mode EC had a strong relationship with $PM_{2.5}$ nitrate ($R^2 = 0.75$), suggesting an anthropogenic source for $PM_{2.5}$ EC, as nitrate is a secondary aerosol formed from nitrogen oxides (NO_x) emitted mainly by traffic sources. One important finding from this study is that the $PM_{10}/PM_{2.5}$ ratios in our study were at least three times higher than the highest ratio when compared with ten previous studies in other locations. The differences between ratios of EC samples were the highest. The $PM_{10}/PM_{2.5}$ ratio in our study was six times higher than the highest ratio among other sites, mainly due to comparatively lower fine-mode EC concentrations in our study.

One limitation with this study is a short sampling time, restricted to a narrow

period of eight days for the observations of day-night and weekend-weekday trends, and

this was mainly due to the financial limitation. Therefore, future studies should

investigate the influence of seasonal variations on the concentrations of these

carbonaceous aerosols. Finally, the formation of SOC via aqueous-phase oxidation of low

volatility organic compounds should also be studied in the future since this process is not

yet well understood.

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