Impact of Mixed Sources on the Atmospheric Aerosols of Urbanized Areas in the Philippines

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ABSTRACT

Southeast Asia (SEA) holds approximately 10% of the global population, who are constantly exposed to severe local and transboundary air pollution. Here, we characterized the physiochemical characteristics of atmospheric aerosols in urbanized areas (Valenzuela, Manila, and Boracay) in the Philippines. The variability of coarse and fine aerosols, black carbon (BC), and trace elements of particulate matter (PM) were analyzed between June 2017 and April 2019. The average fine (coarse) aerosols of Valenzuela, Manila, and Boracay were 26.7 (80.4), 27.9 (86.6), and 20.9 (124.6) µg m–3, respectively, which all exceeded the recent annual limits of the World Health Organization. The average BC level was 6.6 µg m–3 across three sampling sites, ranging between 4 to 83% of the fine PM mass. Vehicular emission predominated at the extreme urban sites as reflected by the high BC levels attributed to transport activities. The conventional receptor modeling procedure was implemented and improved by integrating BC speciation, which distinguished vehicle emission and biomass burning. The new method revealed eight and seven sources influencing the atmospheric conditions of Valenzuela and Boracay. In particular, the elevated zinc and lead highlighted the substantial impact of industrial sources in Valenzuela, attributing more than 9% of PM2.5. For Boracay, construction activities evidently enhanced PM based on the mass burden of calcium. Overall, the results uncovered the origin of PM2.5 in urbanized locations in the Philippines, which will be valuable in reducing the exposure of a significant portion of the global population to harmful pollutants.

Keywords: Southeast Asia, Local pollution, MABI, Urban emissions

1 INTRODUCTION

Southeast Asia (SEA) is one of the most populous regions globally, with an estimated 669 million residents in 2020, according to the United Nations World Populations Projections (UN, 2019). Unfortunately, a substantial portion of the population of SEA is severely exposed to both local and transboundary air pollution, which inflicts several cardiovascular and respiratory diseases. With the unprecedented upsurge in population and urbanization, the World Health Organization (WHO) projected that air pollution causes a yearly 2.4 million premature deaths in SEA. Moreover, in a systematic review of the health effect of air pollution in SEA, an increase of 10 µg m–3 of fine
and submicron aerosols would result in a 1–2% enhancement in the propensity of wheeze-associated disorders (Luong et al., 2019). With the severe impact of air pollution in the SEA region, more in-depth characterization of toxic compounds in the atmosphere should be implemented to reduce mortality and improve the environmental policies in this region.

Among the air pollutants, particulate matter (PM) is one of the most concerning due to its adverse effects on human health (Hamanaka and Mutlu, 2018; Sharma et al., 2020; Pabroa et al., 2022). Unlike other pollutants, PM consists of heterogeneous components such as organic compounds and elemental tracers that individually cause diseases. Also, an evident fraction of PM interacts with radiation, ultimately impacting the global temperature (Salvador et al., 2021). An important component of particulate matter is Black carbon (BC) which has been identified as a major driving force of global climate change as BC has a strong warming influence on the atmosphere (Ramanathan and Carmichael, 2008; Bond et al., 2013). BC can be produced naturally but mostly by human activities such as incomplete combustion of fossil fuels, biofuels, and biomass, some of which are attributed to deforestation and crop residue burning. Reducing emissions of BC can have an immediate near-term impact on atmospheric warming since black carbon remains in the atmosphere for as little as several weeks, unlike CO₂, which has a residence time of about 40 years.

Understanding the status and sources of ambient particulate matter will help determine the specific mitigation measures needed that will reduce PM₂.₅, and PM₁₀ levels below the guideline levels, thus providing suitable air quality. Many source identification and apportionment studies have been done previously in various parts of the world, especially in countries that were participants of the regional project under the Regional Cooperation Agreement (RCA) of the International Atomic Energy Agency (IAEA). In such a global collaborative study, nuclear analytical techniques (NATs) were utilized for air pollution source identification and apportionment studies (Chan et al., 2008; Ramanathan and Carmichael, 2008; Santos et al., 2008; Begum et al., 2010; Cohen et al., 2010). Different countries have distinct air pollution sources, but developing Asian countries such as Indonesia, Bangladesh, Vietnam, Mongolia, and the Philippines reported a substantial effect of vehicle emissions on air pollution.

The source and variability of selected urbanized areas in Southeast Asia were comprehensively evaluated using NATs and receptor modeling for this study. In particular, the atmospheric level of PM and its components (i.e., BC and trace elements) of regions with varying urban level (Metro Manila and Boracay) in the Philippines were assessed to determine the contribution of natural and anthropogenic activities. Few studies reported the in-depth profile of atmospheric aerosols in the megacity in the Philippines (Pabroa et al., 2011; Bautista et al., 2014; Pabroa et al., 2022; Salvador et al., 2022), but no prior study characterized the levels, composition, and sources of PM in an urbanized island with several anthropogenic sources. The comparison will be valuable in evaluating the distinct air pollution of Southeast Asia, which consists of varying urbanization even at remote locations (i.e., touristic spots). Moreover, this study details an improved receptor modeling procedure that integrated multi-wavelength absorption analysis of black carbon. The addition of BC speciation clearly separated the biomass and fossil fuel burning, which is a necessity in improving air quality in urbanized areas.

2 MATERIALS AND METHODS

2.1 Site Description

The locations of the sampling sites in the Philippines are shown in Fig. 1(A). The urban PM samples were collected from two Metro Manila sites (Fig. 1(B)) — (1) the “Valenzuela” site at the Radyo ng Bayan Compound, Don Pedro Subdivision Road, Marulas, Valenzuela (14.7011°N, 120.9830°E, General Ambient Station) and (2) the “Manila” site Pamantasan ng Lungsod ng Maynila or PLM (14.5869°N, 120.9773°E, General/Roadside Ambient Station). The PM samples for the urbanized island were collected at the “Boracay” site located on Boracay Island (11.9674°N, 121.9248°E, Roadside Ambient Station) (Fig. 1(C)). The three sites will be termed Valenzuela, Manila, and Boracay hereinafter. The sampling duration for the Valenzuela, Manila, and Boracay sampling sites was between June 2017 to October 2018, November to December 2017, and December 2017 to April 2019, respectively.
Fig. 1. Geographical locations of study sites – (A) The map of the Philippines. Metro Manila sampling sites – (B) Valenzuela and Manila and (C) Boracay Island sampling site.

Valenzuela City is an industrial site that has been maintained as Philippine Nuclear Research Institute (PNRI) sampling site until October 8, 2018. This site will be used as a reference since previous data is available in this area, and this has been known to have higher Pb levels than other Metro Manila sampling sites (Pabroa et al., 2011). The Manila site is near the coastal area; thus, signatures from ship emissions will be expected. More importantly, Valenzuela and Manila sites are located in Metro Manila Region, which serves as the Philippines’ national capital region. Metro Manila is considered one of Asia’s top-populated metropolitan areas, with more than 13 million residents in 2020. Transportation activities heavily impact the air quality in the region, where many vehicles still utilize engines with pre-EURO emission standards. On the other hand, Boracay Island is one of the most known tourist spots in the Philippines. Therefore, it will be of great interest to assess the air quality in this area specifically impacted by the movement of tourists and local residents using motorcycles and ships/boats. Boats/ships are the primary means of transportation from the mainland to the island, and it could be expected that boats/ships’ emissions would have a profound impact on the area. The volume of tourists coming in and out of the island would also mean that more boats/ships ply the area to cater to the needs of the tourists. Compared to other sites, Manila had a relatively shorter measurement duration. Thus, more focus will be provided on Boracay and Valenzuela sites. However, data from Manila will still be a valuable reference to the other sites, given the highly populated condition of Manila and its designation as the capital of the Philippines.

2.2 Sample Collection and Analysis

Sampling has been done as per the in-house protocol of PNRI, collection by dichotomous sampling (coarse and fine) using the Gent sampler. This method was adapted from the International...
Atomic Energy Agency - Regional Cooperative Agreement (IAEA RCA) project study (Atanacio et al., 2016) and modified to accommodate the atmospheric conditions of the Philippines (i.e., high aerosol loading). The collection period was at different intervals from June 2017 until April 2019 for the three sampling sites. Sampling was done twice a week—one weekday (Wednesday) and one weekend (Sunday), over a 24-hr period at alternating one hour on and off cycle. Due to limited resources, the source apportionment study focused only on the critical PM$_{2.5}$ fraction as this fine fraction is directly correlated with health effects.

Using the microbalance (Mettler Toledo AG245), PM mass was determined by gravimetry with 1.0 $\mu$g sensitivity. A mass correction factor of 1.447 was applied to the PM$_{2.5}$ databases of the three sampling sites similar to the Pabroa et al. (2022) study. This correction factor was estimated from the comparison of the Gent sampler and the co-located sampler of the European Union-GFA Consulting Group GmbH (EU-GFA) at NAMRIA. Such factor also agreed with the estimated correction factor generated from a previous study at the Ateneo de Manila University (ADMU) sampling site. Gent sampler results were also compared with the Aerosol Sampling Program (ASP) sampler of the Australian Nuclear Science and Technology Organization (ANSTO). Black carbon was analyzed using M34D Smokestain Reflectometer with $\varepsilon = 7$ m$^2$ g$^{-1}$ ($\varepsilon$: the average fine particle mass absorption coefficient) and Multi-wavelength Absorption Black Carbon Instrument (MABI). Two of the most important sources of black carbon particles are vehicle emissions and biomass burning (Jain et al., 2018). To ascertain the source of BC, multi-wavelength absorption analysis (MABI) BC was implemented in this study. Three wavelengths were considered to estimate BC concentration from diverse sources, 639 nm, 405 nm, and 1050 nm. More information can be found elsewhere (Manohar et al., 2021). Elemental levels (F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Se, Br, Pb, and Sr) in PM samples were determined using a non-destructive nuclear-related multi-element analytical technique by the energy-dispersive X-ray fluorescence spectrometry (EDXRF). Receptor modeling was done using the Positive Matrix Factorization (PMF) ANSTO macro-assisted PMF2 DOS version. In particular, source apportionment was done using ANSTO macro file-aided PMF2 DOS version, using error value of 0.05 and fpeak ranging from 0.1 or – 0.1. More information regarding the details of the PMF2 methodology can be found in a prior study (Atanacio et al., 2016). The possible transboundary contribution of air pollution sources was determined using the HYSPLIT model (Stein et al., 2015). Back trajectories were calculated for 72 hours, starting trajectories at 1-hr intervals for 24 hours, at starting heights of 100, 300, and 500 mAGL.

3 RESULTS AND DISCUSSION

3.1 Variability of PM$_{10}$ and PM$_{2.5}$ in the Urban and the Holiday Spot in SEA

Figs. 2 and 3 show the PM$_{10}$ and PM$_{2.5}$ mass concentrations of Boracay and Valenzuela. Detailed statistics of the PM are given in the supplement. Average PM$_{10}$ values in Boracay and Valenzuela were 125 ± 67 and 80 ± 28 $\mu$g m$^{-3}$, respectively. For PM$_{2.5}$, the mean values for the two sites were comparable (Boracay: 20.9 $\mu$g m$^{-3}$ and Valenzuela: 26.7 $\mu$g m$^{-3}$). The fine aerosol in Boracay (18.8%) had a lower contribution to coarse aerosol (34.4%), highlighting the influence of particles of larger diameter generated from marine sources and anthropogenic activities (e.g., construction) in the size distribution of PM in the coastal site. The weekend effect was only observed in PM$_{10}$ of Boracay, where t-test analysis indicated a significant difference between the mean mass concentration collected on Sunday (106 $\mu$g m$^{-3}$) and Wednesday (144 $\mu$g m$^{-3}$). This was attributed to the extensive construction activities in Boracay during the sampling period on weekdays, which clearly influenced the variability of coarse particles in the tourist spot. Fig. 2 also shows that the PM$_{10}$ observed in the urban area and a prime tourist spot in the Philippines were evidently elevated compared to some neighboring countries in SEA, such as Malaysia (Azhari et al., 2021), Thailand (Kanjanasiranont et al., 2022), Vietnam (Hien et al., 2019), Indonesia (Santoso et al., 2020), and Myanmar (Sricharoenvech et al., 2020; Lung et al., 2022). Such results accounted that the dominant impact of marine and construction activities in the Philippine sites that enhanced the coarse PM. On the other hand, Boracay and Valenzuela reported a similar magnitude of PM$_{2.5}$ compared to other SEA countries, as shown in Fig. 3 (Hien et al., 2019; Santoso et al., 2020; Azhari et al., 2021; Mueller et al., 2021; Lung et al., 2022).
The health impact of particulate matter in the urban and tourist spots in a SEA country was assessed based on the compliance of the measured mass concentration of PM to the annual and daily limits set by the WHO. For PM$_{10}$, Fig. 2 shows that both Valenzuela and Boracay exceeded the annual guideline value (10 $\mu$g m$^{-3}$). The same conclusion can also be gleaned for fine aerosols (see Fig. 3), where the two sampling sites had PM$_{2.5}$ average levels that do not meet the requirements of the WHO for yearly limits of PM$_{2.5}$ (5 $\mu$g m$^{-3}$). Furthermore, daily variations of PM were evaluated against WHO’s 24-hr guideline values (PM$_{10}$ - 45 $\mu$g m$^{-3}$ and PM$_{2.5}$ - 15 $\mu$g m$^{-3}$). In terms of daily exceedances of PM$_{2.5}$, the Valenzuela and Boracay sites failed 92% and 73% of all days sampled, respectively. For PM$_{10}$, the urban area recorded 93% of all days sampled with more than 45 $\mu$g m$^{-3}$, while the Boracay site surpassed the limit almost all the days (96%). The non-conformity of both the measured fine and coarse aerosols to the PM guideline of WHO indicate that the residents of the urban and tourist spot in the SEA region were extensively exposed to unhealthy air quality, which has a severe impact on human health. On the contrary, only a few days surpassed the national limit set by the Philippine government for PM for both sites. Fig. 2 illustrates that Boracay and Valenzuela sites only reported 25% and 2% of the sampling days that surpassed the threshold for PM$_{10}$ (150 $\mu$g m$^{-3}$). On the other hand, 7% of the measurement days in Boracay and 16% in Valenzuela were higher than 35 $\mu$g m$^{-3}$, which is the 24-hour limit set for PM$_{2.5}$ in the Philippines. The evident disparity in the days of exceedance highlights the need to update national limits for the PM to substantially reduce the ambient concentration of harmful atmospheric aerosols and the mortality burden due to PM in this region.

While it is expected that vehicular emissions contribute a major portion of the PM in urban to highly urbanized areas such as in Valenzuela and Manila, a different scenario occurred in the prime tourist spot which impacted its atmospheric condition. During the sampling period, the Philippine National government placed Boracay Island on a granular lockdown for the island to environmentally recover from the massive anthropogenic emissions that degraded the air and water quality in the area. As a result, local and foreign tourists, sometimes exceeding 20,000 during the peak season, were barred from entering the area to rehabilitate and redevelop the island. Indeed, beachside clearance was successful, where the water quality improved noticeably due to
Fig. 3. PM$_{2.5}$ Levels at Valenzuela and Boracay sampling sites. (Left) Mean PM$_{2.5}$ measured at Boracay and Valenzuela. The average PM$_{2.5}$ observed in the Philippines was compared with prior measurements in Malaysia (Azhari et al., 2021), Thailand (Mueller et al., 2021), Vietnam (Hien et al., 2019), Indonesia (Santoso et al., 2020), and Myanmar (Lung et al., 2022). More information regarding the measurements in other SEA countries are provided in Table A3 in the supplement. The BC contribution in PM$_{2.5}$ for both sites is also shown in the figure. (Right) Integrated 24-hour mass concentration of PM$_{2.5}$ in the urban area and the holiday spot in SEA. A day with %BC of 83% at the Valenzuela site was not included in the plot for a better illustration of the scatter plot. Also shown here is the daily contribution of BC in Valenzuela and Boracay (y-axis), where the substantial mass burden of BC was calculated in Valenzuela. Time series of the PM$_{2.5}$ plots of the two sites are provided in the supplement. Moreover, signifiers of daily and annual limits for PM$_{2.5}$ set by WHO and the National government are shown in this figure.

3.2 Sources of Elemental Tracers in PM

The comparison of the elemental concentrations at the different sampling sites is shown in Fig. 4 for Valenzuela and Boracay, while the descriptive statistics are provided in the supplement. Based on the average values, the decreasing order of the concentrations of the element in Valenzuela are as follows:

S > K > Si > Na > Ca > Fe > Pb > Zn > Al > Cl > P > V > Ti > Mn > Cr > As > Cu > Sc > Ni.

While for Boracay, the order was:

Ca > S > Si > Cl > Na > Fe > K > Al > Sr > Zn > Ti > Mn > V > Cu > Ni > Sc.
Fig. 4. PM$_{2.5}$ multi-element comparison for Valenzuela and Boracay sampling sites. The highest contribution at Valenzuela came from sulfur, while for Boracay, calcium reported the highest mass burden. The “x” symbol denotes the outlier for the box-whisker plot. On one measurement day, calcium in Boracay reached 14.2 µg m$^{-3}$, an outlier not shown here for better visualization of the concentration of elements. Note that Boracay reported below the detection limit (dl) for phosphorous (P) [dl = 6 ng m$^{-3}$] and lead (Pb) [dl = 2 ng m$^{-3}$], while strontium (Sr) was not measurable in Valenzuela.

It can be observed that the highest elemental concentration in Valenzuela was coming from sulfur (1.9 µg m$^{-3}$). In contrast, the highest concentration in Boracay was calcium (1.7 µg m$^{-3}$), although sulfur was still a dominant element in Boracay (0.9 µg m$^{-3}$). Sulfur in PM has primarily been attributed to sulfate aerosols generated from homogeneous processes and multiphase oxidation of SO$_2$ (Hopke et al., 2008; Wang et al., 2016). Sulfate aerosols are of primary interest due to their impact on air quality, climate, and ecosystem (Liu et al., 2021). Assuming that sulfur in PM primarily existed as sulfate, the mass concentration of sulfate in Boracay and Valenzuela were 2.7 and 5.7 µg m$^{-3}$, contributing as much as 13 and 21% of PM, respectively. This calculation is based on the molecular weight (MW) to atomic mass ratio of sulfate (MW = 96.06 g mol$^{-1}$) and sulfur (AM = 32.07 g mol$^{-1}$). A ratio (MW/AM) of 2.99 was applied to the measured sulfur content to derive the sulfate concentration. SO$_2$ emission is expected to be high in urban areas, usually coming from vehicular emissions and the burning of bunker fuel emitted from maritime vessels. The high relative humidity (R.H.) concentration in the Philippines (R.H. > 90%) also induced the formation of sulfate aerosols through the multiphase oxidation of SO$_2$. This enhanced the sulfur levels in both sites, besides the photochemical reaction route (Cheng et al., 2016; Liu et al., 2021).

On the other hand, the elevated calcium concentration in Boracay was credited to the enhanced emission of sea spray aerosols and construction activities. The measurement site in the tourist spot was adjacent to the coast, where sea spray can easily reach the sampling area. The calcium was also hypothesized to be elevated in this region due to rampant construction endeavors that emitted and resuspended particles enriched with calcium.

A striking difference between the two sites was the predominance of lead in Valenzuela, while no single day in Boracay reported above the detection limit. It was observed that lead was quite high (Ave: 0.15 µg m$^{-3}$; Max: 0.38 µg m$^{-3}$) in the Valenzuela site, similar to the results in a prior study (Pabroa et al., 2011). There was a unique source of Pb in Valenzuela, which was ascertained to be a distinct industrial activity that impacted the distribution of elemental tracers in the urban region. Exposure to lead has caused neurotoxic effects, with some patients reported to have enhanced blood pressure and hypertension (Salcedo et al., 2010). Identifying the source of lead in atmospheric aerosols is highly critical in preventing diseases inflicted on nearby residents. Nevertheless, the profile of the major elemental tracers reveals the dominant emission sources...
that influence the atmospheric conditions in Boracay and Valenzuela. This will be expounded later in the receptor modeling section (PMF results).

3.3 Enhanced Black Carbon in Urban Areas

The mean black carbon levels, as measured by reflectometry, found in fine aerosols are listed in Table 1. Higher BC concentration and contribution to PM$_{2.5}$ were observed in Valenzuela compared to measurements in Boracay. The massive vehicular activities in the urban area emitted a substantial level of BC, contributing as much as 30% of the average fine aerosol mass. Compared to other regional sites (see Fig. 5), Manila and Valenzuela sites had comparable BC levels to metropolis regions in Sri Lanka and Bangladesh. The Boracay site exhibited low BC concentration, similar to areas with clean atmospheric conditions (e.g., Australia and New Zealand).

To apportion the sources of Black Carbon, multi-wavelength characterization was implemented to efficiently separate the contribution of biomass and fossil fuel burning. Fig. 6 illustrates the BC comparison profiles between vehicular and smoke sources at Boracay and Valenzuela. In Metro Manila, the MABI indicated that on average, 9.1 µg m$^{-3}$ of BC was accounted for in vehicle emissions while only 0.13 µg m$^{-3}$ was attributed to biomass burning. Valenzuela has always been a heavy-traffic city. In 2017, 9.3 million private motor vehicles were registered in Metro Manila (National Capital Region), a considerable 13% increase compared to 2016. High BC from automobile sources than biomass burning is expected in this region, but the increase in output must be mitigated to address global warming and air quality. For the prime tourist spot, 2.0 and 0.53 µg m$^{-3}$ of the mass of BC were ascertained to the vehicle and biomass burning/smoke emissions. The BC levels of BC are higher in Valenzuela and Manila compared to other regions.

Table 1. Descriptive statistics of black carbon (µg m$^{-3}$) in PM$_{2.5}$ at the sampling sites.

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>Average (n)</th>
<th>Standard Dev.</th>
<th>Confidence interval (95%)</th>
<th>Max/Min</th>
<th>%BC in PM$_{2.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valenzuela</td>
<td>7.6 (110)</td>
<td>3.1</td>
<td>0.58</td>
<td>17.8/1.5</td>
<td>29.1</td>
</tr>
<tr>
<td>Boracay</td>
<td>1.37 (74)</td>
<td>1.5</td>
<td>0.35</td>
<td>11.6/0.50</td>
<td>7.4</td>
</tr>
<tr>
<td>Manila</td>
<td>10.8 (14)</td>
<td>3.0</td>
<td>1.7</td>
<td>16.4/7.1</td>
<td>39</td>
</tr>
</tbody>
</table>

Fig. 5. Comparison of PM$_{2.5}$ black carbon (BC) levels in Valenzuela (Val), Boracay (Bor), and Manila with that of the regional data (2001–2009) (Atanacio *et al.*, 2016). The BC average levels in Manila and Valenzuela sites are above the regional average of 6 µg m$^{-3}$. In addition, the Manila average level is comparable to average levels in Sri Lanka (SRI), Valenzuela with Bangladesh, and Boracay with Australia or New Zealand.
concentrations from automobile sources are comparable with biomass burning except for the evident peak that coincides with months when tourists normally visit the island. Unlike in the metropolis, vehicle activities in less urbanized areas like Boracay are low to moderate, where the main mode of transportation for tourists and locals are motorcycles and tricycles. At the same time, less urbanized areas depend on biofuels for their household cooking, water boiling, cattle feed preparation, etc. (Jain et al., 2018). With the closure of the island in 2018 for its rehabilitation, massive reduction in operating tricycles/motorcycles, automobile emission was reduced, and smoke (or biomass burning) was dominant on some days. Pre-lockdown, the average vehicular contribution to BC was 3.4 µg m⁻³ and subsequently reduced by 46% (1.8 µg m⁻³) during the island’s rehabilitation. More importantly, the reduction in black carbon emissions observed during the rehabilitation will initiate policies regarding the proper utilization of public transportation on Boracay Island. Also, similar tourist spots across the globe, particularly in Southeast Asia, can pursue similar environmental policies for the reduction of emissions of atmospheric pollutants in prime resort regions.

### 3.4 Integration of Multi-wavelength BC Analysis to Traditional Multi-element Source Apportionment

Multi-element and black carbon are the typical input parameters to establish the sources of atmospheric aerosols using PMF. To increase the capacity of the receptor modeling, data from MABI that can distinguish BC sources based on their absorption properties were included in the model instead of the typical BC measured using reflectometry. The corresponding time series plots of the apportioned air pollution sources are shown in Appendix A. – Figs. A6 and A7 for Valenzuela and Boracay, respectively. Source apportionment (Figs. A8 and A9) and time series plots (Figs. A9 and A10) using BC concentration from reflectometry for Valenzuela and Boracay sites are also shown in Appendix A. In general, the “Automobile” factor was easily determined due to the evident contribution of the BC generated from transportation activities. The same goes for the Smoke factor, which was straightforwardly distinguished due to the substantial source fraction from BC from biomass burning. Such results were not evident when BC from the typical reflectometry was utilized. Overall, BC from MABI showed to be source-specific compared to BC from reflectometry. The resulting BC combined with PMF can provide estimates of BC related to the vehicular source and biomass burning.

Fig. 7 shows the PMF-derived air pollution sources for the Valenzuela and Boracay sites, based on the chemical components of PM₂.₅. Valenzuela source apportionment analysis resulted in eight (8) sources of PM—soil, secondary sulfate, aged sea spray, auto or vehicular emissions with
Fig. 7. PM$_{2.5}$ source apportionment results at the Valenzuela and Boracay sampling sites using BC concentration from MABI. Eight (8) pollutant sources were found for Valenzuela (June–November 2016), while seven (7) pollutant sources were found for Boracay (December 2017–April 2019). The industry factor of Valenzuela presented here is a composite of industry, industry-Zn, and industry-Pb variables. Also, the sea spray observed in Valenzuela was aged, according to PMF analysis. The numbers inside the bars are the contribution of each source to the mass of PM$_{2.5}$.

road dust, industry-related sources, industrial Pb, and industrial Zn. Among the determined factors/sources, the most dominant was vehicular emission, contributing as much as 47.08% of PM, corroborating with previous studies (Pabroa et al., 2022). High traffic areas such as Valenzuela release trace elements in ambient air from exhaust emissions (As, Pb, Mn, K, P, and S), vehicular wear and tear (Cu and Zn), and resuspended road dust (Ca, Ti, and Fe) (Gugamsetty et al., 2012; de Miranda et al., 2018; Saggu and Mittal, 2020). On the other hand, industry-related sources are characterized by Ca, Cl, K, Fe, Ni, and Mn (Gugamsetty et al., 2012; Ryou et al., 2018). The Valenzuela sampling site has a distinct industrial source with Pb and Zn as major components. The presence of Pb in the Valenzuela site can be an indication of battery recycling activities in the area (Pabroa et al., 2011, 2022), while the Zn concentration can be associated with the steel industry (Saggu and Mittal, 2020) and plastic molding industry that uses Zn compounds (ZnSO$_4$). A plastic packaging manufacturing company is located less than 1.0 km from the sampling site.

The source apportionment results for Boracay revealed seven (7) sources—seaspray, fine soil, vehicular emissions, smoke, or biomass burning, construction dust, and industrial source, primarily Zn. Unlike in the metropolis area, receptor modeling reported less contribution from vehicle emissions, which only attributed 11.2% to the total pollutant sources. Automobile sources such as tricycles and motorcycles, which are the main mode of transportation on the island, contributed less to the BC vehicular concentration than the jeepneys and buses in Valenzuela. Elevated Zn source can be attributed to two-stroke engines like a motorcycle, a primary mode of transportation on the island, and four-stroke engines like machinery used in construction activities (Gugamsetty et al., 2012). A noteworthy source in Boracay was the construction activities, which were the dominant source of PM (23%). As indicated earlier, widescale road-widening projects were implemented in the area during the sampling period. The high Ca concentration noted in the results can be attributed to the emission and resuspension from the construction project. Road construction sites have high metal enrichment, reflecting the materials and activities involved in such activity (Yang et al., 2020). A closer look at the profile of source apportionment of Boracay reveals the substantial presence of Zn. This element was associated with BC biomass emitted from the burning of the wood, grasses, and leaves, usually used as biofuels for their household requirements. Zn is also an essential element for plant growth. Thus, a high Zn concentration is expected from biomass-burning plumes (Salam et al., 2013). The source of Zn, either produced locally or through transboundary transport, was determined using a back trajectory model. Plume movement analysis showed that air masses
passed through different areas such as Malabon and Navotas (see supplement) where these areas have industrial companies that can be the source of emissions. However, the spatial resolution analysis of HYSPLIT cannot ascertain a specific source for zinc. Thus, local emissions might have contributed to the high zinc. The Zn from the Boracay site may be from activities near the sampling site, such as road widening, instead of long-range transport.

4 CONCLUSIONS AND RECOMMENDATIONS

An extensive characterization of atmospheric aerosols was implemented in Southeast Asia's urban areas. In particular, coarse and fine aerosols were collected for almost two years in Valenzuela and Boracay, Philippines, and subsequently examined the variability of PM mass, BC, and trace elements. Results showed that mean PM$_{10}$ and PM$_{2.5}$ sites in the urban area were non-compliant with the WHO annual limits of 10 $\mu$g m$^{-3}$ for PM$_{10}$ and 5.0 $\mu$g m$^{-3}$ for PM$_{2.5}$. The Boracay site reported an average level much lower than the urban sites but was still above the WHO 1-year guideline value. It can be established from both the PM$_{2.5}$ and PM$_{10}$ concentration levels that the sampling sites in this study have unhealthy air quality levels. Moreover, several daily PM values surpassed the 24-hour limit of WHO during the measurement. PM$_{2.5}$ in Valenzuela and Boracay exceeded the WHO limit 92 and 73% of measurement days, respectively. For coarse particles, 85 and 95% of the study campaign period recorded more than 50 $\mu$g m$^{-3}$. The elevated atmospheric levels observed in the urban sites were well expected due to the extensive vehicle and industrial emissions that enhanced the PM mass concentration. However, the augmented mass of PM in Boracay was surprising given the area's semi-rural condition.

Multi-element profile analysis indicated that the most dominant trace elements were sulfur at the urban sites and calcium for the Boracay sampling site. The sulfur was chiefly attributed to sulfate in aerosols, generated from the oxidation of SO$_2$ emitted from vehicular and industrial activities. The eminent calcium level in Boracay was considered a marker of sea spray aerosols and construction activities. Lead also had a substantial mass burden, particularly in Valenzuela, where several industrial processes (i.e., battery production/recycling) were near the sampling site. Overall, the multi-element analysis revealed the principal endeavors and sources that influenced the variability of the PM in urban and tourist spot in the Philippines.

Black carbon levels (average at 6.6 $\mu$g m$^{-3}$) across the sampling sites varied between 4 to 83% of the fine particulate mass. BC compositions were 29, 7.0, and 39% for Valenzuela, Boracay, and Manila, respectively. BC is a fingerprint of incomplete combustion products, which may originate from vehicular emissions or biomass burning. Vehicular emission predominated the Metro Manila sites, consistent with the extensive automobile endeavors. Less BC mass burden in fine aerosols was calculated in Boracay due to limited transportation endeavors caused by the rehabilitation protocols set by the national government. The reduction in black carbon during the closure was clear evidence that black carbon levels can be brought down with the decrease in vehicular emissions. This will help solidify policies to promote the use of electric vehicles (e.g., tricycles) on the island to reduce black carbon emissions and improve air quality.

Using receptor modeling on the PM$_{2.5}$ dataset with the black carbon data generated from MABI, eight (8) and seven (7) PM were found in Valenzuela and Boracay, respectively. Vehicular emissions dominated the black carbon source in Valenzuela, while both transportation activities and biomass burning had comparable contributions in Boracay. Therefore, a better resolution is afforded for apportioning the black carbon sources using the data from MABI. Fine construction dust is a prominent source in Boracay, considering that various construction activities were ongoing during the sampling period, which impacted the mass concentration of PM. Seaspray with ship emissions fingerprint was determined in Boracay, while aged sea spray was found at Valenzuela. A Pb source, chiefly coming from industrial emissions, was determined for Valenzuela but was absent in Boracay.

This study enhanced the capability of source apportionment studies, which typically employ trace elements and BC concentration. In this study, MABI was more suitable for environments significantly impacted by either vehicle emissions or biomass burning. Furthermore, the results of this study provided new information on local sources of air pollutants in urban and remote
environments in Southeast Asia, a region with substantial air pollution emissions yet with limited research studies compared with other global regions. Even though the measurements were carried out only in the Philippines, the applied methods and data analysis can also be applied to other areas to understand the variability and sources of PM. The information from this study can be used to guide authorities and policymakers in assessing the air quality impact of PM$_{2.5}$ and BC and implementing environmental policies that will mitigate the ambient concentration of toxic atmospheric pollutants.

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REFERENCES


