Particulate air pollution in six Asian cities: Spatial and temporal distributions, and associated sources

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Abstract

A monitoring program for particulate matter pollution was designed and implemented in six Asian cities/metropolitan regions including Bandung, Bangkok, Beijing, Chennai, Manila, and Hanoi, within the framework of the Asian regional air pollution research network (AIRPET), coordinated by the Asian Institute of Technology. As uniform the methodologies as possible were intended with an established QA/QC procedure in order to produce reliable and comparable data by the network. The monsoon effects and seasonal changes in the sources/activities require long-term monitoring to understand the nature of air pollution in the cities. During phase 1 (2001–2004) of the AIRPET around 3000 fine and coarse particulate matter samples were collected from characteristic urban sites, which provide insight into temporal and spatial variations of PM in the cities. In all six cities, the levels of PM\textsubscript{10} and PM\textsubscript{2.5} were found high, especially during the dry season, which frequently exceeded the corresponding 24 h US EPA standards at a number of sites. The average concentrations of PM\textsubscript{2.5} and PM\textsubscript{10} in the cities ranged, respectively, 44–168 and 54–262 $\mu$g m\textsuperscript{-3} in the dry season, and 18–104 and 33–180 $\mu$g m\textsuperscript{-3} in the wet season. Spatial and temporal distribution of PM in each city, the ratios of PM\textsubscript{2.5} to PM\textsubscript{10}, and the reconstructed mass were presented which provide useful information on possible PM sources in the cities. The findings help to understand the nature of particulate matter air pollution problems in the selected cities/metropolitan regions.

Keywords: Monitoring; Particulate matter; Contributing sources; Asian cities; AIRPET

1. Introduction

Atmospheric particles can cause multiple effects on human health and the environment. Particles with the size less than 10 $\mu$m (PM\textsubscript{10}) have long been...
implicated in causing adverse health effects and increased mortality (Dockery and Pope, 1994) whereas fine (PM_{2.5}) and ultrafine particles impose even higher risk (Donaldson et al., 1998; Schwartz and Neas, 2000; Ostro et al., 2006). Atmospheric particles also interact directly and/or indirectly with the Earth’s radiation energy balance and can subsequently affect the global climate (IPCC, 2001; Liu and Daum, 2002). The recently discovered atmospheric/Asian brown cloud, which contains suspended particles as the major component, is believed to cause multiple effects on regional air temperature, precipitation, agriculture, air quality, and health (UNEP and C4, 2002). Due to their ability to absorb and scatter solar radiation the atmospheric particles, especially fine ones, effectively reduce visibility (Watson, 2002; Kim et al., 2001).

There has been a growing concern on monitoring and characterization of size-segregated ambient particulate matter (PM) in the recent years. Efforts and resources are being spent to understand its nature and to develop mechanisms that would help control this harmful pollutant. In many developing countries, however, information on levels of fine particles in the ambient air is still scarce. Until recently, total suspended particulate matter (TSP) was the most monitored and is still a regulated pollutant in most developing countries. However, with the increased awareness of their harmful effects on human health and the environment, there is a tendency toward monitoring fine particles in the ambient air. Fragmented data available in some Asian developing countries suggest high ambient levels of fine particles. A study in Beijing shows that the weekly PM_{2.5} in 1999–2000, at two sites, ranged from 37 to 357 \mu g\,m^{-3} (He et al., 2001). In Vietnam, the averaged level during 1996–1998 for PM_{2.5} and PM_{10–2.5} at a site in Ho Chi Minh city, was 16 and 32 \mu g\,m^{-3}, respectively (Hien et al., 2001), while for a site in Hanoi the corresponding levels, averaged for 1998–1999, were 35 and 50 \mu g\,m^{-3}, respectively (Hien et al., 2002). In Bangkok, Thailand, records show that in the years of 2000, 2001 and 2002, the PM_{10} levels at curbside stations exceeded the 24 h Thai National Ambient Air Quality Standard (120 \mu g\,m^{-3}) with a frequency of 12.8\%, 10.5\%, and 3.8\%, respectively, while at ambient sites the corresponding exceedance frequency was 2.1\%, 0.3\%, and 0.39\% (PCD, 2001, 2002, and 2003). Limited published PM_{2.5} data for Bangkok show that 24 h PM_{2.5} in busy parts of the city may be as high as 100 \mu g\,m^{-3} (Ostro et al., 1999).

There are no systematic and long-term published records of PM mass and composition, which are regionally compatible, in the Asian developing countries. Such records, especially with focus on fine particles, will help to create and enhance scientific knowledge necessary to address the worsening particulate air quality in these countries. In particular, the data will help to understand the nature of the particulate pollution in a city in relation to local sources, long-range transport and atmospheric transformation processes, which is essential for the formulation of effective air quality management strategies.

To partly fill up the gap, the Asian regional air pollution research network, or AIRPET, (http://www.serid.ait.ac.th/airpet), has designed a monitoring program to collect such data. AIRPET, now in phase 2, has one of the main research objectives in providing a comprehensive assessment of PM pollution. The focus is on PM_{2.5} and PM_{10}/PM_{10–2.5} levels and composition with the spatial and temporal distribution in six involved cities/metropolitan regions in Asia, namely, the Bangkok Metropolitan Region (BMR, Thailand), Bandung (Indonesia), Beijing (China), Chennai (India), Metro Manila Region (Philippines), and Hanoi Metropolitan Region (Vietnam). The network is mainly funded by the Swedish International Development Cooperation Agency (Sida) through the Asian Regional Research Program in Environmental Technology (ARRPET) and is coordinated by the Asian Institute of Technology (AIT). This paper presents some findings on levels, composition and possible source contributions of the PM in the six cities during AIRPET phase 1, 2001–2004.

2. Methodology

2.1. Monitoring program design

Six research institutions (NRIs) are involved in this network, including AIT; Institute of Technology of Bandung; Research Centre for Eco-Environmental Sciences/Beijing Normal University, Beijing; Manila Observatory; Hanoi University of Science; and Indian Institute of Technology, Madras. Each institution conducts monitoring for one city/metropolitan region in a country.

The selected cities/regions are different in terms of topography, meteorology, population, energy use, industry, and vehicular mix and density. The climate of the region is dominated by monsoon with
two distinct seasons, dry and wet. Though the dry and wet seasons may cover different months of the year in different countries, it has been decided to have only these two broad season categories for the consistency in intercity comparison of the monitoring results. In all cities, the wet season is within the summer months of the Northern Hemisphere (May–October) and the dry season is the rest of the year, except for Bandung (Indonesia), which is just opposite due to its location in the Southern Hemisphere. Note that even during the wet season, the samples were collected when there was no intense continuous rain.

The PM monitoring program was designed to provide as harmonious data in the six cities/metropolitan regions as possible. Sampling sites are classified into six categories characterizing the urban airshed including the upwind, traffic, residential, commercial, industrial, and urban mixed (downwind) sites. Each city/metropolitan region has 3–5 out of these six site categories. The classification of sites is based on the vicinity of major influencing emission sources/activities, and was done in order to have as much consistency for all six cities as possible. Accordingly, the upwind site refers to the upwind direction of the city in the dry season, the traffic site is located in the city central districts and close to traffic lanes (within 3–10 m), the residential site is in the city crowded area, the commercial site is in the commercial areas in the city center, the industrial site is located in areas with more concentrated industrial activities within the city metropolitan region, and the urban mixed site is located in the downwind direction during the dry season and is affected by most of the important sources in the city/region. It was intended to have the sampling intake located at the height of 3–5 m for all cities. However, due to siting difficulty a few sites were located higher than 5 m, especially the traffic site and the residential site in Beijing, which were at around 40 m above the ground. This, consequently, may cause inconsistency in the comparison of results site by site, particularly for large particles.

In all cities monitoring for PM$_{2.5}$ and PM$_{10}$ or PM$_{10-2.5}$ was conducted using dichotomous (dichot), Minivol, or other equivalent samplers depending upon the availability. Each sampler used in the network was compared with a dichot, as will be discussed later. For consistency, here we present and discuss the 24 h PM$_{2.5}$ and PM$_{10}$ mass concentrations. Fine (PM$_{2.5}$) and coarse (PM$_{10-2.5}$) fractions by dichots were summed up to get the PM$_{10}$ mass concentration. Filter media were selected to suit the subsequent analytical methods. It was intended that all the filters/samples used in the network to be conditioned for about 24 h (temperature 20±5 °C, relative humidity 40±10%) for the gravimetric mass determination, though small deviations were observed depending on the actual conditions at each research institution. The quartz filters were fired at 550 °C for about 6 h prior to conditioning for pre-weighing. The treatment of quartz filters at this temperature is necessary to remove any carbonaceous/organic pollutants and is recommended for samples to be analyzed for organic components. Detail on QA/QC employed is presented in a separate section later.

2.2. Sample analysis

The filter samples were segregated and subjected to multiple compositional analyses. The water soluble ions were analyzed by IC using the procedure given in Chow (1995). Filter samples in Chennai (India NRI), however, were analyzed for NH$_4^+$, sulfate and nitrate using UV-Visible spectrophotometer (Lodge, 1989). Elements were analyzed by ICP-AES (China), ICP-MS (India, Vietnam), PIXE (AIT, Philippines), XRF (Vietnam, Philippines). In Indonesia, the elements were analyzed by both INAA and AAS to detect more elements. Black carbon (BC) was measured using M43D digital smoke stain reflectometers for samples collected by AIT, India, Vietnam, Indonesia, and Philippine NRIs. A number of samples were also analyzed for EC/OC, including samples collected in the dry season at the upwind site of BMR by the thermal/optical transmittance (TOT) method (Sunset analyzer) and samples from Beijing by a C/H/N elemental analyzer following the method described in Dan et al. (2004). Quartz filters were segregated for analysis of ions and EC/OC, while samples on mixed cellulose or Teflon filters were analyzed for elements. The numbers of analyzed parameters are slightly different for different cities due to the availability of the equipment. The network aims at getting as complete data sets as possible on PM composition for receptor modeling purpose which primarily include mass, water soluble ions, elements, and BC and/or EC/OC.
2.3. Quality assurance and quality control (QA/QC)

Data quality is of the foremost concern, and implementation of a harmonized QA/QC procedure is especially important when many research institutions are involved. Common methodology for sampling and analyses, as well as the comparison between different sampling and analytical techniques used by NRIs in the network are important for obtaining a harmonized regional database. The QA/QC of the monitoring scheme were followed at all possible stages from monitoring (siting, sampling method selection, sampler calibration, co-located sampling, selection of filter media, filter preparation, sampling execution, filter weighing, filter segregation) to the chemical analysis. The analytical methods for elements used by different institutions within the network were checked using a standard reference material (SRM), which was the coal fly ash (GBW 08401), provided by the China NRI. All NRIs analyzed this SRM except for the Indonesia NRI which analyzed the NIST SRM #1648 (urban PM). In phase 1 of AIRPET, the PM composition analytical results are considered acceptable if the deviation is within ±20–30% of the certified/reference values for major elements (concentrations >1 μg g⁻¹) and larger deviations (<2 fold) for minor elements depending on the analytical methods used. Taking into account also the standard deviations of both the certified values and the analytical results, it is considered that the SRM analytical results produced by most of the NRIs agree reasonably with the SRM certified values, except for the method used for Chennai samples. The SRM analytical results by this NRI (ICP-MS) are off the range for most listed elements, hence, the PM composition data for Chennai will not be further discussed in this paper.

The M43D Digital Smoke Stain Reflectometer used at AIT was calibrated against the optical spectrometer at Borås, Sweden, which is described in Moloi et al. (2002). Samples from Vietnam were also measured for BC by the AIT equipment. India used the conversion formula obtained based on the AIT reflectometer calibration. The Philippine and Indonesia NRIs measured BC using reflectometers available in the countries through the regional project on air pollution and trends of the International Atomic Energy Agency (IAEA, 2005), which were calibrated following the method prepared by the Max Planck Institute of Chemistry, Germany.

Regular sampler calibration was planned for the whole network. The coarse fraction of dichot samples was corrected for the carried-over fine fraction. Most samples were collected over 24 h period, except for some samples in Beijing, which were taken for 4–8 h due to high PM loadings on filters. The latter were subsequently normalized to 24 h and the data sets for all cities are 24 h averaged.

One filter for about every 20–30 filters in a lot was used as a blank. All the analyzed data were blank corrected. For illustration, the quartz filters at AIT, by ICG, have blank levels for Ca²⁺ and SO₄²⁻ of 0.4–0.5 μg cm⁻² filter area, for Cl⁻, NO₃⁻, and Na⁺ of 0.14–0.15 μg cm⁻², and the lowest for NH₄⁺, Mg²⁺, and K⁺, of around 0.03 μg cm⁻². Mixed cellulose filters for elements, by PIXE, at AIT have the average blank levels for Cl, S, Si, Ca, and Al (listed in the increasing order) of 0.08–0.2 μg cm⁻² filter area, whereas other elements are well below 0.01 μg cm⁻² and basically zero for As, Sb, and Ag. Other NRIs reported the filter blank levels comparable with those of AIT for the same filter types. In addition, the Whatman G/F used in Beijing have high blank levels for Cl⁻, NH₄⁺, NO₃⁻, and SO₄²⁻ (0.5–1 μg cm⁻²).

Each NRI was provided with one Sierra Anderson dichot (series 241), which was used as a reference sampler of the network and was collocated with other samplers used by the NRIs. AIT used two collocated dichots for routine sampling which were compared with the US EPA FRM samplers (RASS and Partisol®-Plus). The dichot results (x-axis) agree well with the FRM and with most of other samplers (y-axis) used by different NRIs yielding a slope of 0.93–1.06 for PM₂.₅, and a slope of 0.97–1.05 for PM₁₀ and PM₁₀₋₂.₅ (R² of 0.86–0.99). In addition, good agreements were also obtained, by AIT, between the ionic composition of PM₂.₅ samples by dichots and those by FRM (Opal, 2002). The results of the collocated sampling by the Indonesia NRI (dichot and LowVol), however, have a slope of 0.84 for PM₂.₅ (R² of 0.57). The medium volume sampler (APM550) used by the India NRI produced higher PM₂.₅ and PM₁₀₋₂.₅ than the collocated dichot with a slope of 1.13 (R² = 0.97) for PM₂.₅ and 1.25 (R² = 0.99) for PM₁₀₋₂.₅. The Philippine NRI used Minivols for routine sampling, which agree reasonably with the dichot with a slope of 0.93 for PM₂.₅ (R² = 0.86). It is noted that the comparison has been made based on over 30 collocated samples collected by each NRI, except for China (5–6 samples) and India.
For the NRIs producing water soluble ion data, the ion charge balance was also checked. The ratios of the sum of the cation equivalents (NH$_4^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) to that of anion equivalents (Cl$^-$, NO$_3^-$, SO$_4^{2-}$) are closer to 1 for PM$_{2.5}$ samples and larger (>1–3) for the coarse fraction. Detail on ion balance will be presented in our forthcoming papers.

3. Results and discussion

3.1. PM levels

Totally, in phase 1 the AIRPET research team collected nearly 3000 PM samples in the six cities, of which around 1650 are PM$_{2.5}$ samples and the rest are PM$_{10}$/PM$_{10-2.5}$. More samples were collected in the polluted dry season than the wet season. Larger numbers of samples were collected at two designated intensive sites in each city, the upwind and the urban mixed site, than other sites. All samples were analyzed for mass and most of the samples were analyzed for the chemical composition. Arithmetic average PM mass concentrations, the standard deviations, and the sample numbers used for average mass calculation for each site in the six cities during the dry and wet season are presented in Figs. 1 and 2, respectively.

PM concentrations in all the cities in the dry season are remarkably higher than those in the wet season. Absence of intensive wet removal, increase in local emission, e.g. coal burning for space heating in China (He et al., 2001) and open biomass burning, more road dust/soil suspension, and stagnant meteorological conditions (Kim Oanh et al., 2005; Hien et al., 2002; He et al., 2001) are some major factors leading to the high air pollution concentrations in the dry season. Long-range transport of pollutants from upwind regions following the Northeast monsoon may also contribute to PM levels in some cities.

Based on the data collected during 2001–2004 by AIRPET, PM$_{2.5}$ in the dry season, on average, was the highest in Beijing (Fig. 1a). During the wet season, the difference in PM$_{2.5}$ between the cities is not so large though Beijing still recorded considerably higher levels (Fig. 2a). PM$_{10}$ results show almost a similar trend as PM$_{2.5}$ with the highest levels in Beijing, followed by Hanoi (traffic and residential site) and Chennai (traffic and industrial site).

Fig. 1. Average concentrations of PM$_{2.5}$ (a) and PM$_{10}$ (b) in the dry season in six cities. (Whiskers represent one standard deviation, SD, of the mass concentration data series at each site. Note that SD mainly indicates the variations in daily concentrations due to changing emission and meteorology conditions throughout a season).
The high PM levels in Beijing, remarkably higher than BMR and Manila which have the comparable population, may be attributed to both natural and man-made factors. Extensive coal burning in Beijing during the cold winter, when there is notably limited dispersion, may cause high PM levels during this period of the year, and the dust storms may contribute significantly to PM in the spring (He et al., 2001; Sun et al., 2004). The high PM levels observed at the upwind site of Beijing in the dry season also reflect the impacts of PM transport from outside into the city. In addition, the low annual average precipitation in Beijing as compared to other cities would limit the wet removal of air pollutants. Though relatively small in size and population, Hanoi recorded high PM levels during the dry season. Cold winter and more stable atmosphere under the influence of a high-pressure ridge with the limited vertical dispersion due to radiative and subsidence inversion (Hien et al., 2002) enhance the high PM build up in Hanoi in the dry season. The highest PM$_{2.5}$ was observed at the residential site, 200 $\mu$g/m$^3$ (averaged for 10 samples), which implies a high exposure for people and also suggests a local contribution, most probably from domestic cooking in the nearby living compounds. More samples, however, are required to produce a reliable average PM at this site. Note that during the dry season some weak influence of the high-pressure ridge may be felt in BMR which may reduce the pollutant dispersion. However, the coastal location would enhance the dispersion in the four cities (Bangkok, Bandung, Chennai, and Manila). Coupled with the warm climate (no space heating), this may substantially lower ambient air pollution even though traffic and other stationary sources in these cities may be significant.

Remarkably higher concentrations of PM$_{2.5}$ and PM$_{10}$ at the traffic sites, during both seasons, in Bangkok and Manila, and PM$_{10}$ in Hanoi (no PM$_{2.5}$ data) reflect a relatively high contribution from the traffic. In the wet season, the difference in PM levels between the traffic site and other sites in these three cities is even more pronounced, meaning the higher relative influence of traffic, which is most probably caused by a lesser intensity of other local and long-range transport contributions. In Bandung, the

![Diagram]

Fig. 2. Average concentration of PM$_{2.5}$ (a) and PM$_{10}$ (b) in the wet season in six cities (Whiskers represent one standard deviation, SD, of the mass concentration data series at each site. Note that SD mainly indicates the variations in daily concentrations due to changing emission and meteorology conditions throughout a season).
PM\textsubscript{2.5} and PM\textsubscript{10} levels in both seasons were relatively low and are comparable between the sites. Average levels at different sites in Beijing are also comparable but are high at all sites. It is noted that the sampling intake at both the traffic and the residential sites in Beijing was high (40 m), which may not produce comparable results with other sites. In Chennai, higher PM levels, especially PM\textsubscript{10}, were observed at the industrial site, suggesting an important contribution from industry. However, small numbers of samples collected at the sites in Chennai during both seasons may not yet produce representative results.

PM levels varied significantly from day to day at each site during a season, which is seen in the large standard deviations in Figs. 1 and 2. Especially in Beijing during the dry season, when PM\textsubscript{2.5} from time to time reached above 400 \(\mu\)g m\(^{-3}\) and PM\textsubscript{10} reached above 1400–1600 \(\mu\)g m\(^{-3}\) (for example, at the upwind site and the traffic site in December 2001). Highly fluctuating PM levels in the cities are the reflection of the changes in the meteorology and emission throughout a season with some sources that are discontinuous and episodic in nature, such as dust storms or biomass burning.

Average PM\textsubscript{2.5} and PM\textsubscript{10} concentrations across the cities (averaged for all sites in a city) in each season are presented in Table 1 together with the major PM compositions. To reduce the bias related to the difference in sample numbers at different sites across a city the average was calculated from the seasonal averaged PM\textsubscript{2.5} and PM\textsubscript{10} at each site (not from the 24 h data series). PM\textsubscript{2.5} averaged for the dry season was the highest in Beijing (168 \(\mu\)g m\(^{-3}\)) followed by Hanoi (124 \(\mu\)g m\(^{-3}\)), which well exceeded even the short-term ambient air quality standard of the US EPA, 24 h PM\textsubscript{2.5} of 65 \(\mu\)g m\(^{-3}\). For PM\textsubscript{10} in the dry season, the highest was in Beijing (262 \(\mu\)g m\(^{-3}\)) followed by Hanoi (186 \(\mu\)g m\(^{-3}\)) and Chennai (169 \(\mu\)g m\(^{-3}\)), which are even higher than the US EPA 24 h standard of 150 \(\mu\)g m\(^{-3}\). In the wet season, the PM\textsubscript{2.5} level in Beijing was also the highest, 104 \(\mu\)g m\(^{-3}\), while in other cities the levels did not differ much with the average of less than 45 \(\mu\)g m\(^{-3}\). For PM\textsubscript{10}, the highest level was in Beijing (180 \(\mu\)g m\(^{-3}\)), which is closely followed by Chennai (145 \(\mu\)g m\(^{-3}\)). It is noted that the numbers of samples differ from a site to another, and between the cities with the smallest numbers of samples collected in Chennai. The intensive sites generally have more than 40 samples during the dry season and above 25–30 samples during the wet season, but the mixed site in Manila has above 160 PM\textsubscript{2.5} samples in each season. The seasonal average levels calculated based on small numbers of 24 h PM samples are not likely to be highly representative. Long-term monitoring is desired to produce large numbers of samples at the selected sites and hence reliable seasonal averages, which is one of the objectives of AIRPET phase 2.

TSP was also monitored in BMR, Bandung, Beijing, and Chennai. Beijing recorded an average TSP of 305 \(\mu\)g m\(^{-3}\) (58 samples) in the wet season and 440 \(\mu\)g m\(^{-3}\) (34 samples) in the dry season. Samples collected at Chennai during December–February in 2001–2002 showed an average TSP level of 367 \(\mu\)g m\(^{-3}\) (77–863 \(\mu\)g m\(^{-3}\)). In Bandung, the TSP level during the dry season (July–October 2002) was 121 \(\mu\)g m\(^{-3}\) (85–191 \(\mu\)g m\(^{-3}\)) based on 26 samples. TSP in BMR was in the range 60–140 \(\mu\)g m\(^{-3}\) during the wet season and 100–300 \(\mu\)g m\(^{-3}\) during the dry season.

### 3.2. PM\textsubscript{2.5} to PM\textsubscript{10} ratio

The average ratio of PM\textsubscript{2.5} to PM\textsubscript{10} (PM\textsubscript{2.5}/PM\textsubscript{10}) was calculated for each site based on simultaneous pairs of PM\textsubscript{2.5} and PM\textsubscript{10} samples, and the results are presented in Table 2. PM\textsubscript{2.5} constitutes a larger fraction of PM\textsubscript{10} in most of the cities with the city wide average ratios generally \(\leq 0.6\) except for Chennai where the ratio was only 0.3–0.32. The citywise as well as the sitewise average ratios for the wet season are lower than those for the dry season in BMR, Beijing, Bandung, and Hanoi. In Manila, lower average ratios were obtained for the dry season at every site but with larger standard deviations than the wet season, while in Chennai the ratios obtained for both season are more or less the same.

The fine (PM\textsubscript{2.5}) and coarse particles (PM\textsubscript{10–2.5}) are relatively different in their physical and chemical compositions. They generally originate from different sources or by different activities within the same source. Coarse particles are normally generated by mechanical activities such as grinding or wind blowing, and are dominated by materials of geological origin (Chow, 1995). Fine particles mainly consist of secondary particles, which are formed in the atmosphere by chemical reactions (e.g., sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate), and primary organic carbon and elemental carbon. Due to the
time period required for the formation and atmospheric mixing processes, the secondary particles are expected to have a rather uniform spatial mass distribution in the cities at a given time. The fluctuation in PM$_{2.5}$/PM$_{10}$ ratios from one site to another is largely due to the primary sources, especially those contributing to the coarse particles. Lower PM$_{2.5}$/PM$_{10}$ ratios at all sites in Chennai indicate significant contributions from primary sources such as resuspended soil/road dust (unpaved roads), and other mechanical activities. Higher PM$_{2.5}$/PM$_{10}$ obtained in other cities suggests relatively high contributions from secondary particles and the combustion sources. For examples, high ratios of PM$_{2.5}$/PM$_{10}$ at the traffic sites in BMR and Manila in both seasons may be attributed to the emission from the vehicular fuel combustion. Likewise, the high PM$_{2.5}$/PM$_{10}$ ratio at the residential site in Hanoi, 0.91, suggests again a direct contribution from the surrounding residential fuel combustion. Higher PM$_{2.5}$/PM$_{10}$ ratios in some cities during the dry season as compared to the wet season may be attributed to higher fossil fuel combustion emission; more secondary particles formation due to more intensive photochemical reactions, e.g. higher ozone levels in BMR in dry

<table>
<thead>
<tr>
<th>City</th>
<th>PM$_{2.5}$ Dry</th>
<th>PM$_{10}$ Dry</th>
<th>PM$_{2.5}$ Wet</th>
<th>PM$_{10}$ Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bangok</td>
<td>181 50</td>
<td>181 76</td>
<td>106 18</td>
<td>106 33</td>
</tr>
<tr>
<td>Beijing</td>
<td>142 168</td>
<td>132 262</td>
<td>115 104</td>
<td>89 180</td>
</tr>
<tr>
<td>Chennai</td>
<td>83 46</td>
<td>83 169</td>
<td>10 42</td>
<td>10 145</td>
</tr>
<tr>
<td>Bandung</td>
<td>106 53</td>
<td>106 83</td>
<td>38 38</td>
<td>38 62</td>
</tr>
<tr>
<td>Manila</td>
<td>407 44</td>
<td>407 169</td>
<td>376 43</td>
<td>376 145</td>
</tr>
<tr>
<td>Hanoi</td>
<td>75 124</td>
<td>75 122</td>
<td>21 33</td>
<td>63 79</td>
</tr>
</tbody>
</table>

$n$ is total number of samples taken for the average; (——) data not available; blank cells: data are not presented due to high uncertainties.

*Average of all sites in the city.

$^b$Na analyzed by method other than IC.

$^c$Sulfur element content only.

$^d$Si data is not available hence is not included.

$^e$Value is for AIT site with OC data, average of other sites without OC data is in parentheses.

$^f$No EC and OC data was included for this average calculation, in parentheses is % contribution of EC and OC alone to mass.

$^g$These values are given as additional information. They are partly included in the previous columns on crustal (K) and trace elements, respectively.
months (Zhang and Kim Oanh, 2002); less wet removal; and possible long-range transport of fine particles during the NE monsoon.

3.3. Major chemical components and reconstructed PM mass

By chemical composition the major components of PM$_{10}$ in most urban areas can be presented in several groups: (i) geological material (oxides of Al, Si, Ca, Ti, and Fe), (ii) organic carbon (OC), (iii) elemental carbon, (iv) sulfate, (v) nitrate, and (vi) ammonium (Chow, 1995). In this study, to account for the PM nature and origin, hence to gain certain insights into the contributing sources, the final groups used include the crustal, organic matter (OM), soot, sea-salt, NH$_4^+$, SO$_4^{2-}$/C$_0$, NO$_3^-$/C$_0$, and ‘trace elements’ (the rest of the elements, depending on the analytical methods used by NRIs).

It is noted that in some cities the composition data are not available for all ‘n’ samples presented in Table 1, which were used for the average mass concentration calculation. For example, the average element composition presented in Table 1 for Manila was calculated based only on around 25% of the PM$_{2.5}$ samples at each site in the dry season, and 15% in the wet season, for which the data are available. Only a few PM$_{10}$ samples have the composition data and a limited number of PM$_{2.5}$ samples in Manila have the ionic composition data, hence the related parameters are not displayed in the table. For Hanoi, the element data are available for all samples but ionic data are available for only around 25–30% samples at each site.Datasets of Bandung, Beijing, and BMR are more complete for all ‘n’ samples. However, Beijing has EC/OC data only for about 30% of samples and no BC data. For BMR, the composition data is available for all reported samples, except for EC/OC, which is available only for samples at the upwind (AIT) site in the dry season. Consequently, in some cases the average computed from a subset of samples at a few sites in a city was used to represent the citywise PM composition, which may be biased. The use of different methods for PM$_{2.5}$ and PM$_{10}$ sample collection, non-simultaneous sampling of these two PM parameters in some cases, and different numbers of PM$_{2.5}$ and PM$_{10}$ samples at a given site, may together cause inconsistency in the citywise average values of the reconstructed terms.

The crustal group includes oxides of Al, Ca, Si, Ti, Fe, Na, Mg, and K. Following Chan et al. (1997), the crustal matter in this study is estimated as 1.16 (1.9Al+2.15Si+1.41Ca+1.67Ti+2.09Fe), where the factor of 1.16 is used to compensate for those crustal oxides (including K$_2$O) that were excluded. As expected, the crustal group contributes much less to PM$_{2.5}$ than to PM$_{10}$, which indicates that the crustal elements are present mainly in the coarse fraction. The dry season has higher crustal matter levels than the wet season. The highest values in μg m$^{-3}$ were obtained for Beijing but the relative

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Average and variation (1 standard deviation) of PM$<em>{2.5}$-to-PM$</em>{10}$ ratios at different sites in six cities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upwind</td>
</tr>
<tr>
<td><strong>Dry season</strong></td>
<td></td>
</tr>
<tr>
<td>Bangkok</td>
<td>0.62±0.1</td>
</tr>
<tr>
<td>Beijing</td>
<td>0.55±0.27</td>
</tr>
<tr>
<td>Chennai</td>
<td>0.39±0.07</td>
</tr>
<tr>
<td>Bandung</td>
<td>0.73±0.07</td>
</tr>
<tr>
<td>Manila</td>
<td>0.54±0.19</td>
</tr>
<tr>
<td>Hanoi</td>
<td>0.69±0.10</td>
</tr>
<tr>
<td><strong>Wet season</strong></td>
<td></td>
</tr>
<tr>
<td>Bangkok</td>
<td>0.32±0.1</td>
</tr>
<tr>
<td>Beijing</td>
<td>—</td>
</tr>
<tr>
<td>Chennai</td>
<td>0.43±0.16</td>
</tr>
<tr>
<td>Bandung</td>
<td>0.68±0.16</td>
</tr>
<tr>
<td>Manila</td>
<td>0.60±0.14</td>
</tr>
<tr>
<td>Hanoi</td>
<td>—</td>
</tr>
</tbody>
</table>

(—) either or both PM$_{2.5}$ and PM$_{10}$ data not available for the ratio calculation. The ratios were calculated based on daily PM$_{2.5}$/PM$_{10}$ at each site.
contributions of the crustal group in this city are in the same ranges as in other cities: around 5% of the PM$_{2.5}$ and 15% of PM$_{10}$ mass. Note that, Si is reportedly high in the Asian dust (Ma et al., 2001) hence it may be high in Beijing. However, the Si data was not available for Beijing samples to be included in the 'crustal' mass, which may substantially reduce the estimated 'crustal' contribution to PM in this city. Examining the crustal group at each site in the cities reveals that often the traffic sites have the highest contribution of the crustal matter to PM$_{10}$, followed by industrial and mixed urban sites, especially those near construction sites, which indicate an important contribution from road dust resuspension and construction activities to PM.

The OM group is obtained by multiplying the OC content by a factor, which is in the range 1.4–2.1 (Turpin and Lim, 2001). The factors may vary widely between the cities and from one season to another depending on the nature of PM emission sources and chemistry. However, in this study, for simplicity, a factor of 1.7 (Hopke, 2005, personal communication) was used for both cities reporting OC data, BMR (the upwind site in the dry season) and Beijing (a subset of PM$_{2.5}$ samples at every site). OM has a large relative contribution to PM mass in the cities, from around 20% to above 42%. Availability of OC data improves the mass enclosure substantially. Thus, during the dry season, with OC data the average mass explained for samples at the AIT site is 78–80% as compared to 41–45% obtained for other sites in BMR with no OC data. For Beijing, the EC and OC alone contribute on average 50% of PM$_{2.5}$ mass in the dry season and 30% in the wet season. Without EC and OC composition, the average mass explained for PM$_{2.5}$ and PM$_{10}$ in Beijing was around 40–57% in both seasons.

'Soot' is the BC or EC (if the EC data are available). The majority of soot is found in PM$_{2.5}$ with higher levels (in µg m$^{-3}$) obtained for the dry season. However, the difference in 'soot' levels between the two seasons is not so pronounced in each city except for PM$_{2.5}$ in Beijing. This suggests that the major contributors to soot, such as traffic, remain relatively constant throughout the year in the other cities while in Beijing the soot in the dry season may also come from other seasonal sources such as combustion for space heating. Soot is the highest for Manila, where it contributes 49% of PM$_{2.5}$ mass in the dry season and 52% of PM$_{2.5}$ in the wet season, which is mainly due to high-average BC at the traffic site (above 40 µg m$^{-3}$ in both seasons). For other cities, the relative contributions of soot are 11–19% of PM$_{2.5}$ during the dry season and 5–33% during the wet season, with the lower values obtained for Beijing.

The sea-salt contribution is commonly estimated by applying a factor of 2.54 to the water soluble sodium (Na$^+$) concentrations (Ho et al., 2003; Chan et al., 1997) which are measured by the ion chromatography (IC). In this study the Na$^+$ data were available for PM$_{2.5}$ and PM$_{10}$ samples of BMR and Beijing, and for PM$_{10}$ in Hanoi, during both seasons. Therefore, for other cities the elemental Na concentrations analyzed by other methods (than IC) were used to estimate the sea-salt contribution. This in turn can introduce some uncertainty as the elemental Na may also be originated from soil, which is location specific though is generally believed to be small. Some sea-salt contribution was found in PM$_{2.5}$, but the large difference between sea-salt content in PM$_{10}$ and in PM$_{2.5}$ indicates that a larger portion of sea-salt in most cities, as expected, was in the coarse fraction, PM$_{10-2.5}$. The sea-salt levels in PM$_{10}$ were highest in Bandung, the city surrounded by the sea, and the second highest in BMR. The reported sea-salt levels of BMR are close to those reported for Brisbane, 0.7 µg m$^{-3}$ in the fine and 2.5 µg m$^{-3}$ in the coarse fraction (GU site, Chan et al., 1997), which may be a reflection of the coastal location of both cities. Besides, the sea-salt levels (in µg m$^{-3}$) in PM for BMR are more or less the same in both seasons, which may be due to the general weak large-scale wind in BMR (NE and SW monsoons) and rather strong effects of sea-land breeze.

The highest NO$_3^-$ and SO$_4^{2-}$ in PM$_{2.5}$ and PM$_{10}$ were reported for Beijing in both seasons, which indicate a significant contribution of secondary particles. Higher NO$_3^-$ and SO$_4^{2-}$ content in the dry season as compared to wet season may be partly linked to more coal burning during winter in this city. The levels found in this study are comparable with those presented by He et al. (2001). During the dry season, Hanoi also reported high nitrate and sulfate levels in PM$_{10}$ (and high S in PM$_{2.5}$). The regional transport of particles to the city following the NE monsoon as well as the precursors emission from local sources, such as SO$_2$ from residential coal briquettes burning, in the Hanoi Metropolitan Region are some of the causes for this high secondary particles mass. Relatively large amounts of NO$_3^-$ and SO$_4^{2-}$ ions are also found in the coarse
fraction ($PM_{10-2.5}$) in all cities. For comparison, coarse particles in Brisbane have been reported to share above 20% of total sulfate and 60% of total nitrate in $PM_{10}$ (Chan et al. 1997). Higher values of $NO_3^–$ and $SO_4^{2–}$ in $PM_{2.5}$ were observed in the dry season than the wet season in all the cities, which may partly be due to less wet removal and higher emission of the gaseous precursors. In addition, the increased atmospheric photochemistry in the dry season (seen in higher ozone levels, Zhang and Kim Oanh, 2002) would enhance conversion of the gaseous precursors to sulfate and nitrate particles. Note that for cities, which do not have sulfate data, elemental sulfur (S) is presented and also included in the reconstructed mass.

$NH_4^+$ is present mainly in the fine fraction, as ammonium salts, hence the difference between the concentrations in $PM_{2.5}$ and $PM_{10}$ is small. $NH_4^+$ was the highest in Beijing for both seasons. Note that, apart from differences in emission, the lower ambient temperature in Beijing may reduce the volatilization loss of ammonium (nitrate) during the sampling, which results in the high $NH_4^+$ (and $NO_3^–$) in PM. Use of appropriate sampling methods to reduce the ammonium (nitrate) loss during sampling should be considered for better results.

The trace elements group includes all elements except for Na, S and those listed in the crustal group mentioned above. The elements that belong to this group vary depending on analytical methods by the NRIs but generally it includes Mg, V, Mn, Ni, Zr, Sn, Sb, Cu, Zn, As, Se, Br, Rb, and Pb. The presence of this group in $PM_{2.5}$ suggests that some contribution may come from combustion sources. Hanoi shows the highest values of this group, which may be partly due to the high number of analyzed elements by both ICP-MS and XRF.

Due to the importance of the biomass burning source in the study region the ‘smoke’ term was also calculated following Chan et al. (1997). The method assumes that the crustal matter would have the average ratio K/Fe of 0.6 and the excess of K, i.e. [Total K–0.6Fe], can be assigned to the biomass burning contribution (of K). It is noted that the reference ratio of K/Fe for the crustal matter may be location/city specific, which needs further investigation, but for simplicity this formula is applied for all cities. It is understandable that the ‘smoke’, calculated based only on the K content, is just an indicator or surrogate of the biomass burning but not its absolute contribution to ambient PM levels and it was not accounted for in the reconstructed mass. (The potassium content of the PM was already accounted for in the ‘crustal’ group.) The ‘smoke’, as expected, was found predominantly in the fine fraction ($PM_{2.5}$). In the case of BMR, where all $PM_{2.5}$ and $PM_{10-2.5}$ were collected simultaneously by dichots, the smoke contribution to each coarse fraction sample was close to zero. For Beijing, due to the lack of element K data, the water soluble K$^+$ was used instead which may reduce the ‘smoke’ term in this city. Nevertheless, the levels in Beijing are still the highest during both seasons, around 2 $\mu g m^{-3}$ in the dry season and 1 $\mu g m^{-3}$ in the wet season, which are about two fold the corresponding levels in other cities. The percentage of ‘smoke’ to the PM mass is less than 1–2% in all cities. Lower percentage of ‘smoke’ was reported for Brisbane, Australia (Chan et al. 1997), namely, 0.34% of $PM_{2.5}$ mass and 0% of the coarse fraction. Note that the PM concentration mass reported for Brisbane was only around 10–15% of those recorded in the cities in this study.

Due to its toxicity, the seasonal average of Pb in the cities is also presented separately in Table 1, though Pb was already included in the ‘trace elements’ group for the reconstructed mass. It is noted that different methods used for the Pb analysis may not render the full compatibility of the concentration data. For $PM_{2.5}$, the Pb levels found for Bandung, Beijing, and Hanoi are comparable while lower levels are found in BMR. Since the analytical method used by the Philippine NRI did not detect Pb in SRM, the Pb results of Manila samples are not presented in Table 1. For $PM_{10}$, the highest seasonal average Pb levels were obtained at the upwind site in Hanoi where the maximum 24 h average was 4.7 $\mu g m^{-3}$ in the wet season and 1.0 $\mu g m^{-3}$ in the dry season, which are higher than the traffic site (maximum 24 h average of 0.6–0.7 $\mu g m^{-3}$ in both seasons). This suggests that the Pb found in Hanoi $PM_{10}$ samples may come also from other sources than only the traffic. It is noted that in all six cities, only Bandung still uses leaded gasoline. Leaded gasoline has already been phased out in others cities for some time, e.g. Thailand phased out leaded gasoline in 1996 (Supat, 1999), Vietnam in 2001 (ADB, 2002), Metro Manila in April 2000 and the Philippines nationwide in December 2000 (EMB, 2003), Beijing since 1999 and China nationwide since January 2001 (ABSC, 1998), India nationwide since 2000 (Parivesh, 2001).
Thus, in general for all cities, the major components of PM$_{2.5}$ and PM$_{10}$ are OM, soot (EC/BC), SO$_4^{2-}$, NO$_3^-$, and crustal. Mass enclosure is much improved for the site/cities where all these components are available. OM and EC may come from various sources such as traffic, open biomass burning, and domestic fuel combustion. In particular, substantial OM may be formed and present as the secondary organic aerosols in the atmosphere. The ‘smoke’, estimated based on K content of PM, may provide additional indicator for the biomass burning contribution.

The PM spatial and temporal distribution, and the reconstructed mass give qualitative information on major contributors to PM levels in a city. The high PM$_{2.5}$/PM$_{10}$ ratios in the cities indicate the contribution of secondary particles and fuel combustion sources. The quantitative source apportionment results by receptor modeling for the cities will be published in our forthcoming papers. Note that the major contributors obtained by receptor modeling agree with those identified in this paper. The preliminary results show that the traffic, biomass burning and secondary particles (ammonium sulfate and ammonium nitrate) are the largest contributors to PM$_{2.5}$ pollution in most of the cities in both the dry and wet seasons with a collective share of around 60–90% of the PM$_{2.5}$ mass.

4. Summary and conclusions

The designed monitoring program has captured the urban PM pollution characteristics in the six cities, which show high levels of PM$_{2.5}$ and PM$_{10}$, especially in the dry season. PM$_{2.5}$ and PM$_{10}$ concentrations fluctuated from one site to another within a city reflecting the influence of primary PM from sources in the vicinity of the sites. Inter city comparison shows the highest levels of PM$_{2.5}$ and PM$_{10}$ in Beijing in both seasons followed by Hanoi and Chennai. Both natural and man-made factors play important roles in the PM build up in the cities leading to the large differences in pollution levels between them. The PM$_{2.5}$ constitutes a larger fraction of PM$_{10}$ in most of the cities. The major chemical components of PM$_{2.5}$ across six cities are OM, soot, NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$. The crustal group is also significant in PM$_{10}$. Analysis of the spatial and temporal variations of the PM levels, the PM$_{2.5}$/PM$_{10}$ ratios, and the reconstructed mass provide insight into the contributors/sources. The major contributors to PM levels in the cities include the traffic, secondary sulfate and nitrate particles, biomass burning, and soil dust. Contribution of other sources such as stationary fuel combustion for space heating, sea-salt, and industry may be significant in some cities. Continuous update and refinement of the PM ambient data with emphasis on QA/QC are still required to improve the AIR-PET monitoring results. The outcome of this study, however, provides useful information to understand the nature of PM pollution in the region.

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University of Technology; Emmanuel G. Anglo, James Bernard B. Simpas, Rikki Pamela L. Piñeda Genevieve H. Lorenzo at the Manila Observatory.

Appendix A. Supplementary data

Supplementary data associated with this article, including the general information on the 6 cities, detail on PM sampling and SRM analysis results, can be found in the online version at doi:10.1016/j.atmosenv.2006.01.050.

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