Elemental Composition of Particulate Matter Air Pollution Collected Around Industrial Area in East Java

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Abstract. Air pollution is one of the key environmental and public health concerns in urban areas in Indonesia. The environment impacts are particularly severe in Java region where the cities have a combination of intense industrial activities, large populations, and increase of motor vehicle usage. This paper describes results from a detailed elemental characterization study conducted in Surabaya, East Java. Samples of airborne particulate matter, PM_{2.5} and PM_{2.5-10} were collected once a week using a Gent stacked filter sampler during 2012-2015. The samples were analyzed for their elemental composition and black carbon (BC) content by Energy Dispersive X-ray Fluorescence (EDXRF) and light absorption, respectively. The mass concentration of PM_{2.5} and PM_{10} ranged from 4.8 to 30.8 μg/m³ and 9.4 to 114.9 μg/m³, respectively. The annual average PM_{2.5} obtained during over the period of 2012 to 2015 would be in violation of the Indonesian annual average standard concentrations of 15 μg/m³. The distributions of the ratio of PM_{2.5} to PM_{10} is less than 0.5. The average ratio of BC concentrations compared to the PM_{2.5} concentrations was 22.6 %. Several composition of elemental concentration were also determined and the results showed that lead level in PM_{2.5} and PM_{2.5-10} was significantly higher with the maximum concentrations were 2779 and 2258 ng/m³ respectively. These results could be used to provide an overview of the measurements of the concentrations and composition of particulate air pollution in Surabaya and as a key in identification and estimation of pollutant sources to design the appropriate and right policies.

Keywords: pollution, PM_{2.5}, PM_{2.5-10}, Energy Dispersive X-ray Fluorescence, black carbon

1. Introduction
In Indonesia, air pollution is one of many serious environmental problems faced by major urban cities. There are several factors that cause this pollution and the main factors were population growth and rapid urbanization. In 2015, the population of Indonesia was estimated to reach 255.4 million and about 58 % live on the island of Java [1]. Therefore, increased economic development in Indonesia, especially in Java, has led to rapid and unplanned urbanization. The change of urban economic structure will increase
the transportation, energy consumption and also caused severe environmental pollution, particularly air pollution.

Air pollution in an urban area is a dynamic mixture of pollutants emitted from numerous sources including motor vehicles and other anthropogenic activities. The impact of air pollution can be one of the reasons for civilization diseases [2]. Health effects are mostly associated with the particles in the size range of about 10 µm and 2.5 µm (PM$_{10}$ and PM$_{2.5}$). High concentration of particulate matter, particularly PM$_{2.5}$ have raised great attention. Santoso et al. in 2008 reported the composition and source apportionment of fine and coarse particle samples collected in Bandung and Lembang [3], while the PM$_{2.5}$ concentration in Serpong Tangerang, especially with respect to high concentration of Pb were reported in 2011 [4]. However, monitoring PM$_{2.5}$ in Indonesia were rare and limited.

Surabaya as second largest city in Indonesia was also face the environmental problem especially air pollution. Syafei et al. reported the spatial and temporal factors of air quality in Surabaya and the trend of air pollution indicates a strong increase in daily concentration proportionally to the growth of Surabaya’s vehicle volumes [5]. Airborne particulate matter characterization and preliminary study of the determination of pollutant sources in Surabaya have been carried out for the October 2012 - February 2014 monitoring period [6]. To monitor air quality, the environmental protection agency of Surabaya has introduced Air Quality Management System (AQMS), continuous automated monitoring for CO, SO$_{2}$, NO$_{x}$, O$_{3}$, and PM$_{10}$. This system itself had limitation and could not monitor particulate matter smaller than 2.5 micrometers. Therefore it could not detect a range of potentially harmful air pollutants. The main objective of this research was to provide an overview of particulate air pollution especially PM$_{2.5}$ in this city from the results of 4 years monitoring in 2012-2015. This report describes the distribution of mass and some major species concentration across this region.

2. Materials and methods

2.1. Sampling

Air particulate samples were collected using a Gent stack filter unit particle sampler capable of collecting PM$_{2.5-10}$ and PM$_{2.5}$ size fractions. The samples were collected on an 8 µm and 0.4 µm pore nucleopore filter for the coarse fraction (PM$_{2.5-10}$) and the fine fraction (PM$_{2.5}$) sample respectively. The samples were collected for a 24 h period, once per week in Surabaya at an area of local EPA of East Java province (07°20.770' S, 112°44.024' E) between March 2012 to November 2015 (Figure 1). Surabaya is a capital of East Java and as second largest city in Indonesia covers the area 374.78 km$^2$ with over 3 million in population. Surabaya industrial area located in the Surabaya city territory with an area of 245 hectares accommodates more than 300 companies and about 70 % of the total land is used for industry while the rest is for public use. Surabaya features a tropical wet and dry climate, with distinct wet and dry seasons. The wet season is usually established from November to June, while the dry season covers the remaining five months. The average temperatures are very consistent throughout the year from 26 °C to 31 °C [5,6].

2.2. Mass and Black Carbon measurement

PM mass of each samples were determined by weighing the filter using a microbalance (Mettler Toledo XP6) in the Center for Applied Nuclear Science and Technology Laboratory, National Nuclear Energy Agency (BATAN), Bandung Indonesia. The aerosol masses of both PM$_{2.5-10}$ and PM$_{2.5}$ fractions were determined by weighing the filters before and after exposure. The difference in weights for each filter was calculated and the mass concentrations for each samples were determined, then divided by the volume of air passing through the filter to obtain the concentration of PM$_{2.5}$ and PM$_{2.5-10}$ (µg.m$^{-3}$). The PM$_{10}$ concentration was obtained by summing these two values. Black carbon concentration on a filter was measured by an EEL-type Smoke Stain Reflectometer (Diffusion Systems, Ltd). Secondary standards of known black carbon concentrations were used to calibrate the reflectometer [7]. The concentrations are defined based on the amount of reflected light that is absorbed by the filter sample and an assumed mass absorption coefficient. It is related to the concentration of light absorbing carbon through standards of carbon with known areal density [8].
2.3. Elemental Analysis

The elemental analysis were all carried out in BATAN Bandung that has implemented ISO/IEC 17025:2005 accredited by National Accreditation Body. The analysis was conducted using Epsilon 5 EDXRF spectrometer from Panalytical, which has a 100kV excitation source and a polarising optical path give detection limits in the low ng/cm$^2$ range for most elements. EDXRF Epsilon 5 with its polarization method produces an indirect excitation/secondary target excitation gives significantly lower background. A special sample insert enables air filters to be fitted directly into the sample cup. No additional sample preparation is needed and the sample changer makes continuously analysis possible. The EDXRF Epsilon 5 installed in BATAN Bandung has 9 secondary targets i.e: $\text{Al}_2\text{O}_3$, $\text{Fe}$, $\text{CaF}_2$, Ge, Zr, CeO$_2$, Mo, Ag and Al. The calibration was set up using multi-standard reference material, standard Micromatter® and a blank standard for each element: Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Pb. The validation of XRF measurements in this application was applied using standard reference material SRM NIST 2783 Air Particulate on Filter Media [9].

3. Results and Discussion

The annual average of PM$_{2.5}$ and PM$_{2.5,10}$ at Surabaya over the period of 2012 to 2015 were 20.71, 14.55, 16.95, 14.86 and 30.59, 14.80, 21.93, 21.91 respectively. Adding these two values together estimates of PM$_{10}$ and the annual average of PM$_{10}$ were 51.29, 29.35, 38.88 and 36.77. The detail on the number of samples collected during period of study and the range of twenty-four hour mass concentrations are provided in Table 1. The Indonesian National Ambient Air Quality Standards (NAAQS) for annual average PM$_{2.5}$ is 15 µg/m$^3$, while the 24 h standard is 65 µg/m$^3$. It can be seen that the data provided by 2012 and 2014 would be in violation of the Indonesian annual average standard for PM$_{2.5}$, while the values for 2013 and 2015 almost reach the threshold. It should be noted that Gent sampler will underestimate PM$_{2.5}$ since the 50% collection point is closer to 2.2 µm [10]. Therefore, there is a strong indication that in this area there was problem with air quality.

The mass concentration for 2012 was found higher than the values for 2013 to 2015. The annual average of PM$_{2.5}$ at Surabaya in 2012 was also higher than the value in several urban areas in Indonesia over the period of 2011 as reported by Santoso [7]. The average PM$_{2.5}$ concentrations for Bandung, Jakarta, Serpong, and Yogyakarta were 18.35, 16.50, 16.68, and 8.78 µg/m$^3$ respectively. While for PM$_{10}$ at these areas were 35.81, 41.58, 32.05, and 20.13 µg/m$^3$. The higher mass concentration during 2012 could be due to a longer period of dry season and less rainfall during the period of 2012.
Table 1. Mass concentrations of PM$_{2.5}$ and PM$_{2.5-10}$ in Surabaya during 2012-2015.

| Year | n  | PM$_{2.5}$ (ng/m$^3$) |   | PM$_{2.5}$-10 (ng/m$^3$) |   |
|------|----|------------------------|---|--------------------------|---|
|      |    | Mean ± Range           |   | Mean ± Range             |   |
| 2012 | 17 | 20.71 ± 3.86           | 16.30 - 30.85 | 30.59 ± 14.66 | 12.71 - 71.03 |
| 2013 | 42 | 14.55 ± 4.76           | 4.92 - 22.45 | 14.80 ± 5.98  | 4.47 - 30.82  |
| 2014 | 38 | 16.95 ± 4.19           | 8.11 - 24.55 | 21.93 ± 15.09 | 6.15 - 99.33  |
| 2015 | 22 | 14.86 ± 3.86           | 6.17 - 20.95 | 21.91 ± 8.81  | 5.66 - 34.57  |

The average ratio of PM$_{2.5}$ to PM$_{10}$ at Surabaya site were 0.46 and in general, the ratio is less than 0.5. This values indicating there are higher coarse particle (PM$_{2.5-10}$) masses. The urban site in Australia, Bangladesh, Malaysia, India, Pakistan, Sri Lanka, Thailand, and Vietnam have ratio of PM$_{2.5}$ to PM$_{10}$ values lower than 0.5 [11], while for Jakarta and Yogyakarta were 0.4 and 0.48 [7]. These values were similar with the results obtained for Surabaya site.

The time variations of monthly PM$_{2.5}$ and PM$_{2.5-10}$ concentrations over the period of 2012 to 2015 are shown in Figure 2 and Figure 3. Due to technical issues, the samples were not collected during the period of January to February 2012, July to August 2012, January 2015, March 2015 and December 2015. Eventhought the annual average of PM$_{2.5}$ was slightly fall the Indonesian NAAQS, however, none of daily concentrations exceed the 24 h Indonesian NAAQS for PM$_{2.5}$ (65 µg/m$^3$). In Figure 2 and Figure 3, the seasonal variations are also clearly shown, where the average monthly data for the total PM$_{2.5}$ and PM$_{2.5-10}$ concentrations are plotted as a function of time for the Surabaya site. Dry seasons peaks (June to August) in the PM$_{2.5}$ and PM$_{2.5-10}$ concentrations are clearly visible with wet variations being more than a factor of two in some years. The seasonal variation obtained in this research were also similar with the results for Bandung sites [12].

There are several high concentration of PM$_{2.5}$ and PM$_{2.5-10}$ levels in Surabaya were also observed from Figure 2 and Figure 3. The high mass concentration at November 2013, February 2014, July 2015
and November 2015 were resulted from the samples collected during the volcano eruption at Mount Merapi, Kelud volcano, Raung volcano, and Rinjani volcano, respectively. Mount Merapi is the most active volcano in Indonesia located on the border between Central Java and Yogyakarta. On November 18, 2013, mount Merapi ejecting smoke up to a height of 2000 meters. While, Kelud volcano erupted on February 13, 2014, destroying the lava dome and ejecting boulders, stones, and ashes up to west Java about 500 kilometers from mount Kelud. The Kelud eruption has also significantly influenced the air quality in Java area especially at Yogyakarta in central Java, due to the volcano spit ash up to 17 kilometers into the sky and the wind was strongly blown to the west direction [13]. Raung is one of the most active volcanoes on the Java island and located in the province of East Java. Raung standing almost 3332 meters above sea level. The volcano eject material causing a dust cloud during June to July 2015 that influences the air quality to the residents surrounding the volcano. Several airports throughout Indonesia were also closed due to the ash being produced by the Raung volcano eruptions. Mount Rinjani is an active volcano on the island of Lombok Indonesia, started erupting on 31 October 2015. After that a lot of major activities had occurred in November 2015 and this eruption has forced the closure of Ngurah Rai airport in Bali and disrupted international flights in and out of Bali. During the periods of study, several volcanoes eruptions in Java and surrounding areas were significantly influence mass concentration of PM$_{2.5}$ and PM$_{2.5-10}$, such as high level coarse particle (100 ug/m$^3$) was observed during Kelud volcano eruption at February 14, 2014.

**Table 2.** Black carbon and elemental concentrations of fine and coarse in Surabaya during 2012-2015

| Element | PM$_{2.5}$ (ng/m$^3$) | Range | Mean | Range |
|---------|------------------------|-------|------|-------|
| Na      | 534 ± 412              | 17    | 2237 | 524 ± 405 |
| Mg      | 42 ± 39                | 0.4   | 259  | 113 ± 68  |
| Al      | 59 ± 46                | 0.3   | 341  | 358 ± 379 |
| Si      | 132 ± 103              | 16    | 1026 | 954 ± 990 |
| S       | 711 ± 279              | 167   | 1487 | 299 ± 164 |
| K       | 231 ± 111              | 4.3   | 632  | 161 ± 110 |
| Ca      | 125 ± 59               | 16    | 298  | 628 ± 343 |
| Ti      | 4.37 ± 2.97            | 0.2   | 20   | 32 ± 21   |
| Mn      | 9.29 ± 7.40            | 0.1   | 47   | 18 ± 12   |
| Fe      | 124 ± 84               | 6.8   | 568  | 486 ± 320 |
| Zn      | 285 ± 205              | 8     | 1091 | 290 ± 236 |
| Pb      | 420 ± 518              | 2.4   | 2779 | 234 ± 399 |
| BC      | 3472 ± 1036            | 673   | 7427 |

Table 2 shows the mean and range of values black carbon (BC) concentration for PM$_{2.5}$ and the elemental concentration for PM$_{2.5}$ and PM$_{2.5-10}$ at Surabaya site over the period of 2012-2015. The BC content of the samples were measured using a reflected light instrument and BC was measured only for the fine fraction filters (PM$_{2.5}$). The average and range concentration of BC were 3472 and 673 to 7427 ng/m$^3$. While the average ratio of BC concentrations compared to the PM$_{2.5}$ concentrations was 22.6 %. The highest BC concentration was found in June 2012 and July 2015, it could be due to forest fires from surrounding areas of Surabaya. It can also be shown from Table 2 that there are several samples have high concentration of crustal elements especially Si. The high concentration of crustal elements was observed from the samples collected during the eruption episode, especially from mount Kelud at February 2014. The high amount of silica should be considered due to its impact on human health. These are free crystalline silica known to cause silicosis, a disabling and potentially fatal lung disease typically
found in miners and quarry workers exposed to high concentrations of siliceous dust over long periods of time [14].

Figure 4. The distributions of Pb in PM$_{2.5}$ at Surabaya site during 2012-2015.

Figure 5. The distributions of Pb in PM$_{2.5}$-10 at Surabaya site during 2012-2015.

Figure 4 and Figure 5 shows the measured distributions of lead for the fine and coarse particle fractions. The result obtained from this study showed that the average level of lead in PM$_{2.5}$ and PM$_{2.5}$-10 collected during 2012-2015 in Surabaya site were 420 and 234 ng/m$^3$, respectively. While the maximum concentration observed were 2779 ng/m$^3$ in PM$_{2.5}$ and 2258 ng/m$^3$ in PM$_{2.5}$-10. In Figure 5, It could be shown that lead concentration was also high in the coarse fraction and the distributions have the same pattern with the fine fraction. The lead in coarse particle could arise from road dust that has been re-suspended by the motion of tires over the road surface [4]. The annual average of lead in PM$_{2.5}$ and PM$_{2.5}$-10 during 2012 to 2015 were 560, 323, 417, 525 and 422, 124, 244, and 448 ng/m$^3$ respectively, while the maximum concentrations were 2662, 1911, 2119, 2779 and 2258, 835, 1446, 1924 ng/m$^3$ respectively. These annual average values were significantly higher and several data fall to the 24 h National Ambient Air Quality Standard of Indonesia for lead in total suspended particulate matter (2000 ng/m$^3$). These results revealed that lead concentration in Surabaya were much higher compared to other cities in Asia countries [12] and even higher than Tangerang that already polluted with lead [4]. The results of the preliminary study of source apportionment in Surabaya showed that biomass, vehicle, soil and industrial activities are the main sources [6]. To improve health protection for at-risk group, especially children, In 2008, the USEPA has revised NAAQS for Lead in total suspended particulate matter 10 times tighter than previous standards (from 1500 to 150 ng/m$^3$ as a quarterly average value). The results obtained from this study showed that the annual average lead in Surabaya site during 2012 to 2015 have exceeded the US standard (150 ng/m$^3$). Much of lead in fine fraction was due to emissions from the emissions of vehicles burning fuel containing tetraethyl lead. However, Indonesia has eliminated leaded gasoline, the high lead concentrations could be from other lead sources such as smelter industry and battery recycling plant, as reported in the previous studies related the high Pb concentration in Tangerang [4]. This finding gave very important information as early warning and scientific research based references to avoid greater financial disadvantage and human health impact. A better solution and proper action should be taken into this matter. The local government institution and Ministry of Environment have to take the follow up of this fact.

4. Conclusions
The annual mean concentrations of PM$_{2.5}$ collected at Surabaya sites during March 2012 to November 2015 showed that majority exceeded the annual air quality standards (15 µg/m$^3$). In general, the ratio of PM$_{2.5}$ to PM$_{10}$ were less than 0.5, while the average ratio of BC concentrations compared to the PM$_{2.5}$ concentrations was 22.6 %. The elemental concentrations of Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Zn

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and Pb in PM$_{2.5}$ and PM$_{2.5-10}$ were determined and the results showed that high concentration of crustal element, especially Si were observed in samples collected during volcanic eruption episode. While the lead level in PM$_{2.5}$ and PM$_{2.5-10}$ at Surabaya site showed significantly higher than in other sites and should be further followed by identification and quantitative apportionment of the particle sources. Through these results, important finding related to heavy metal pollution in Surabaya were achieved and these results could significantly support national program of air quality improvement.

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