Identification of Trace Element in Ambient Air Case Study: Industrial Estate in Waru, Sidoarjo, East Java

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ABSTRACT

Metal is one of the air pollutants found in air particulates. The presence of heavy metals in air can be due to human activities or natural factors. Heavy metals can affect human health, causing respiratory disease and even death. The purpose of this study was to determine daily particulate matter (PM) concentrations in ambient air at the Waru Industrial Estate, analyze the results, and then characterize and estimate the locations of pollutant sources. PM was collected for 24-hour periods with Gent stacked filter units. Filters were analyzed via X-ray fluorescence (XRF) to find concentrations of metal particles. The measurement data were analyzed via principal component analysis (PCA) and the conditional probability function (CPF) method in order to identify and estimate the industrial pollutant sources that contribute to these metal particles being in the ambient air. Results arrange PM_{2.5} concentrations from 2.65 to 32.68 µg m^{-3}, with an average daily concentration of 17.67 ± 7.29 µg m^{-3}, whereas PM_{10} concentrations ranged from 14.69 to 72.27 µg m^{-3}, with an average daily concentration of 40.70 ± 13.78 µg m^{-3}. The elements identified with XRF were Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb, and Cl. The PCA results explain that there are four main components (factors) which then become a potential source of pollutants, namely the first is a marker of industrial activity, the second indicates the activity of the metal smelting industry, third shows the contribution of sea salt. Fourth shows the biomass combustion emissions. The results of the CPF method show that the first factor originates from north to northeast with a probability of 0.5. The second factor comes from west to southwest with a probability of 0.4. The third factor comes from northeast to east with a probability of 0.4–0.45.

Keywords: Particulate matter; Metal; Industry; PCA; CPF.

INTRODUCTION

Pollution caused by metal particles in Indonesia has worsened due to increased economic activity, rapid population growth, urbanization, and industrialization. Metal is one of the air pollutants found in air particulates. The presence of metals in the air can be due to human activities or natural factors such as volcanoes, ocean aerosols, chemical reactions in the atmosphere, and so forth (Santoso and Lestiani, 2014). Some studies have shown that ±20 metal particles are present in the air, including Al, Ag, As, Br, Ca, Co, Cr, Cs, Fe, Hg, I, K, La, Mg, Mn, Na, Nb, Sc, Sm, Ti, Si, Ni, S, V, Sr, and Zn (Santoso and Lestiani, 2014). The metal particles are PM_{2.5}, which is particulate matter containing fine particles with diameters of less than 2.5 µm (WHO, 2007). These metals are emitted by either anthropogenic or natural sources (Deshmukh et al., 2010).

Fine particles that contain metals can affect human health if they are inhaled and penetrate the lungs. Particles can cause acute respiratory infections (ARIs), symptoms of anemia, barriers to growth, a weak immune system, symptoms of autism, lung cancer, and even premature death (Mukhtar et al., 2013). Schaumann et al. (2004) reported that fine particles containing metals could trigger the oxidant radical generation of bronchoalveolar lavage fluid cells. Cytokine concentrations in bronchoalveolar lavage fluid were elevated after the introduction of PM_{2.5} into the Hettstedt area (Schaumann et al., 2004). Hassanvand et al. (2015) revealed that Si, Fe, Zn, Al, and Pb were the most abundant metal materials measured in a retirement home and school dormitory in Tehran, Iran. A multi-city study conducted in Europe (29 cities) and the United States (20 cities) reported a short-term mortality effect for PM_{10} of 0.62%, with a 0.46 percentage point increase for every 10 µg m^{-3} increase in PM_{10} concentration (24 hours, on average) (Samet et al., 2009). A Harvard study of 24 cities in the US indicated that long-term...
exposure to PM resulted in an increase in the occurrence of respiratory disease in children (Dockery et al., 1993).

Over the past several decades, multivariate analysis has been widely used to identify sources of particles in ambient air, one of which is the application of principal component analysis (PCA). PCA analysis was carried out in identifying sources of PM$_{2.5}$ emissions which produced five factors of sources of PM$_{2.5}$ emissions in the City of Anglet located in the southwest of France. The five factors are factor 1: soil dust, factor 2: combustion, factor 3: industry, factor 4: vehicle, factor 5: sea (Chavent et al., 2009). To estimate the location of local pollutant sources can be done by combining elemental concentration data with meteorological data of wind direction and speed, better known as the CPF (Conditional Probability Function) method. The CPF method was used by Pekney et al. (2006) in Pittsburgh, the results of his study showed that the source of PM$_{2.5}$ pollutants is likely to come from the southeast with a probability of 0.70, in the southeast there is a coal-fired power plant, which allows the combustion of rock these embers can contribute to PM$_{2.5}$.

PM$_{2.5}$ concentration in Surabaya for 2012 to 2014 was 15.05 µg m$^{-3}$, so PM$_{2.5}$ had exceeded the quality standard yearly, based on PP 41 1999, U.S. EPA and WHO (Ahmad and Santoso, 2016). The results of a study on PM containing heavy metals in the Serpong industrial area, which was characterized by fine particulates (PM$_{2.5}$), identified five factors in the spread of Pb, namely, the smelting industry (9.61%), soil dust (17%), a mixture of metal smelting and sea salt industries (13.02%), transportation (44.36%), and burning of biomass (22.58%). PM quality studies in Surabaya found 12 metal elements in PM$_{2.5}$ and PM$_{2.5-10}$ including Na, Al, Si, K, Ca, Ti, Mn, Fe, Cu, Zn, and Pb (Santoso et al., 2016).

Increasing industrial development activities have the consequence of increasing waste generated by the industry, including air pollutants that can change ambient air quality (Mukono, 2011). Industrial activities are complex and involve various processes. The use of fuel, incineration processes or the combustion of raw materials with high temperatures are generally found in industrial activities (Zannaria et al, 2009). Emissions from industry are believed to be one of the main contributors to pollutant sources to air particulates (Santoso et al., 2013).

One of the main industrial zones in the south of Surabaya is in the District of Waru. Waru is also known as the buffer zone of Surabaya City from the southwest (Mojokerto / Madiun / Kediri / Solo / Yogyakarta) and from the south (Malang / Banyuwangi). This sub-district is a border area between South Sidoarjo and Surabaya and is an area that is experiencing rapid development. In addition to its strategic location, with a variety of potentials such as in the industrial sector from the metal industry and shoes/sandals, trade, as well as regional small and medium businesses as well as adequate human resource support, the Waru District is one of the strategic areas for development economy. Fig. 1 shows the location of the sampling site around the Waru Industrial Estate (7°20′43.64″S, 112°45′21.55″E). The gent stack had a place data height of 5.5 meters from the ground within 1–2 km of industries that pollute the air (SNL19-7119.6-2005). The sample analysis was carried out at the Center for Applied Science and Technology: National Nuclear Energy Agency (PSTNT-BATAN) in Bandung.

The air particulate test sample was obtained by using the gent stack, which was able to capture PM$_{2.5}$ and PM$_{2.5-10}$. Samples were taken every 24 hours over a period of 35 days from March 14, 2019, to May 18, 2019. Overall, 35 samples were collected at the site.

The Gent SFU Sampler consists of two main parts namely the black receptacle and the pump system which regulates with the timer. Gent SFU Sampler is a dichotomous sampler which is a type of sampler that can collect air particles with a size of less than 2.5 µm and particulates with a size of 2.5–10 µm. Gent stack had an impactor-stage inlet-cut-off point system on the head of the outer part of its container that only allowed dust below 10 µm in diameter to enter. These dust particles first encountered coarse filter size of 2.5–10 µm, and those particles able to pass through the first filter then accumulated on a fine filter of less than 2.5 µm in size. The flow rate used in the gent stack was 18 L min$^{-1}$ (Hopke et al., 1997). Wind speed and direction were assessed using a Kestrel 5500 at the same elevation as the gent stack. The average wind speed ranged from 0 to 6 m s$^{-1}$ (with a mean of 1 m s$^{-1}$), the average temperature ranged from 23.2°C to 37.7°C, and the relative humidity ranged from 48.3% to 100% (mean value: 81.47%).
All filters were conditioned for 24 hours in a clean room equipped with a dehumidifier and an air conditioner to control air humidity in the range of 40–50% and temperatures in the range of 18–25°C, respectively. Filters were then weighed using a Mettler Toledo micro balance with a precision of up to six digits because the samples weighed very little.

Each filter set was then arranged in a filter cassette with the coarse filter placed on the outside or at the top. The fine filter was placed on the inside of the filter cassette. After the cassette filters were filled, they were connected to the Gent SFU Sampler for sampling. Samples were collected using a Gent SFU capable of collecting particulate matter in the PM$_{2.5-10}$ and PM$_{2.5}$ size fractions (Hopke et al., 1997). Sampling was performed at a flow rate of 15–18 L min$^{-1}$ for 24 hours over 3 month periods. There were a total of 35 pairs of PM$_{2.5-10}$ and PM$_{2.5}$.

**Sample Analysis**

The PM$_{2.5}$ concentrations were determined via the gravimetric method, namely, by balancing the samples on the fine filters with a fine, smooth flange weight. For PM$_{10}$, the concentrations were obtained by using both the fine and rough filters. X-ray fluorescence (XRF) spectroscopy was used to determine mass concentrations and identifications of the metal particle elements in the samples. The XRF analysis method is based on the emission of X-rays by atoms which are excited by high-energy photons such as X-rays and $\gamma$-rays (Santoso et al., 2010). XRF can detect various elements in air particles and produce a data set of 25–30 elements in the identification of sources of air pollutants (Santoso et al., 2014). The principle of XRF spectroscopic analysis is to utilize the emission of radiation emitted from secondary characteristics X-rays that characterize each element of a material. The secondary characteristic X-rays are produced by the process of excitation or ionization of the innermost skin electrons due to the emission of primary X-ray radiation emission at certain energies towards a target called the photoelectric effect. Secondary X-ray radiation is then detected by an X-ray detector into electrical pulses. The pulses are reinforced by the initial amplifier and the final amplifier. Electric pulses that have been strengthened by the final amplifier are used as input for the Analog to Digital Converter (ADC) to be converted into digital numbers and then processed by the computer into an area of the spectrum of analysis results (Rixson et al., 2015).

The XRF used for metal analysis contained in the PM was the XRF spectrometer Epsilon5 PANalytical. The XRF Epsilon5 is a type of XRF Energy Dispersive System (EDXRF) that can separate the characteristic radiation energy originating directly from the sample.

**Statistical Analysis**

Determination of pollutant sources was carried out with the help of principal component analysis (PCA) and conditional probability function (CPF). The purpose of PCA is to obtain the maximum number of components that can explain the variations in the data (Thurston and Spengler, 1989). The source profile is then estimated by finding a profile with the same characteristics as in the literature (Reff et al., 2007). The CPF determine pollutant sources based on plots of wind direction and speed.
PCA is part of a multivariate technique that can reduce dimensions in data groups by identifying new data from several independent variables that explain the covariance of the original data (Lau et al., 2012). Principal component analysis (PCA) and cluster analysis (CA) were carried out using the SPSS statistical software package version 13.0 for Windows. The PCA model is a statistic that identifies data patterns and shows differences and similarities in data. The main purpose of a PCA application is to obtain a number of component values that can explain the maximum data inheritance (Thurston and Spengler, 1989). The PCA model does not change, reduce, or add data but only replaces variables that are correlated with data that are not correlated through linear combinations of original variables. The first variable resulting from dimension reduction should explain almost all data variability. The result of PCA is the eigenvalues and eigenvector of the matrix (Henry and Hidy, 1979). The correlation matrix always has at least one non-zero eigenvalue, and all these non-zero values are positive. The matrix of the diagonal transformation is derived from the eigenvector as a column/row depending on the original vector of the variables. The principal component (PC) has the greatest association with the eigenvalue. This value is a linear combination of variables that produces the maximum value of the total data. These characteristics were seen through the element markers in each type of source. In general, pollutants can be characterized singly or in combination (Seinfeld and Pandis, 2006). After the elements in PM are identified, the XRF measurement results are then analyzed using PCA. PCA was carried out using SPSS 17.0 to identify sources that contribute to air pollution around the Waru Industrial Estate, Sidoarjo. The XRF measurement data is the standard for generating all the variables of identical variation and calculating the associated eigenvalues.

PCs consisting of different sources were analyzed by applying orthogonal rotation varimax with an identical number of eigenvalues. The number of PCs is determined by extracting them with a PC eigenvalue greater than 1, the Kaiser criterion. It contains the original variable value (source of emissions) on each PC counted. Loading values greater than 0.5 are considered to be strong correlations between PCs and emission sources.

PCA is widely used to reduce data dimension in metal distribution studies, it extracts a small number of latent factors, referred to principal components to analyze relationships among observed variables (Yeung et al., 2003; Han et al., 2006; Meza-Figueroa et al., 2007). The concentrations of heavy metals investigated in this study vary by different orders of magnitude, and PCA assists the identification of pollutant sources. Despite that PCA suffers in terms of method in which its eigenvector analysis is based on unweighted least-square fit to the data, which may not provide best estimators for parameters of interest (Hopke and Jaffe, 2020), its usage remains important to provide first step of a more complex process, provided with other tool such as PMF, in quantifying the sources (Chavent et al., 2009).

The CPF determine pollutant sources based on plots of wind direction and speed. To identify possible sources of heavy metals based on the wind speed and direction, a CPF receptor model is used. The conditional probability function (CPF) seen in Eq. (1) calculates the probability that a source is located within a particular wind direction sector, $\Delta \theta$:

$$CPF = \frac{M_{\theta_0}}{n_{\theta_0}}$$

where $n_{\theta_0}$ is the number of times that the wind passed through the direction sector $\Delta \theta$, and $M_{\theta_0}$ is the number of times that the source contribution peaked while the wind passed through sector $\Delta \theta$ (Ashbaugh et al., 1985). To use the CPF method, the 24-hour averaged source contribution data were applied to all 30-minute wind direction averages measured at the site on each date. All time periods with wind speeds less than 1 m s$^{-1}$ were removed from the data set. To calculate $M_{\theta_0}$, the highest 25% of the source contribution concentrations were used. CPF is useful in determining the direction of a source from a receptor site (Begum et al., 2010).

Estimation of the location of local pollutant sources is done by combining the polluted source mass concentration data with meteorological data on wind direction and speed hour period. The second analysis of the data uses the CPF method with the help of Microsoft Excel software. The CPF method is to divide the number of events in a particular wind direction with the largest contribution of factor mass concentration with wind direction and velocity above 1 m s$^{-1}$ to the total factor mass concentration in the direction and wind speed greater than 1 m s$^{-1}$.

**RESULTS AND DISCUSSION**

**Particulate Mass Concentrations**

A total of 35 samples of PM$_{2.5}$ and PM$_{10}$ aerosols were collected from March 2019 to May 2019 at the Waru Industrial Estate sampling site. The concentrations of PM$_{2.5}$ and PM$_{10}$ ranged from 2.65 to 32.68 $\mu$g m$^{-3}$ and from 14.69 to 72.27 $\mu$g m$^{-3}$, respectively. Respective daily mean concentrations of 18.26 ± 6.40 $\mu$g m$^{-3}$ and 43.59 ± 14.53 $\mu$g m$^{-3}$ were recorded for PM$_{2.5}$ and PM$_{10}$.

When compared with the daily quality standard (24 hours) of 25 $\mu$g m$^{-3}$ published by the WHO, there were three days for which the PM$_{2.5}$ concentrations exceeded the quality standard, namely, on April 14 and 15,2019 and May 6, 2019, with concentrations of 28.44, 32.68, and 25.05 $\mu$g m$^{-3}$, respectively. There were decreases in the concentration on several days, namely, on March 17, 20, 23 and April 3, 7, 16, 18, 28, 2019, to 6.00, 4.81, and 13.46 $\mu$g m$^{-3}$ respectively. For PM$_{10}$, when its concentrations are compared with the daily standard (24 hours) of 50 $\mu$g m$^{-3}$ published by the WHO, there were 12 days for which the concentrations exceeded the quality standard, namely, on March 14, 24, 28 2019, April 4, 14, 15, 2019, and May 4, 6, 8, 9, 11, 13, 2019, with PM$_{10}$ concentrations of 66.53, 53.05, and 55.03, 56.06, 52.41, and 68.71 $\mu$g m$^{-3}$; and 56.60, 65.65, 72.277, 53.74, 53.18, and 55.76 $\mu$g m$^{-3}$, respectively. There were decreases in the concentration on several days, namely, on March 17, 20 and
April16, 18, 19, 2019, of 21.74 and 30.83 µg m⁻³, and 14.69, 17.25, and 31.48 µg m⁻³, respectively. Based on the calculations of the PM₁₀ concentrations during the study period around the Waru Industrial Estate, Sidoarjo, the PM₁₀ concentration had an average concentration value of 43.59 µg m⁻³, with the lowest concentration value of 14.69 µg m⁻³ and the highest concentration value of 72.27 µg m⁻³. When compared with the Government Regulation No. 41/1999 concerning air pollution control quality standard for PM₁₀ of 150 µg m⁻³ over a 24-hours period, the concentration of PM₁₀ in the vicinity of the Waru Industrial Area, Sidoarjo, is still below the quality standard. This result is consistent with the research conducted by Ahmad and Santoso (2016), which showed that the average PM₁₀ concentration in Surabaya during the period from October 2012 to February 2014 was 30.41 µg m⁻³, well below 1999’s 150 µg m⁻³, the U.S. EPA’s 150 µg m⁻³, and the WHO’s 50 µg m⁻³ (Ahmad and Santoso, 2016). This finding is also supported by Pitakola and Adiriyani (2016), who showed that the PM₁₀ concentrations in the Ready Mix Concrete area of Waru, Sidoarjo amounting to 0.032 mg Nm⁻³ did not exceed the threshold value set by the Ministry of Man power and Transmigration’s Regulation No. PER.13/MEN/X/2011 of 0.26 mg Nm⁻³ over 24 hours.

The mean of the values of the PM₂.₅ and PM₁₀ concentrations were compared with six cities (Table 1). The mean PM₂.₅ concentrations in Waru, Sidoarjo, Bandung, Jakarta, Palangkaraya, Serpong, and Yogyakarta were 18.26, 18.35, 16.50, 7.74, 16.50, 7.74, 16.68, and 8.78 µg m⁻³, respectively, while the mean PM₁₀ concentrations were 43.59, 35.81, 41.58, 17.58, 32.05, and 20.13 µg m⁻³, respectively. The PM₂.₅ concentrations for Waru, Sidoarjo, Bandung, Jakarta, and Serpong are higher compared with those for Palangkaraya and Yogyakarta, indicating that Waru, Sidoarjo, Bandung, Jakarta, and Serpong are more polluted than Palangkaraya and Yogyakarta. The PM₁₀ concentrations in Waru, Sidoarjo, Jakarta, Bandung, and Serpong were also higher than they were for Yogyakarta and Palangkaraya. It should be noted that the amount of industrial activity in Yogyakarta and Palangkaraya was less than that in Waru, Sidoarjo, Jakarta, Bandung, and Serpong. The rapid growth of industry, the population, and motor vehicle usage in Waru, Sidoarjo, Bandung, Jakarta, and Serpong has affected their environmental quality considerably. The imbalance between the number of motor vehicles and available roads has created traffic problems in almost every section of these cities and resulted in air quality deterioration (Santoso et al., 2013).

The decreasing and increasing patterns seen in the PM₂.₅ and PM₁₀ concentrations around the Waru Industrial Estate occurred on almost the same dates, as can be seen in Fig. 2. The pattern could have been influenced by meteorological parameters at the time of the measurements. When the PM concentration is high, the wind speed ranges from 0.5 to 2.1 m s⁻¹, and the dominant wind direction comes from the west with a temperature of 27°C–30°C and a humidity of 70%–85%, whereas when the PM concentration is low, the wind speed ranges between 2.1–3.6 m s⁻¹ and the dominant wind direction comes from the east with a temperature of 27°C–29°C and a humidity of 70%–80%. These results are consistent with research conducted by Proias et al. (2010) that concluded that wind direction and speed correlate significantly with the average daily PM concentration. During the measurement period, it rained for several days, such as on April16, 2019, when it rained at a temperature of 27°C, and the PM concentration experienced a small decrease. Rain greatly affects the concentration of PM because it causes air borne particulates to float in the air bound to rain drops, which then descend toward the surface of the earth (Holst et al., 2008).

The correlation test for the PM₂.₅ and PM₁₀ concentrations showed significantly high correlations between their concentrations. Determination coefficient (R²) gives the meaning of the percentage effect of mass concentration PM₂.₅ on PM₁₀. The relationship pattern between the two is the root of the value R². In Fig. 3, the PM₁₀ value of 67.50% is influenced by changes in the mass concentration variable PM₂.₅ while 32.50% is influenced by other variables, as shown in Fig. 3.

**Multi-elemental Analysis of Particulates**

The elements identified by XRF spectroscopy for the PM₂.₅ fine particle fractions and PM₂.₅,PM₁₀ coarse particle fractions were Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb, and Cl. The box and whisker plots in Fig.4 illustrate the distributions for each element. Multi-element analysis reveals that the dominant substance in PM₂.₅ was S and that the dominant metal in PM₂.₅,PM₁₀ was Si, as shown in Table 2.

Based on the XRF test results, there are 15 elements in PM₂.₅ and PM₂.₅,PM₁₀. Of these 15 elements, Pb, Mn, and Cr already have quality standards for ambient air in several countries. The National Ambient Quality Standards (NAAQS) of the USEPA state that the Pb concentration within a measurement period of three months should not exceed 0.15 µg m⁻³. The average Pb concentrations measured in PM₂.₅ and PM₂.₅,PM₁₀ for the sampling period were 0.1655 µg m⁻³ and 0.0862 µg m⁻³, respectively. Hence, the Pb measured in PM₂.₅ exceeded the established quality standards NAAQS.

### Table 1. The mean of the PM₂.₅ and PM₁₀ concentrations.

| Location      | PM₂.₅ (µg m⁻³) | PM₁₀ (µg m⁻³) | Literature          |
|---------------|---------------|---------------|---------------------|
| Waru, Sidoarjo| 18.26         | 43.59         | In this study       |
| Bandung       | 18.35         | 35.81         | Santos et al. (2013)|
| Jakarta       | 16.50         | 41.58         | Santos et al. (2013)|
| Palangkaraya  | 7.74          | 17.58         | Santos et al. (2013)|
| Serpong       | 16.68         | 32.05         | Santos et al. (2013)|
| Yogyakarta    | 8.78          | 20.13         | Santos et al. (2013)|
and the measurement results in one sample for PM$_{2.5}$ and PM$_{2.5-10}$ indicated Pb concentrations of 0.6471 µg m$^{-3}$ and 0.3112 µg m$^{-3}$, respectively, also exceeded the NAAQS quality standard. If the Pb concentrations are compared instead with the Indonesian standard during the 24-hours measurement time of 2 µg m$^{-3}$, then one of them exceeded this standard. The WHO’s 24-hours standard for Mn concentrations is 0.018 µg m$^{-3}$, while the Mn concentrations measured by PM$_{2.5}$ and PM$_{2.5-10}$ were 0.0094 µg m$^{-3}$ and 0.023 µg m$^{-3}$, respectively, meaning that the quantity of Mn in PM$_{2.5-10}$ exceeded the established quality standards. The 24-hours standard for Cr concentrations of the Ontario Ministry of the Environment Ambient Air Quality Criteria/Texas Commission on Environment Quality (OAQC/TCEQ) is 1.5 µg m$^{-3}$, while the Cr concentrations measured by PM$_{2.5}$ and PM$_{2.5-10}$ are 0.0016 µg m$^{-3}$ and 0.0038 µg m$^{-3}$, respectively, indicating that the quantity of Cr has not exceeded the established quality standards.

Based on the XRF plots used in the identification of the metal elements in PM$_{2.5}$ (Fig. 4), the seven elements with the highest concentrations (in order from greatest to smallest concentrations) are S > Na > K > Zn > Si > Fe > Pb. S has the highest concentration at 2080.2 ng m$^{-3}$, with a mean value of 1090 ng m$^{-3}$. This element is one of the markers of vehicle activity conducted with low quality fuel. Emissions from the transportation sector that contain high quantities of S are transformed in the atmosphere into SO$_2$. This finding is backed by de Bruin et al. (2006) and the International Council on Clean Transportation (ICCT). A report by Miller and Jin. (2018) states that Indonesia has a high sulfur average, especially because it uses EURO II vehicles that run on diesel fuel with high S content (> 500 ppm).
Fig. 4. (a). Box and whisker plot for PM$_{2.5}$. (b) Box and whisker plot for PM$_{2.5-10}$.

Table 2. Mass concentrations of elements in PM$_{2.5}$ and PM$_{2.5-10}$.

| Element | PM$_{2.5}$ (ng m$^{-3}$) | PM$_{2.5-10}$ (ng m$^{-3}$) |
|---------|--------------------------|-----------------------------|
|         | Mean         | STD          | Min          | Max          | Mean        | STD           | Min          | Max          |
| Na      | 753.1        | 429.2        | 148.8        | 1748.2       | 763.5       | 437.4         | 251.1        | 1641.2       |
| Mg      | 34.7         | 18.8         | 6.5          | 99.6         | 112.2       | 46.5          | 53.9         | 235.2        |
| Al      | 105.8        | 63.6         | 5.1          | 230.5        | 642.5       | 300.5         | 113.1        | 1500.7       |
| Si      | 182.2        | 87.8         | 11.2         | 350.0        | 1305.0      | 600.6         | 280.8        | 2767.8       |
| S       | 1090.0       | 393.2        | 177.5        | 2080.2       | 525.1       | 201.1         | 188.5        | 945.1        |
| K       | 262.6        | 106.6        | 36.6         | 556.6        | 239.7       | 77.5          | 81.5         | 433.5        |
| Ca      | 81.8         | 33.4         | 13.6         | 156.0        | 765.2       | 302.3         | 215.7        | 1583.7       |
| Ti      | 9.3          | 3.8          | 2.7          | 21.2         | 50.2        | 20.9          | 12.6         | 120.0        |
| Cr      | 1.6          | 1.2          | 0.1          | 4.3          | 3.8         | 2.2           | 0.3          | 7.9          |
| Mn      | 9.4          | 9.3          | 0.3          | 40.0         | 23.3        | 18.0          | 4.7          | 77.4         |
| Fe      | 167.1        | 109.2        | 8.4          | 445.4        | 800.0       | 413.9         | 138.2        | 1931.3       |
| Cu      | 3.5          | 2.0          | 0.4          | 7.1          | 6.7         | 4.1           | 0.1          | 16.3         |
| Zn      | 282.1        | 250.0        | 28.5         | 1091.5       | 439.5       | 441.8         | 36.6         | 2160.2       |
| Pb      | 165.5        | 160.4        | 9.8          | 647.1        | 86.2        | 78.8          | 1.6          | 311.2        |
| Cl      | 20.6         | 13.4         | 1.7          | 61.9         | 588.5       | 411.1         | 112.7        | 1752.7       |
Based on the XRF plots for the identification of metal elements in PM$_{2.5-10}$ (Fig. 4), the seven elements with the highest concentrations are Si > Fe > Ca > Na > Al > Cl > S. The Si element has the highest concentration of 1305 ng m$^{-3}$, with a mean value of 2767.8 ng m$^{-3}$. In general, the Si element is derived from soil dust particles but can also come from industrial sources that release Si, depending on area conditions. This research was carried out in the Waru Industrial Zone, which has approximately 235 companies with a variety of industrial activities, including the manufacture of paper, glass, dye, and cosmetics. Some of these industrial activities can contribute to the Si found in PM$_{2.5-10}$ around the Waru Industrial Area, Sidoarjo. As a comparison, the concentration of Si in PM around the Industrial Zone of the city of Raipur, Central India is very high, ranging between 6.6–102 µg m$^{-3}$ (Patel et al., 2016).

**Principal Component Analysis (PCA)**

After the elements in PM are identified, the XRF measurement data are then analyzed using PCA to identify sources that contribute to air pollution around the Waru Industrial Area, Sidoarjo. PCA has been used widely in the study of particulate matter composition in the air (Hopke, 1999). PCA is widely used to reduce data dimension in metal distribution studies, it extracts a small number of latent factors, referred to as principal components to analyze relationships among observed variables (Yeung et al., 2003; Han et al., 2006; Meza-Figueroa et al., 2007). The PCA results can explain how much information is explained by four main components (factors) based on the values of the eigenvalues (root characteristics) for each major component.

Initial eigenvalue values greater than one identifies factors one to four, which then become the potential sources of pollutants. Markers are selected for the factors based on loading values > 0.5, and the loading values for the elements meeting this criterion are given in bold type in Table 3.

The first factor consists of the elements Fe, Ca, Al, and Si, Ti, Mn, Cr, Mg, and Cu. Elements Fe, Ca, Al, and Si are markers of industrial activities. Paper, glass, cosmetics, and electronics industries which can contribute to the source of these pollutants, especially the Si concentrations, are located around the sampling locations. The elements Si, Fe, Ca, and Al are markers of industrial activities around the Industrial Zone of the city of Raipur, Central India (Patel et al., 2016). Si is usually used for various purposes in various sizes, depending on the application, in the tire, ceramics, rubber, glass, textiles, paper, cosmetics, electronics, toothpaste, and other industries (NIOSH, 2002). The Ti and Mn elements in the first factor are markers derived from soil dust (de Bruin et al., 2006). The soil dust can come from activities around the sampling location. A field about 60 meters from the sampling location is being used for the construction of housing. The first factor also includes Cr, Mg, and Cu, which indicate soil as well as the vehicle sources (de Bruin et al., 2006). Around the Waru Industrial Estate, vehicles are used to transport goods, and vehicles from outside also pass through the streets within the Industrial Estate because they lead to the airport and out of town. After work hours, the streets are congested with frequent traffic jams. These vehicle activities can contribute to this pollutant source. It can be concluded that the first factor is a combination of industrial activities, soil dust, and vehicle activities. The correlation matrix in Table 3 shows the strength of the relationships between elements, and the values in bold indicate strong relationships between variables (correlation > 0.5). It can be seen from the correlation matrix that the elements Al, Si, Ca, Ti, and Fe are strong, so it is possible that these elements come from one source, most likely soil dust.

The second factor consists of the elements S and Pb, where Pb can come from activities in the metal smelting industry. There is a metal smelting industry within 2–6 km of the sampling location, so the Pb in the PM mostly likely came from this industry. Pb in PM can also come from iron and steel industry activities (Dai et al., 2015). S in this second factor indicates that there is a contribution from

**Table 3.** Factor analysis for PCA.

| Parameter | Component |
|-----------|-----------|
|           | Factor 1  | Factor 2  | Factor 3  | Factor 4  |
| Fe        | .976      | .029      | -.094     | -.021     |
| Ti        | .944      | -.196     | -.105     | .096      |
| Ca        | .944      | -.234     | -.072     | .056      |
| Al        | .924      | -.234     | -.098     | .106      |
| Si        | .914      | -.245     | -.148     | .127      |
| Cr        | .836      | .084      | -.316     | -.238     |
| Mn        | .817      | .404      | -.033     | -.295     |
| Cu        | .726      | .325      | -.378     | .023      |
| Cl        | .723      | -.121     | .561      | .164      |
| Mg        | .689      | -.390     | .409      | .308      |
| Zn        | .625      | .606      | .076      | -.400     |
| S         | -.379     | .718      | -.256     | .334      |
| Pb        | .033      | .573      | .422      | .103      |
| Na        | .478      | .563      | .520      | -.128     |
| K         | .253      | .571      | -.177     | .633      |

Note: Numbers in bold are loading values for elements that meet the criteria.
diesel vehicles (Chueinta et al., 2000; Begum et al., 2014). Around this sampling location, many diesel vehicles are used as means of transporting industrial products/services that will be distributed to the Surabaya area or other cities outside East Java. Indonesia still has a high S content in diesel fuel (5,000 ppm) (Santoso et al., 2008).

The third factor consists of Na and Cl, which indicates that there is a contribution of sea salt to air pollution around the Waru Industrial Area. The contribution of sea salt comes from sea water evaporation (Mukhtar et al., 2013). Na evaporation usually coincides with Cl (Santoso et al., 2008).

The fourth factor consists of K, which indicates biomass combustion emissions (Santoso et al., 2008). K is present in biomass smoke and is the result of an incomplete, open combustion process, such as open air burning of garbage, forest fires, and cigarette smoking.

**Conditional Probability Function (CPF)**

The following are the results of using the CPF method, with the help of Microsoft Excel, for estimating PM pollutant sources based on wind direction and velocity data. The results are in the form of a radar plot graph that uses 16 cardinal directions as a prediction of the direction of the pollutant source. The plot is based on the element that has the highest concentration and contributes to each factor.

The first factor consists of the elements Fe, Ca, Al, Si, Ti, Mn, Cu, Cr, Zn, and Mg from industrial activities and soil dust. Of these, Si, Al, and Fe have the highest concentrations. Si, Fe, and Al (Fig. 5) are estimated to originate from the north to northeast with a probability of 0.5. An industrial estate lies north to northeast from the sampling site. The industrial processes there can release Si, Fe, and Al particles into the air, so it is entirely possible that the estate could be the source.

The second factor consists of Pb and S, which come from the smelting industry and diesel vehicles. S has a higher concentration than Pb. The results of overlaying CPF radar plot graphs for the elements Pb and S can be seen in Fig. 5, respectively. The results indicate that the Pb pollutant sources (non-ferrous metal industry activities) are from the west to southwest with a probability of 0.4. A steel smelting plant is 2–6 km from the sampling location in that direction, and in the southwest, there is also a metal village 2.3 km from the sampling location. Surabaya is flanked by industrial regions, such as Gresik and Sidoarjo, in that direction, which house Rungkut Industri Raya and Brebek Industry as well as steel smelting (Ahmad and Santoso, 2016).

In addition to contributions from the non-ferrous metal industry, pollutant emission source factors in the second factor can also come from diesel vehicles, because high concentrations of S are present. The result of overlaying the CPF radar plot graph for the S element can be seen in Fig. 5. An industrial estate lies in the north to northeast direction for the sampling location. Many vehicles pass through the industrial estate because its roads lead to the airport and out of town. These S concentrations are likely the result of high S concentrations in motor vehicle fuels used by the many vehicles passing through the area. Thus, the locally formed S condenses on to the surfaces of the existing particles (McMurry and Friedlander, 1979).

Fig. 5. CPF plot for the estimated location of the source of pollutants.
The third factor consists of the elements Na and Cl, which are contributions from sea salt. The CPF radar-plot-overlay results for Na and Cl can be seen in Fig. 5. The sea salt arrived from the northeast to the east with a probability of 0.4–0.45. Sea salt is made possible because the area borders the Madura Strait to the east, this conclusion is supported by Ahmad and Santoso (2016).

CONCLUSIONS

PM$_{2.5}$ and PM$_{10}$ concentrations around the Waru Industrial Area ranged from 2.65 to 32.68 µg m$^{-3}$ and from 14.69 to 72.27 µg m$^{-3}$, respectively. Mass concentrations for PM$_{2.5}$ and PM$_{10}$ at the time of measurement in the form of time series did not exceed the Indonesian quality standard but did exceed the WHO quality standard. XRF spectroscopy identified 15 metal elements in fine particles (PM$_{2.5}$) and coarse particles (PM$_{2.5-10}$), namely, Na, Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Pb, and Cl. The multi-element concentrations were analyzed using PCA to produce four components of PM pollutant sources around the Waru Industrial Area, Sidoarjo, East Java. A mixture of industrial activities, soil dust, and vehicle activity contributed to the first factor; metal smelting and diesel vehicle emissions contributed to the second factor; sea salt contributed to the third factor; biomass combustion emissions contributed to the fourth factor. Estimations of the locations of pollutant sources using the CPF method show that the PM pollutants come from industrial activities, vehicle activities, metal smelting activities, and sea salt emissions.

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