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CHARACTERISTICS OF THE PM_{10} IN THE URBAN ENVIRONMENT OF MAKASSAR, INDONESIA

Sattar Yunus[1*], Mohd Rashid[2], Ramli Mat[3], Sabariah Baharun[2] and Hasfalina C. Man[4]

[1]*Department of Environmental Engineering, Universitas Muslim Indonesia, Makassar, Indonesia*
[2]*Air Resources Research Laboratory, Malaysia-Japan International Institute of Technology, UTM Kuala Lumpur, Malaysia*
[3]*Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, UTM Johor Bahru, Malaysia*
[4]*Department of Biological and Agricultural Engineering, Universiti Putra Malaysia, Serdang, Selangor, Malaysia*

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Abstract: Ambient PM_{10} samples were collected in Makassar, Province of South Sulawesi to examine the chemical characteristics of the airborne particulates in the area. The PM_{10} was monitored on a weekly basis for a period of one year from February 2012 to January 2013. A total of nineteen elemental constituents (i.e Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Ti, and Zn) along with black carbon and ionic components $SO_4^{2-} > NO_3^- > Cl^- > NH_4^+$ were analyzed in the sample. The average PM_{10} concentration was found to be 32.92 µg/m3, lower than those found in other major cities of the world. The black carbon represents 6.1% of the PM_{10}, the highest concentration, followed by SO_4^{2-} (4.5%), NO_3^- (3.4%), and Cl^- (2.7%) while each of the elemental concentrations represent less than 2% of the PM_{10} at the site. The descending order of elemental concentration found at the site was Ca > Si > Na > Al > Fe > K > Mg > Zn > Ti > Pb > Ni >Mn> Ba > Cu > Cr > B > Ag > Cd > Co. The elemental enrichment factors indicated that most of these elements were enriched relative to soil origin illustrating their possible associations with other sources such as marine and anthropogenic derived aerosols. A better understanding of the potential air pollution sources in the city of Makassar was revealed in the study.

Keywords: Air Pollution; PM_{10}; Black carbon; Elemental components; Ionic Species.

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* Correspondence to: Sattar Yunus. +62-82187010203. E-mail: sattaryunus71@gmail.com

INTRODUCTION

Urban atmosphere is a highly complex system, composed of gaseous and airborne particulate matters which are made up of a wide variety of organics and inorganics compounds of natural and anthropogenic origins. The anthropogenic are man-made sources of air pollution caused by transportation, stationary combustion, space heating, biomass burning, and industrial and many other sources of emissions. Several studies have demonstrated that concentrations of outdoor pollutants are higher for urban sites whilst non-urban areas are characterized by lower concentrations (Sharma and Kulstsrestha, 2014; Pratt *et al.*, 2018). Haze is a common phenomenon afflicting Southeast Asia (SEA), including Malaysia, and has occurred almost every year within the last few decades (Latif *et al.* 2018; Ku Yusof *et al.*, 2018).

The most critical air pollutant in many cities in Southeast Asian is the airborne particulate matter, which is unique among air contaminants because of its complexity in terms of physical properties and chemical composition. Dadhich *et al. (*2017) reports that the urban air quality pattern results indicate that PM_{10} and Suspended Particulate Matter (SPM) concentrations have the greatest effects on the air environment in comparison to gaseous pollutants. The human respiratory health is affected by airborne particulates. More importantly, the finer particulate size fractions with an aerodynamic diameter of less than 10 μm or PM_{10} are able to penetrate deep inside the lungs (Zanobetti *et al.*, 2003; Mar *et al.*, 2003). In addition, studies have found that PM_{10} have long been implicated in causing adverse health and the increase in mortality and morbidity rate (Dockery *et al.*, 1992; Dockery and Pope, 1994). Several studies have observed a statistically significant association between long-term exposure to PM air pollution and causes of death (Hoek *et al.*, 2013; Beelen *et al.*, 2014; Theodosi *et al.*, 2018). Previous studies have also shown that the ambient air quality has a considerable effect on the indoor air quality due to the extensive infiltration of outdoor pollutants (Chen and Zhoa., 2011; Saraga *et al.*, 2017). Ahmat *et al.* (2015) estimated that the number of days when the concentration of PM_{10} exceeded the Malaysian Ambient Air Quality Guidelines (MAAQG) of 150 mg/m3 are between ½ and 1½ days for the Southern Region of Malaysia. Similar findings were reported by Safari *et al. (*2017).

Understanding the physical and chemical characteristics of the ambient particulate matter is important in the development of a rational control strategy. Informed decision-making concerning the improvement of air quality demands precise knowledge of particulate matter chemical speciation and source attribution (Hime *et al.*, 2018). This is particularly important in any city, however, this study regarding air pollution in the city is limited to Makassar city, South Sulawesi Province, Indonesia (Sattar *et al.*, 2012). Hence, studies on elemental composition and concentration in airborne particulate are important in understanding the contribution and effects of air pollution sources in a given locality, so the findings reported in this paper are related to the elemental and ionic components of PM_{10} samples that were collected on a weekly basis for a period of one year from February 2012 to January 2013 in the Makassar city and are very important in providing fundamental information for regulatory agencies to mitigate PM air pollution in this area.

MATERIALS AND METHODS

Sampling

The 24-hr period of once a week PM_{10} sampling was performed by using a standard size-selective high volume air sampler (Sierra Andersen) with a glass type fiber filter (20.3 × 25.4 cm) as the collection medium. The sampler was sited at Daya, a mixed urban, commercial, and industrial area in Makassar City, Province of Sulawesi (**Fig. 1**). The city of Makassar consists of fourteen districts with a total area of approximately 176,000 square km.

Analysis of Samples

The particulate mass concentration of PM_{10} was determined based on gravimetric by dividing the net particulate weight gained on a filter paper to the total volume of air sampled. The filter was analyzed for black carbon (BC) concentration using a Smoke Stain Reflectometer (Model 43D) based on a reflectance method (Lestiani *et al.*, 2007; Lestari and Mauliadi, 2009; Kothai *et al.*, 2011), while the elemental constituents in the particulate sample were analyzed by using the Inductively Coupled Plasma Optical Emission Spectrometry (VARIAN Model 715-ES). One half of the PM_{10} sampled filter paper was cut into small pieces and digested in concentrated nitric acid (HNO_3) and hydrofluoric acid (HF) in a capped flask and microwaved for 20 min. Once cooled, it was filtered using a Whatman filter paper and made up to a final solution of 50 mL. The blank field filter was also subjected to the same experimental procedures to determine the elemental background level. The final elemental concentration was obtained by subtracting the blank from the sampled filter. A total of nineteen elements were determined in the PM_{10} sample, namely Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Ti, and Zn.

The analysis for ion chloride (Cl-), nitrate (NO3-), ammonium (NH_4^+), and sulfate (SO_4^{2-}) in the PM_{10} sample was performed using Ion Chromatography (DIONEX, Model DX500). A quarter of the PM_{10} sampled filter paper was cut into small pieces, placed

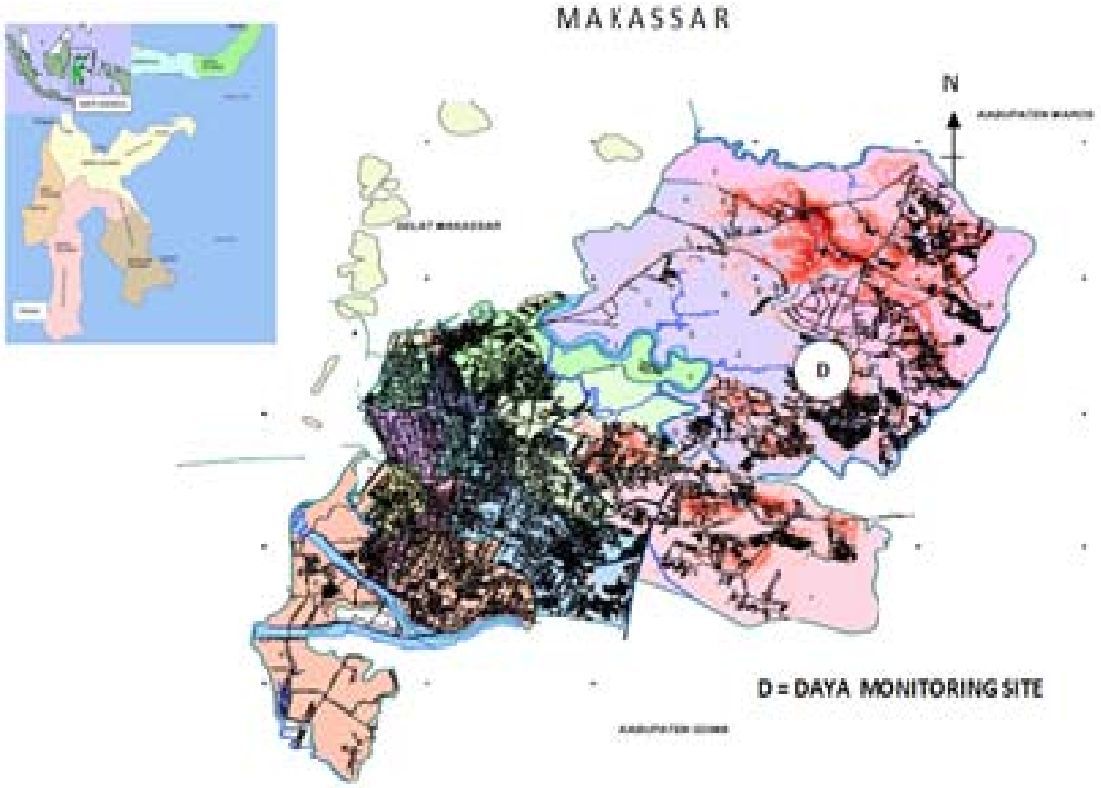

Fig. 1 Location of the sampling site at Daya, Makassar.

into a 100 mL conical flask with 25 mL of deionized water added to it. The sample was immediately transferred for ultrasonic vibration extraction for at least 30 minutes at room temperature to dissolve the ionic components. Then, the sample was filtered and analyzed for the ionic content. Similarly, the blank filter was subjected to the same experimental procedures (Rashid *et al.*, 2014).

RESULTS AND DISCUSSION

Constituents of PM_{10}

Table 1 presents the mean and standard deviation of PM_{10}, black carbon, ions, elemental concentrations, and their respective contributions in PM_{10} which show that BC accounted for 6.1%, the highest percentage in PM_{10}, followed by SO_4^{2-} (4.5%), NO_3^- (3.4%), and Cl^- (2.7%) while each of the elemental constituents represented less than 2% of the PM_{10} concentration at the site.

As shown in **Table 1**, typically major constituents found in ambient air like BC, Ca, Si, Na, Al, Fe, K, and Mg were found to have a high concentration in the PM_{10}, with an average concentration of 2.01 ± 0.93 µg/m3, 0.64 ± 0.50 µg/m3, 0.60 ± 0.43 µg/m3, 0.54 ± 0.48 µg/m3, 0.50 ± 0.51 µg/m3, 0.43 ± 0.30 µg/m3, 0.36 ± 0.41 µg/m3, and 0.24 ± 0.24 µg/m3, respectively. Particularly, elemental Al, Ca, Si, and Fe were comparatively high in concentration, as they are known to be soil-derived elements (Rashid *et al.*, 1997a). Mohd Tahir *et al.* (2013) categorized Al, Ca, Fe K, Mg, and Na as major elements and Mn, Cd, Ni, Cr, Pb, and Cu as minor elements in their study on atmospheric particulate matter collected in the eastern coast of Peninsular Malaysia.

Table 1. Mean, and standard deviations, of PM_{10} concentration and other ambient constituents at Daya, Makassar

Element	Average	Median	Std deviation
PM_{10}	32.9 [100]	31.8	11.0
BC	2.0132 [6.11]	1.7846	0.9273
Cl^-	0.8662 [2.68]	0.7328	0.9066
SO_4^{2-}	1.4453 [4.47]	1.0005	1.0381
NO_3^-	1.1095 [3.43]	1.2109	1.0586
NH_4^+	0.4883 [1.51]	0.0793	0.6412
Ag	0.0029 [0.01]	0.0028	0.0021
Al	0.5047 [1.53]	0.2548	0.5065
B	0.0038 [0.01]	0.0027	0.0041
Ba	0.0092 [0.03]	0.0073	0.0101
Ca	0.6362 [1.93]	0.3710	0.5060
Cr	0.0069 [0.02]	0.0068	0.0046
Cu	0.0079 [0.02]	0.0031	0.0189
Fe	0.4276 [1.30]	0.3519	0.2976
K	0.3578 [1.09]	0.1860	0.4137
Mg	0.2395 [0.73]	0.2185	0.2379
Mn	0.0165 [0.05]	0.0125	0.0199
Na	0.5451 [1.65]	0.4964	0.4779
Ni	0.0209 [0.06]	0.0069	0.0279
Pb	0.0297 [0.09]	0.0221	0.0211
Si	0.6074 [1.84]	0.4764	0.4326
Ti	0.0377 [0.11]	0.0116	0.0641
Zn	0.0395 [0.12]	0.0430	0.0270

Number of samples = 53; Unit = µg/m^3; [ ] = weight percent of PM_{10}

Table 2. Comparison of PM and element concentrations (μg/m^3) in the aerosol with other studies

PM, Element	This study, Makassar, Indonesia	Lembang, Indonesia (a)		Bandung, Indonesia Dry season (b)		Kuala lumpur, Malaysia (c)		Baoshan District, China (d)	Athabasca Region, Canada (e)
	PM_{10}	Coarse	Fine	Coarse	Fine	Coarse	Fine	PM_{10}	$PM_{10-2.5}$
PM_{10}	32.92	-	-	-	-	-	-	159	7.56
Coarse	-	7.10	-	19.0	-	22.47	-	-	-
Fine	-	-	11.8	-	48	-	26.85	-	-
BC	2.0132	-	-	-	11.26	0.578	4.230	-	-
Cl^-	0.8662	-	-	0.99	-	-	-	0.979	-
SO_4^{2-}	1.4453	-	-	1.76	-	-	-	14.38	-
NO_3^-	1.1095	-	-	1.25	-	-	-	1.071	-
NH_4^+	0.4883	-	-	0.32	-	-	-	-	-
Ag	0.0029	-	-	-	-	-	-	-	-
Al	0.5047	0.367	0.058	0.59	3.712	0.817	0.146	0.720	0.311
B	0.0038	-	-	-	-	-	-	0.742	-
Ba	0.0092	-	-	-	-	-	-	0.173	0.0027
Ca	0.6362	0.234	0.023	1.07	4.641	0.985	0.131	1.159	0.387
Cr	0.0069	0.015	0.005	0.04	0.056	0.011	0.005	0.009	0.001
Cu	0.0079	-	-	0.02	0.041	0.010	0.017	-	0.001
Fe	0.4276	0.198	0.088	0.31	6.827	0.443	0.112	1.385	0.311
K	0.3578	0.039	0.086	0.08	2.583	0.410	0.394	3.637	-
Mg	0.2395	-	-	0.15	3.378	0.234	0.124	0.039	0.066
Mn	0.0165	0.007	0.001	0.02	0.189	0.009	0.005	0.038	0.006
Na	0.5451	0.178	0.067	0.43	7.047	0.361	0.278	3.675	-
Ni	0.0209	-	-	0.01	0.032	0.004	0.003	0.056	0.0004
Pb	0.0297	-	0.016	0.01	0.137	0.022	0.032	0.232	-
Si	0.6074	-	-	0.50	-	1.703	0.317	-	0.892
Ti	0.0377	0.036	0.005	0.03	-	0.044	0.008	-	0.013
Zn	0.0395	0.018	0.011	0.40	0.590	0.030	0.039	2.348	0.0018

(a) Santoso *et al.*, 2008; (b) Lestari and Mauliadi., 2009; (c) Rahman *et al.*, 2011; (d) Wang *et al*., 2013; (e) Landis *et al*., (2017)

Sulfate (SO_4^{2-}) represents the most dominant component among the ionic species followed by NO_3^-, Cl^-, and NH_4^+ with a concentration of 1.44 ± 1.04 μg/m^3, 1.11 ± 1.06 μg/m^3, 0.87 ± 0.91 μg/m^3, and 0.49 ± 0.64 μg/m^3, respectively. In China, sulfate was found to be the major constituent at four monitoring sites comprising 23.8–46.7 % of $PM_{2.5}$ and 18.3–30.7 % of PM_{10} and it was determined to have sea salt and non-sea salt origins (Wang *et al.*, 2006). Rashid *et al.* (1997b) also reported that SO_4^{2-} originated from both natural or sea salt sources, ranging from 0.37–0.50%, while the anthropogenic or non-sea salt aerosol ranged between 3.31–8.28 % of the PM_{10} sampled in Johor Bahru, Malaysia. The contribution of the sea salt sulfate in this study may be significant given the location of Makassar, which is surrounded by seas.

Meanwhile, Al, Ca, Fe, K, Mg, Na, and Si are the major elements found among the elemental components with an average concentration of 0.50 ± 0.51 μg/m^3, 0.64 ± 0.50 μg/m^3, 0.43 ± 0.29 μg/m^3, 0.36 ± 0.41 μg/m^3, 0.24 ± 0.24 μg/m^3, 0.54 ± 0.47 μg/m^3, 0.61 ± 0.43, respectively. In most cases, these elements are said to be associated with a natural origin such as soil dust, sea spray, and biomass burning. The average elemental concentration, in descending order, observed in this study was as follows: Ca> Si > Na > Al > Fe > K > Mg > Zn > Ti >Pb> Ni >Mn> Ba > Cu > Cr > B > Ag > Cd > Co.

PM_{10} Concentration

Table 2 presents the concentration of PM_{10} obtained from other studies and shows that the concentrations found in the Baoshan District, Shanghai, China (Wang *et al.*, 2013) are higher than the ones in Makassar by five orders of magnitudes. Meanwhile, the concentration in the study is higher than the one of the Athabasca Oil Sands Region, Canada (Landis *et al.*, 2017). Another study that was not listed in **Table 2** (i.e. in the Subway Tunnel in Seoul, Korea) reported the concentration of PM_{10} to be 44.0 μg/m3 (Lee *et al.*, 2018) higher than the one in this study. The PM_{10} concentration was influenced by meteorological factors (Schiliro *et al.*, 2015).

The concentration of black carbon in PM_{10} of Makassar was merely 2.01 μg/m^3 (6.11 % of PM_{10}), compared to Bandung's 11.26 μg/m^3 (25.12%) and Kuala Lumpur's 4.81 μg/m^3 (18.4 %). The BC was predominantly found in the fine particulate size fraction and in a higher concentration in other cities area

suggesting that the city of Makassar is relatively less urbanized compared to other cities like Kuala Lumpur and Bandung.

Black Carbon, Ions, and Elemental Components

Carbon Black Component

As presented in **Table 1,** on average BC, ionic species and elemental concentration constitute 9.42 µg/m^3 or 28.8% of particulate PM_{10} mass concentration at the site. The dominant components in the particulate matter are black carbon followed by ionic species SO_4^{2-}> NO_3^->Cl^- > NH_4^+, and the elemental components Ca> Si > Na >Al >Fe > K >Mn.

Black Carbon is a nonvolatile fraction of the particulate matter also known as elemental carbon (EC) (Begum *et al.*, 2009). It is emitted in the atmosphere due to the incomplete combustion of sources such as diesel engines, biomass burning (Gray and Cass, 1998; Kirchstetter, et al, 2003; Lestari and Mauliadi, 2009), and pyrolysis of biological material during combustion processes (Harrison and Jones, 2005). It is reported that the main source of black carbon in the urban environment is represented by automobile emissions from transportation.

Figure 2 presents the mean of black carbon and ionic species concentrations during the dry and wet season, which showed that a higher concentration of BC was observed during the dry season (i.e. 2.34 µg/m^3) compared to the wet season (i.e. 1.78 µg/m^3). Likewise, nitrate and sulfate, as well as ammonium recorded a higher concentration in the dry season than in the wet season. Kim Oanh *et al.* (2006) similarly reported that NO_3^- and SO_4^{2-} in $PM_{2.5}$ and PM_{10} were higher in concentration during the dry season compared to the wet season in Beijing, China. The authors stated that this was partly linked to more burning in this area during dry weather conditions. On the contrary, chloride was observed to have a lower concentration during the dry season compared to the wet season because chloride vaporizes easily in a dry and hot weather condition. Thus, a depletion of Cl^- was observed in this case, especially during the dry season months in the region.

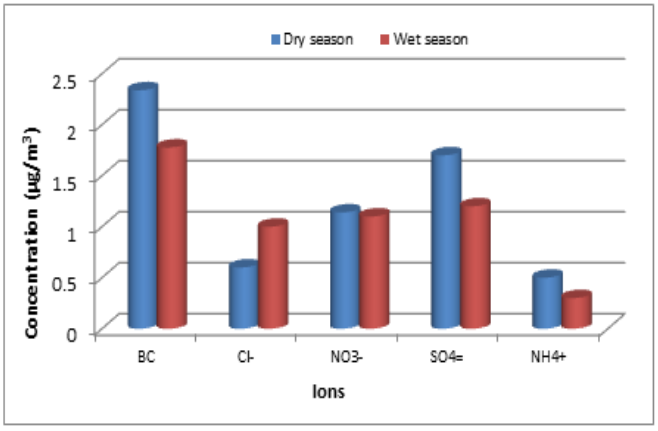

Fig. 2 Mean of BC and ionic species during dry and wet

Ionic Component

Chloride is normally derived from sea salt (SS) and non-sea salt (NSS) sources that are related to industrial emissions like coal combustion (Wang *et al.*, 2006). In this study, it was observed that the monthly mean Cl^- concentration in Makassar was the highest during the wet season, sometimes in November (1.42 ± 1.40 µg/m3), and the lowest in the dry season, namely in August (0.07 ± 0.007 µg/m3). The presence of Cl^- is believed to be caused by the wind passing through the Makassar area from the sea, bringing along sea sprays.

However, there was no meaningful correlation between Na and Cl found in this study. A similar observation was noted between Na and Mg or Mg and Cl, although all these three elements are said to be originating from marine sources. Nevertheless, the average molar ratio of Cl/Na = 1.60 that was slightly lower than the sea salt spray (Cl/Na=1.8) illustrates that Cl is lost (i.e. volatile) easier than Na, especially in the tropical climate (Rashid *et al.*, 1997b).

The concentration of NH_4^+ observed in this study ranged from 0.0250 to 2.7119 µg/m^3. Ammonium originated mainly from ammonia gas, such as combustion products rather than from wind erosion. Unlike chloride, ammonium concentration and its size distributions appeared to be location dependent, and strongly influenced by localized sources. Ammonium and ammonia nitrogen are closely related (Walworth, 2013) with NH_4^+ as predominant in fine particles with aerodynamic diameter less than 2 µm (Wall *et al.*, 1998). In addition, NH_4^+ aerosols affect the earth's radiative balance, both directly by scattering incoming radiation and indirectly by acting as cloud condensation nuclei (CCN). They also contribute to the long-range transport of acidic pollutants, because the atmospheric lifetime of ammonia is short (< 24 h), while NH_4^+ salts might last for a few days (Alves *et al.*, 2007).

Long-range transport results in deposition of NH_4^+ salts far away from the emission sources. Upon deposition, NH_4^+ aerosols can contribute to soil acidification, forest decline, and the eutrophication of the waterways (Marley and Gaffney, 2004).

The concentration of nitrate and sulfate at the sampling site reached the highest in May 2012 (2.14 µg/m^3) and July 2012 (2.37 µg/m^3), respectively. In addition, their concentrations were higher during the dry season than the wet season. Nitrate and sulfate (marine is also a main sulfate contributor) in the atmosphere generally originate from high-temperature combustion processes produced from the conversion of NOx and SOx gases. A significant portion of nitrate results from the atmospheric conversion of nitrogen oxides ($NO+NO_2$) and ammonia (Seinfeld and Pandis, 1998; Han *et al.*, 2009).

In addition, nitrate came from both primary and secondary sources, with the coarse mode nitrate

generated from sea salt sprays and the fine mode nitrate produced from photochemical reactions. Sulfate in the coarse mode may be attributed to the reaction of $CaCO_3$ with H_2SO_4 to form $CaSO_4$ in coarse particles (Tsai *et al.*, 2012), apart from the sea salt origin (Wang et al, 2006). Furthermore, ammonium nitrate and ammonium sulfate are said to be the dominant constituent in the particle size of PM_{10} (Tsai *et al.*, 2012). It was observed that both Na and sulfate were positively and significantly correlated ($r=0.277$, $p \leq 0.01$), indicating their common source origin, which is from marine sources. Interestingly, the ratio of overall mean sulfate to Na concentration (see **Table 2**) was found to be 2.65, which is higher than the molar ratio of sodium sulfate salt (2.09). This finding indicates that there is an excess of sulfate salt (i.e. 0.56) compared to Na, suggesting that there are other sulfate contributors in the study area. Taking this into consideration, the contribution of the sulfate marine and non-sulfate marine source, in this case, is approximately 79% and 21%, respectively, supporting the fact that Makassar is strongly influenced by the marine environment surrounding it.

Elemental Components

Similarly, the major elemental components found i.e. Ca, Al, K, Fe, and Mg had a higher mean concentration during the dry season compared to the wet one (**Fig. 3**). On the contrary, Na and Si had a higher concentration during the wet season compared to the dry one. The higher amount of the Na element may be caused by the sea spray (Na origin) that is carried along with rainfall into the site during the wet season. However, no explanation can be given in the case of Si, which is a dominant soil origin element.

Calcium is one of the elements known as a soil derived constituent. Its presence is more as coarse than fine size fraction and it is slightly enriched in the suspended particulate compared to its crustal origin, with the presumption that Ca originates from soil (Rashid *et al.*, 1986). Similarly, other studies also reported that Ca originated from soil (Han *et al.*, 2006), including a study in Bandung, Indonesia. However, it was also observed that the presence of Ca can be attributed to cement plants (Santoso *et al.*, 2008; Lestari and Mauliadi, 2009). Construction activity and wind-blown road dust material are also responsible for Ca as well as for Al (Wang *et al.*, 2013).

The monthly variations of Ca are presented in **Fig. 4** which shows that the highest concentration of Ca was in June 2012 (i.e., 1.25 ± 0.09 µg/m^3). The presence of Ca on the site might probably come from soil and cement. All the three soil-related elements i.e. Ca, Si, and Al were positively correlated in the study. Evidently, there were many construction activities within a 200 m radius at the time of the study, which may have contributed to a constant amount of Ca during the study period as can be seen in **Fig. 4**.

Aluminum (Al), silicon (Si), and titanium (Ti) are dominant as soil components and may originate from paved road dust, unpaved road dust, construction, agricultural soil, and natural soil (CCPA, 2001; Song *et al.*, 2006; Chelani *et al.*, 2008; Kothai *et al.*, 2011). Al and Si are reported as the main constituents in the re-suspended soil material (Schneidemesser *et al.*, 2010). Both are the main crustal elements with high level of concentrations (Huang *et al.*, 2010) and are predominant in the coarse fraction of atmospheric aerosol (Rashid *et al.*, 1997a). The presence of Al and Si at the sampling site might also possibly come from the construction and transportation activities that bring about the suspension of soil dust material into the atmosphere. The monthly variations of Al and Si are presented in **Fig. 5** which showed that both elements were consistently distributed throughout the months at the study site. This illustrates that their source of origin is associated with an area source which is well distributed around the sampling site. As expected, Si is more dominant than Al, representing 1.84% and 1.53% of the particulate mass concentration of PM_{10}, respectively. Interestingly, the ratio of Al/Si = 0.83 found in the study was in good agreement as reported in the crustal earth, supporting their common source of soil origin. The concentration of Ti was 0.11 % in the particulate mass concentration with a range of 0.0012 to 0.2872 µg/m^3.

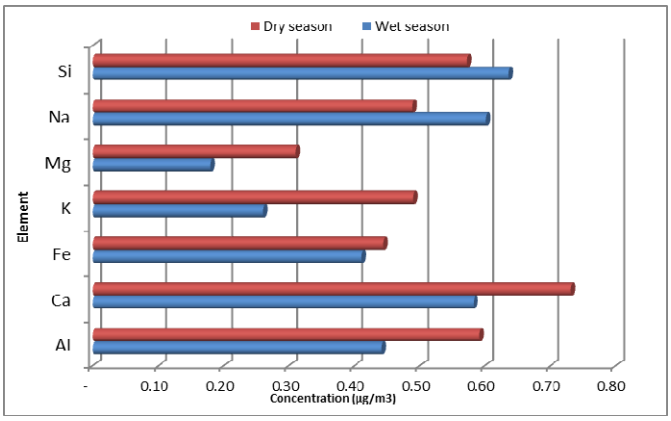

Fig. 3 Mean of dominant elemental components during dry and wet season

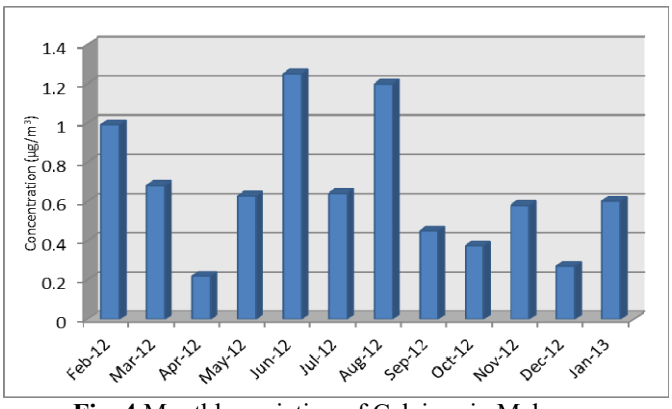

Fig. 4 Monthly variation of Calcium in Makassar

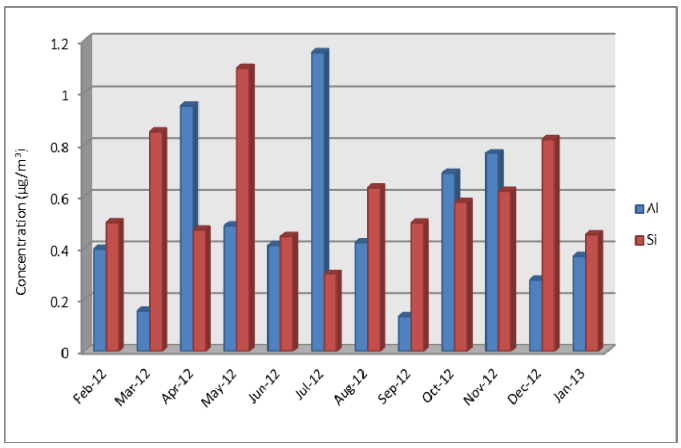

Fig. 5 Monthly variation of Al and Si in Makassar

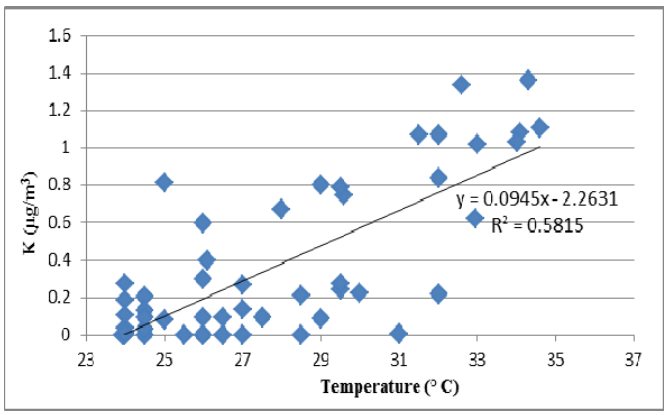

Fig. 6 Relationship between K and ambient temperature in Makassar

Generally, sodium (Na) in the atmospheric particulate is usually assumed to be of marine origin (Pant and Harrison, 2012; Lestari and Mauliadi, 2009; Chelani *et al.*, 2008). This is a true case for Makassar as it is fully surrounded by sea. In this study, the concentration of Na obtained was between 0.0109 and 1.5476 µg/m^3. The highest monthly concentration of Na was in February 2012 and the lowest in June 2012. The monthly concentration of Na during the wet season was higher than the one in the dry season with an average of 0.60 and 0.49 µg/m^3, respectively. The association of Na with sulfate of marine origin has been presented in the previous section.

Fe and Mn generally come from natural sources, road dust, and industrial emissions (Chelani *et al.*, 2008; Jorquera, 2009; Lestari and Mauliadi, 2009; Yu *et al.*, 2013). It was observed that the concentration of Fe and Mn ranged from 0.0142 to 1.2730 µg/m^3 and 0.0001 to 0.0938 µg/m3, respectively. In addition, Fe and Mn along with Cr, Cd, Co, Cu, Zn, and Ni were reported to be associated with industrial source emissions (Rahman *et al.*, 2011; Wang *et al.*, 2013). Furthermore, Yatkin and Bayram (2008) stated that Zn, Cu, Fe, and Mn were found to be associated with traffic emissions.

Potassium is mainly derived from biomass burning (Song *et al.*, 2006; Karanasiou *et al.*, 2009). Thus, it is expected that the concentration of K would be higher during the dry season rather than the wet one. Evidently, as observed in this study, the concentration of elemental K was constantly high during the dry season where rampant biomass or even forest fires are common occurrences. A significant correlation between K and the ambient temperature observed in this study supports the above finding (**Fig. 6**).

The presence of lead and magnesium in the atmospheric particulate is due to fuel combustion in both diesel and gasoline vehicles, especially Pb, principally from the combustion of leaded gasoline in automobiles (Yu *et al.*, 2013). In this study, the concentrations of Pb and Mg range from 0.0008 to 0.0820 µg/m^3 and 0.0007 to 1.2670 µg/m^3, respectively.

The annual ambient Pb concentration (0.0297 µg/m^3 ± 0.0211) in Makassar is within the Indonesian Ambient Air Quality Standard of 1.0 µg/m^3. Since July 2006, the government made the decision to reduce the lead content in gasoline in order to help decrease the Pb in the ambient air (JCFLGP, 2006). The total concentration of Mg observed during the dry season (April-September) was higher than the wet season with 0.31 and 0.18 µg/m^3, respectively. Like Pb, magnesium is believed to originate from automobile emissions apart from marine sources.

The potential source for Ag, B, and Ba in the region are not fully understood. Their presence in the area can be attributed to many possible sources. Silver, B, and Ba can originate from incinerators, coal-fired power plants, and other specialized metal industries. However, these elements can also come from road dust (paved road dust, unpaved road dust, agriculture soil) and even from marine sources and they can be found in coarse and fine or PM_{10} (CCPA, 2001). In this study, Ag, B, and Ba represent 0.01%, 0.01%, and 0.03%, in the particulate mass concentration, respectively.

Enrichment Factor

An Enrichment Factor (EF) technique was used to indicate whether the element is of naturally derived soil origin or otherwise. The EF was calculated by comparing the relative abundance of the element of interest in the air to its crustal rock composition with Si, which is the most common element of soil, taken as the reference element. The EF was estimated using the following equation: $Ef_{crust} = (C_x/C_{Si})_{air}/(Cx/C_{Si})_{crust}$, where $(C_x/C_{Si})_{air}$ are the ratio of the concentrations of element X to Si in the particulate air sample, and $(C_x/C_{Si})_{crust}$ are concentrations of element X to Si in an average crustal rock composition (Mason and Moore, 1982). An EF of equal or less than 1.0, indicates a soil-derived origin or dust (or other crustal matter such as road dust) whereas an EF greater than 1.0 indicates that the element would have a significant contribution from non-crustal sources (Mkomas *et al.*, 2010).

Figure 7 presents the value of EF which shows that none of the elements (other than Si as the reference element) has an EF less than 1.0, suggesting that most of the elements are not associated with soil origin. Nevertheless, Al, Fe, and Ti with EF of less than 5 to a certain extent originated or are classified as soil origin. Meanwhile, the bulk of the elements can be considered of non-crustal origin, alternatively marine or anthropogenic derived elements, especially Ag, B, Cd, Cr, Cu, Ni, Pb, and Zn, which are known to be associated with man-made activities (Nayebare *et al.*, 2016).

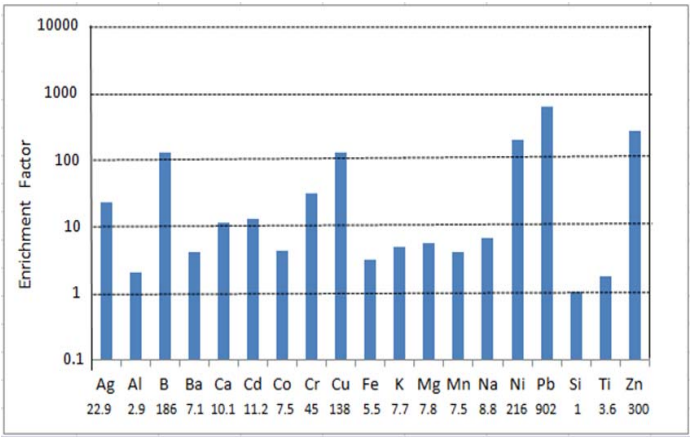

Fig. 7 Enrichment factors of elements in PM_{10} of Makassar

CONCLUSIONS

The ambient PM_{10} particulate matter collected over a period of one year (i.e. February 2012 - January 2013) at Daya, a mixed commercial-residential-industrial site in Makassar, Province of South Sulawesi Indonesia has been reported in this paper. The overall average of PM_{10} concentration was found to be 32.92 $\mu g/m^3$, lower than those found in other major cities of the world. The black carbon constituted 6.1%, the highest percentage in PM_{10}, followed by SO_4^{2-} (4.5%), NO_3^- (3.4%), and Cl^- (2.7%) while each of the elemental concentration represented less than 2% of the PM_{10} at the site. The enrichment factors of the elemental components suggested that most of the elements were not associated with soil origin but to be from marine or anthropogenic sources.

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