Atmospheric Pollution Research 5 (2014) 245–252

Atmospheric Pollution Research

www.atmospolres.com

Carbonaceous particulate matter characterization in an urban and a rural site in the Philippines

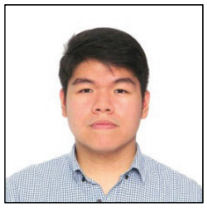
Angel T. Bautista VII [1,2], Preciosa Corazon B. Pabroa [1], Flora L. Santos [3], Joseph Michael D. Racho [1], Leni L. Quirit [4]

[1] *Philippine Nuclear Research Institute, Commonwealth Ave., Diliman, Quezon City, Philippines*
[2] *Institute of Environmental Science and Meteorology, University of the Philippines, Diliman, Quezon City, Philippines*
[3] *Notre Dame de Vie Institute, Brgy. Encanto, Angat, Bulacan, Philippines*
[4] *Institute of Chemistry, University of the Philippines, Diliman, Quezon City, Philippines*

ABSTRACT

Concentrations of organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ were measured at an urban (Valenzuela City, Metro Manila) and a rural (Angat, Bulacan) site in the Philippines from September 2011 to August 2012 by thermal–optical reflectance analysis following IMPROVE–A protocol. Results show that OC (8.00 μg m^{-3}) and EC (6.63 μg m^{-3}) levels in Valenzuela were 2–3 times higher than those in Angat (OC: 4.08 μg m^{-3}, EC: 2.29 μg m^{-3}). The total carbon contributions (OC+EC) to $PM_{2.5}$ mass for the urban and rural site were 38.9% and 19.7% respectively. Compared to neighboring countries in Asia, the Philippine sites have intermediate OC concentrations and greatly elevated EC levels. These suggest the presence of highly inefficient combustion sources and highlight the need for the regulation of such emissions. Valenzuela was dominated by OC2, OC3, and EC1 (carbon fractions evolving at 280 °C and 480 °C in pure He phase and 580 °C in He/O_2 phase of the analysis, respectively) which points to vehicular, industrial, and cooking sectors as the possible main sources. While generally having lower concentrations and being less EC–dominated, Angat had remarkably higher levels of the EC2 fraction which suggests a unique EC source in the area. Conditional Probability Function (CPF) for Valenzuela OC and EC show similar results pointing towards the 30°, 150°, and 210° direction, indicating common sources for these species. Detailed survey of the surrounding area is needed to ascertain the identities of the sources present in these directions.

Keywords: *Carbonaceous particulate matter, organic carbon, elemental carbon, $PM_{2.5}$, Philippines*



Corresponding Author:
Angel T. Bautista VII
☎ : *+632-929-6011*
🖷 : *+632-926-7343*
✉ : *atbautistavii@gmail.com*

Article History:
Received: 30 July 2013
Revised: 31 December 2013
Accepted: 01 January 2014

doi: 10.5094/APR.2014.030

1. Introduction

Carbonaceous particulate matter is carbon–containing solid or liquid particles dispersed in the atmosphere. On the average, they have been found to constitute about 10–20% and 30–40% of the total rural and urban particulate mass, respectively (Cao et al., 2004; Yu et al., 2004; Perez et al., 2008; Saarikoski et al., 2008; Sanchez de la Campa et al., 2009; Ram and Sarin, 2010). These particulates are broadly classified into two main fractions: organic carbon (OC) and elemental carbon (EC). OC is emitted directly to the atmosphere through the combustion of biomass/fuels and it is also formed by secondary atmospheric process such as photo-chemical oxidation (Castro et al., 1999). EC, on the other hand, is produced through the incomplete combustion of carbon–containing fuels in an oxygen–starved environment (Chow et al., 2001). As such, typical sources of carbonaceous particulates in urban and rural environments are biomass burning, traffic, industries, and secondary formation accompanying long–range transport (Saarikoski et al., 2008; Ram and Sarin, 2010).

Aside from forming significant portion of the particulate mass, carbonaceous particulates also have profound effects on health, climate, and visibility. These particulates have been reported to be possible carcinogens (Birch and Cary, 1996) and mitigation measures for black carbon (BC, closely related and almost analogous to EC) are estimated to prevent about 0.6–5 million premature deaths by 2030 (Anenberg et al., 2012). In terms of climate impacts, BC is considered to be the second strongest contributor to global warming next to CO_2 as it causes net positive global forcing, affects regional climates, and accelerates the melting of snow and sea ice upon deposition (Ramanathan and Carmichael, 2008). These are all consequences of the particulates' light–absorbing properties and indeed, BC reduction is identified to be among the top solutions against climate change. This is exemplified by the fact that its residence times are several orders of magnitude lower compared to other greenhouse gases (GHGs) which means that the results of cutting down BC emissions will show effects much faster compared to GHG reduction. This makes BC or EC mitigation a short–term solution that can delay warming and its potential irreversible, catastrophic events for several decades (Baron et al., 2009). Particularly, EC accounts for effectively all (>95%) of the total aerosol light absorption, which is in turn responsible for about 13% and 30% of the total light extinction in rural and urban areas, respectively (Japar et al., 1986). Thus, these particles greatly affect visibility which is another parameter being monitored and protected globally.

Philippines is one of the countries with the highest emissions of BC in the Asian region (Hopke et al., 2008). This makes the country more susceptible and more responsible to the particles' negative impacts. BC levels are being monitored by the Philippine Nuclear Research Institute (PNRI) and the Manila Observatory (MO) along with atmospheric elemental composition and PM_{10} and $PM_{2.5}$ levels for use in receptor modeling studies such as source

apportionment and location (EMB, 2009; Pabroa et al., 2011; Kim Oanh, 2013). BC in these studies is measured using reflectometry which is based on particulate light absorbance. This method however, has inherent limitations as it uses a single fixed mass extinction coefficient which assumes that particulates have generally the same degree of light–absorbing property. OC/EC speciation is thus beneficial as it gives more detailed information about carbonaceous particulate species.

Given Philippines's high BC levels and that studies regarding OC/EC speciation and characterization are very limited in the country, obtaining data on this particular group of atmospheric particulates would be a great leap in terms of atmospheric quality characterization. This would also improve source apportionment receptor modeling in the country by providing specific information about OC and EC. Considering the implications brought by these particulates, obtaining these data would lead to increased understanding and better management of emissions in both urban and rural areas of the country.

This study therefore aims to generate baseline information of OC and EC concentrations and their different fractions in urban and rural settings in the Philippines. This is done to observe spatial and temporal variations of the parameters and to obtain inferences relating to the possible sources of carbonaceous particulate matter. Data obtained were compared to existing OC and EC measurements from neighboring countries in Asia to give perspective on the level of carbonaceous particulate emission in the country.

2. Methodology

Ambient 24–hour carbonaceous particulate sampling was done over a one–year period from September 2011 to August 2012 (twice a week – Wednesdays and Sundays) in two sites namely, Valenzuela City, Metro Manila and Angat, Bulacan. Valenzuela City is an urban site located in the National Capital Region of the Philippines and it has a population of 575 356 and a population density of about 13 000 km^{-2} (NSCB, 2010a). The sampling site is surrounded by industrial and residential buildings and on its east is a major national highway. Angat, Bulacan on the other hand, is a rural municipality area with a population of 55 332 and a population density of about 720 km^{-2} (NSCB, 2010b). The sampling site is within the compound of Notre Dame de Vie Institute and the probable main sources of carbonaceous matter are light road traffic north of the site, biomass burning in surrounding farmlands, cooking with firewood in residential areas, and a tire recycling facility situated at the south. In both sites, sampling was done considerably away from any direct influence of primary sources.

Pallflex quartz–fiber filters pre–baked at 900 °C for three hours (to remove adsorbed carbonaceous material) were used for the study. Sampling was done in the $PM_{2.5}$ range using a Gent sampler with a PM_{10} impactor installed on top of the sampling head assembly. A Nucleopore coarse filter (8 µm pore size) placed before the actual quartz filter removes particles in the $PM_{2.5–10}$ range. Filters were weighed before and after sampling using a Mettler MT5 micro analytical balance with 1 µg sensitivity.

Analyses for OC and EC concentrations were done using a Sunset Laboratory OC–EC Aerosol Analyzer. The method used is thermal–optical analysis (Birch and Cary, 1996) using reflectance correction and following the IMPROVE–A protocol (Chow et al., 2007). This method differentiates and measures OC and EC by controlling the temperature and atmosphere within the instrument. The analysis results in four OC fractions (OC1, OC2, OC3, and OC4 evolving at 140 °C, 280 °C, 480 °C, and 580 °C, respectively, during the pure helium atmosphere phase of the analysis), three EC fractions (EC1, EC2, and EC3 evolving at 580 °C, 740 °C, and 840 °C, respectively, during the 2% oxygen/98% helium atmosphere phase of the analysis), and a pyrolized carbon fraction (portion of the OC that has undergone pyrolysis and transformed into EC during the analysis – co–evolves with EC1). Therefore, total OC=OC1+OC2+OC3+OC4+pyrolized carbon; total EC=EC1+EC2+EC3–pyrolized carbon; Corrected (true) EC1=EC1–pyrolized carbon. This corrected EC1 will be the one referred to as "EC1 fraction" for the remaining parts of this paper. Quality assurance/quality control procedures are summarized in Table S1 (see the Supporting Material, SM).

3. Results and Discussion

3.1. Baseline OC and EC measurements

A total of eighty–four (84) samples were collected in Valenzuela over the one–year sampling while thirty–five (35) samples were concurrently obtained in Angat in the same semiweekly manner, albeit in discrete intervals spread throughout the sampling period. Time series plots for OC and EC of Valenzuela and Angat are shown Figure 1a and 1b. As expected, the urban Valenzuela site resulted in higher OC and EC values of 8.00 µg m^{-3} (21.2% of the $PM_{2.5}$ mass) and 6.63 µg m^{-3} (17.7%), respectively, compared to Angat's OC of 4.08 µg m^{-3} (12.8%) and EC of 2.29 µg m^{-3} (7.0%). The total carbonaceous particulate $PM_{2.5}$ mass contribution for Valenzuela and Angat is thus equal to 38.9% and 19.7%.

Comparing these values with measurements done in neighboring countries in Asia as seen in published works (Figure 2, Kim et al., 1999; He et al., 2001; Lee and Kang, 2001; Lin, 2002; Park et al., 2002; Ye et al., 2003; Cao et al., 2004), Valenzuela has intermediate OC values but extremely high EC concentrations. Particularly, Valenzuela EC is comparable to that of Guangzhou and Shanghai and only next to Seoul and Beijing (Valenzuela having 31.6% and 70.6% of Beijing's OC and EC concentrations, respectively). The same is observed for Angat in comparison with the other two rural sites (Hong Kong and Cheju). These results agree with that of Hopke et al. (2008) which showed that the Philippines is among those with the highest emissions of BC in the Asian region. This observation can also be expressed in terms of OC/EC ratios which showed that Valenzuela has the second lowest ratio value (1.27) among all regions in comparison. Angat has an expected relatively higher ratio of 1.95 since rural areas normally have low EC levels and hence higher OC/EC ratios. Still, this value is lower when compared to the other two rural sites. These findings suggest that the combustion sources in the Philippines are less efficient compared to those of other countries, thus resulting in more EC–dominated emissions. Considering that most of the regions in comparison are highly urbanized and populated cities, these results demonstrate that carbonaceous particulate matter pollution, particularly EC, is ubiquitous in the Philippines and there is a need to better regulate its emissions.

3.2. Secondary OC formation

OC/EC ratios close to unity commonly indicates dominance of primary sources since most of OC and EC come from the same source. It is also thus expected that OC and EC are highly correlated to each other. This however, seems not to be the case for Valenzuela as the R^2 value of its OC vs. EC is only 0.559. Angat on the other hand, has an expectedly small R^2 value of 0.112, most likely attributed to secondary organic particulate matter formation. To investigate this further, following equation for the quantification of secondary organic carbon (SOC) as proposed by Castro et al. (1999) was used:

$$SOC = OC - EC\left(\frac{OC}{EC}\right)_{min} \quad (1)$$

This equation makes use of the minimum OC/EC ratio of the whole dataset of each site and is based on the assumption that carbonaceous particulate matter contribution is mainly from