Black carbon and elemental concentration of ambient particulate matter in Makassar Indonesia

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Abstract. Airborne particulate matter with aerodynamic diameter of less or equal to 10 um or PM_{10}, has been collected on a weekly basis for one year from February 2012 to January 2013 at one site of Makassar, Province of South Sulawesi Indonesia. The samples were collected using a size selective high volume air sampler sited at Daya, a mixed urban, commercial and industrial area in the city of Makassar. The concentration of black carbon (BC) along with a total of 14 elements (i.e Al, Ba, Ca, Cr, Fe, K, Mg, Ba, Na, Ni, Pb, Si, Ti and Zn) were determined from the sample. Results showed that the average particulate mass concentration was 32.9 ± 11.6 μg/m^3, with BC and elemental concentration constituted 6.1% and 10.6% of the particulate concentration, respectively. Both BC and elemental constituents contributed 16.7% while 83.3% of the particulate matter remained to be counted for. The black carbon concentration was higher during the dry months which may be attributed to rampant biomass burning during hot and dry weather conditions, apart from other possible sources. Most of the elements were enriched relative to soil origin illustrating of their possible associations with other sources such as marine and anthropogenic derived aerosols, particularly Cr, Ni, Pb, and Zn, which are known to originate from man-made activities.

Keywords : Air Pollution, Particulate Pollution, Black Carbon, PM_{10}, Elemental pollution.

1. Introduction
Air pollution has also now become a serious and worsening situation in rapidly growing cities of developing countries especially in major cities that experience rapid urbanization [1]. Ambient particulate matter represents a complex mixture of organic and inorganic substances, which are defined as "a mixture of solid, liquid or solid and liquid particles suspended in the air [2].

Particles can be characterized and classified into several categories such as size, density, shape and composition. PM_{10} is referred to as ambient particulate matter having particulate size of equal or less than 10 micrometers which could cause adverse human health impact. The health effects on human not merely depend on particle size but also on the concentration and elemental constituents of the particulate matter. Thus, the understanding on the physical and chemical characteristic of ambient particulate matter is important in the development of a rational control strategy.
This is particularly important in Makassar, where studies regarding air pollution in the city are limited. Thus, this paper presents the study on the atmospheric particulate and its elemental concentration in the city of Makassar sampled over a period of one year.

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2. Material and Methods

2.1. Sampling site

Makassar city has a strategic position because it is located near from the south and north in the provinces of Sulawesi. In fact, it is near from the western region to the eastern region of Indonesia and from the northern to the southern region of Indonesia. Makassar is located between 119° 24′ 38" East longitude and 5° 8′ 19" South latitude this regency bounded by Maros Regency at the North Side, Maros Regency at the East Side, Gowa Regency at the South Side, and Makassar Strait at the West Side. The area of Makassar is 175,77 square km which include fourteen districts. The sampling was carried out at Daya in Makassar, known to be a mixed urban, commercial and industrial area.

2.2. Sampling

The PM_{10} sample was collected using a standard size-selective high volume air sampler using a glass fiber filter (8x10in) as the collection medium. The sampler provides for the measurement of the mass concentration of the particulate matter with an aerodynamic diameter less than or equal to a nominal 10 micrometer (PM_{10}) in ambient air over a 24-hour period with a sampling frequency of once a week. The particulate concentration was determined by dividing the particulate mass collected with the total volume of air sampled.

2.3. Analysis of Sample

The black carbon (BC) concentration in PM_{10} sample was measured using a Smoke Stain Reflectometer (Model 43D) based on a reflectance method [3-5]. The elemental analysis was performed using the Inductively Coupled Plasma Optical Emission Spectrometry or ICP-OES (VARIAN Model 715-ES). A total of fourteen elements were determined in the PM_{10} sample, which include Al, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Si, Ti and Zn.

3. Results and Discussion

3.1. Particulate Matter (PM_{10})

Figure 1 presents the monthly variation of the particulate matter PM_{10} concentration over the sampling period from February 2012 to January 2013 at Daya, Makassar which showed that the highest average monthly concentration was in June while the lowest was in February, conforming with the dry and wet season experience in the region, respectively. The overall average particulate concentration was 32.9 ± 11.6 $\mu g/m^3$, exceeding the WHO guidelines limit of 20 $\mu g/m^3$. Infact, it was observed that only one of the months was in compliance with the guidelines. However, the concentration of PM10 particulate matter found in this study was much lower than those found in Mumbai and Shanghai [6-7].
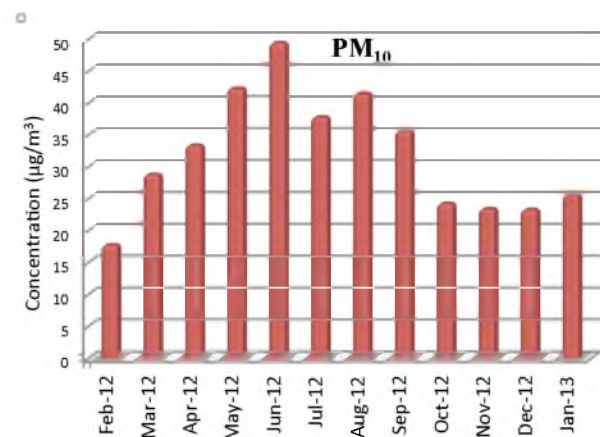

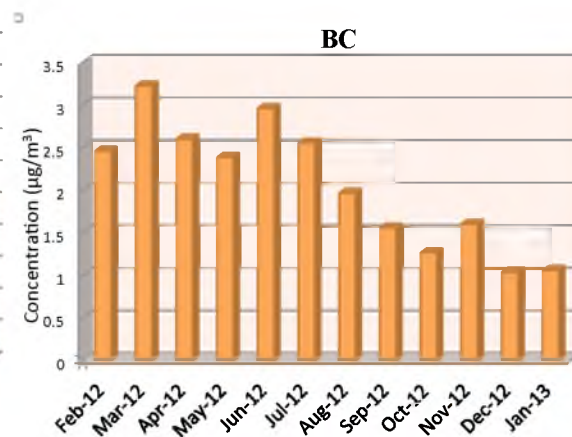**Figure 1**. The monthly PM_{10} in Makassar　　　　**Figure 2.** The monthly average BC concentrations.

3.2. Black Carbon

Black Carbon is a non-volatile fraction of the particulate matter, also known as elemental carbon [8]. It is emitted to the atmosphere due to incomplete combustion from sources such as diesel engines, biomass burning [9-10] and pyrolysis of biological material during combustion processes [11]. It is reported that the main source of black carbon in the urban environment is due to automobile emission from transportation.

Figure 2 presents the monthly average BC concentration variations in Makassar showed that decreasing BC concentration towards the wet season in the region. The high BC concentration was observed during dry months from March to July i.e 3.2 ± 0.8 μg/m^3, 2.6 ± 0.1 μg/m^3, 2.4 ± 1.3 μg/m^3, 2.9 ± 0.9 μg/m^3, 2.6 ± 0.4 μg/m^3, respectively. This observation may be attributable to rampant biomass burning especially during these dry weather conditions, apart contributions from other possible sources like automobile. On the global scale, the black carbon aerosol is considered to be the second largest radiative forcing agent after carbon dioxide and it reported that 85 % of black carbon total forcing is anthropogenically derived [12-13].

Table 1 presents the mean, standard deviation and ranges of the pollutants concentration through out the sampling period, which showed that BC contributes 6.11%, the highest percentage among the other components. The BC contributed 4.9 % of the PM10 concentration sampled in Ashaiman, a Semi-Urban Area of Ghana, but a higher percentage of 18.4% was in the lower PM$_{2.5}$ particulate size fraction [14]. The reported that a high percentage of BC of 25.1 % was found in the PM$_{2.5}$ particulate matter sampled in Bandung Indonesia [15], concurring the BC is associated with combustion sources which predominantly resides in the finer size fraction of the particulate matter.

Table 1. Mean, standard deviations, minimum and maximum concentration of pollutant concentration at Makassar.

Element	Mean	Std deviation	Minimum	Maximum
PM$_{10}$	32.92 (100)	11.06	13.29	63.02
BC	2.0132 (6.11)	0.9273	0.5924	4.3919
Al	0.5047 (1.53)	0.5065	0.0412	1.6092
Ba	0.0092 (0.03)	0.0101	0.0004	0.0729
Ca	0.6362 (1.93)	0.5060	0.1092	1.7336
Cr	0.0069 (0.02)	0.0046	0.0012	0.0186
Fe	0.4276 (1.30)	0.2976	0.0142	1.2730
K	0.3578 (1.09)	0.4137	0.0013	1.3639
Mg	0.2395 (0.73)	0.2379	0.0007	1.2670
Mn	0.0165 (0.05)	0.0199	0.0001	0.0938
Na	0.5451 (1.65)	0.4779	0.0109	1.5476
Ni	0.0209 (0.06)	0.0279	0.0012	0.0926
Pb	0.0297 (0.09)	0.0211	0.0008	0.0820
Si	0.6074 (1.84)	0.4326	0.0489	1.9656
Ti	0.0377 (0.11)	0.0641	0.0012	0.2872
Zn	0.0395 (0.12)	0.0270	0.0002	0.0974

Number of samples = 53
Unit = μg/m^3
( ) = percent of PM$_{10}$

As in Table 1, the percentage contributions from the naturally soil derived elements like Ca (1.93%), Si (1.84%), Al (1.53%), Fe (1.30%), K (1.09%) and sea salt derived elements Na (1.65%), Mg (0.73%) were also significant at the site. Ca, Si, Fe and K were soil derived elements in their studies of atmospheric aerosols in Kuala Lumpur, although Ca could also originated from cement related

industry [16]. Interesting to note that the combined contribution of both BC and elemental component only represent 16.7% (i.e 6.1%+10.6%) of the total mass concentration of the PM_{10} sampled at the site, whilst 83.3% are still unexplained, which needs further investigation.

Table 2. Comparison of elemental concentrations (μg/m3) in Makassar with other cities of Indonesia.

Element	This Study, Indonesia	Lembang, Indonesia[a]	Bandung, Indonesia[b]
Al	0.5047	0.425	0.870
Ba	0.0092	-	-
Ca	0.6362	0.257	1.555
Cr	0.0069	0.065	0.070
Fe	0.4276	0.286	0.825
K	0.3578	0.125	0.315
Mg	0.2395	-	0.295
Mn	0.0165	0.008	0.035
Na	0.5451	0.245	1.110
Ni	0.0209	-	0.050
Pb	0.0297	0.016	0.040
Si	0.6074	-	0.870
Ti	0.0377	0.041	0.080
Zn	0.0395	0.029	0.760

[a] [17]; [b] [15]; '-' not analyzed

Table 2 presents the comparison of elemental concentration found in other cities in Indonesia with respect to those from Makassar showed that the ambient elemental concentrations were higher in Bandung compared to Makassar and Lembang. As expected, Bandung is the third largest city in Indonesia (after Jakarta and Surabaya) is more developed and industrialized as compared to Makassar (the seventh largest city).
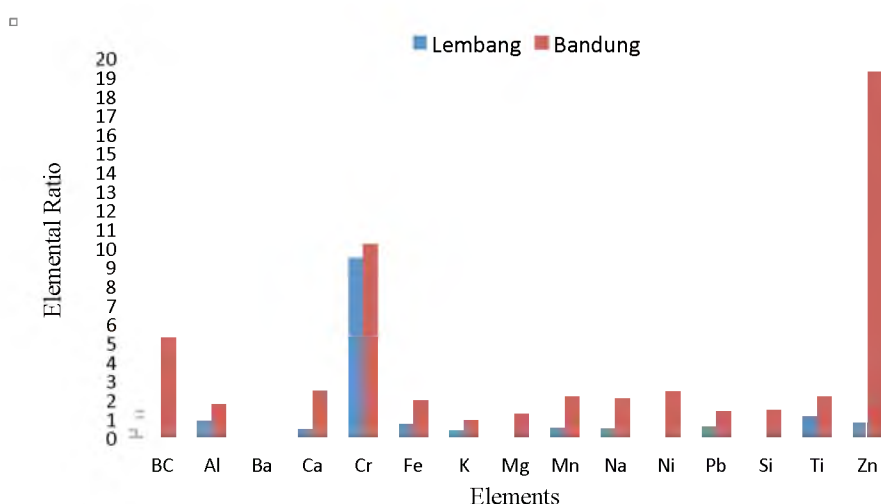

Figure 3. Elemental ratio in Bandung and Lembang with respect to Makassar.

Figure 3 presents the elemental concentration ratio between the cities in Indonesia with respect to Makassar which clearly illustrates that the contributions of air pollution sources are siginificant in a

larger and developed city center. As depicted in Figure 3, the elemental ratio were mostly higher in Bandung compared to Lembang with respect to Makassar which indicates that the level of air pollution sources is influenced by the development of a particular region.

3.3. Enrichment Factors
An Enrichment Factor (EF) technique was used to indicate the whether the element is naturally derived soil origin or otherwise. The EF is calculated by comparing the relative abundance of the element of interest in air to its crustal rock composition, with Si which is the most common element of soil, taken as the reference element. The EF is estimate 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 and Si in the particulate air sample, and $(C_x / C_{Si})_{crust}$ are concentrations of element X and Si in average crustal rock composition [18]. 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 EF exceeding greater than 1.0 indicates that the element would have a significant contribution from non-crustal sources [19].
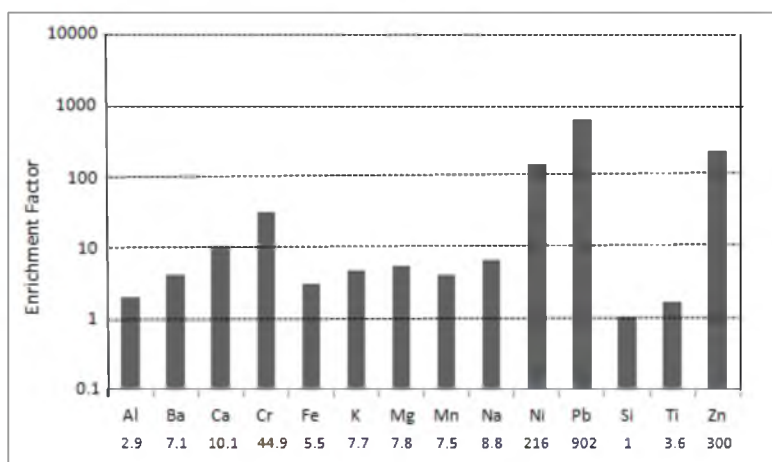

Figure 4. Enrichment factors of elements in PM_{10} of Makassar.

Figure 4 presents the calculated EF which showed that none of the element (other than Si as the reference element) having EF less than 1.0, suggesting that most of the elements are not associated with soil. Nevertheless, Al and Ti with EF of less than 5, could to a certain extend originate or classified as soil origin. While the bulk of the elements can be considered as non-crustal origin alternatively marine or anthrophogenically derived elements especially Cr, Ni, Pb, and Zn, which are known to associate with man-made activities.

4. Conclusion
Airborne particulate matter with aerodynamic diameter of less or equal than 10 um or PM_{10}, collected over a period of one year at one site of Makassar, Province of South Sulawesi Indonesia has been reported in this paper. The overall average particulate concentration was $32.9 \pm 11.6\,\mu g/m^3$, exceeding the WHO guidelines limit of 20 $\mu g/m^3$. The black carbon concentration was found to constitute 6.1% of the particulate mass. Similarly, the black carbon concentration was higher during the dry months which may be attributed to rampant biomass burning during hot and dry weather conditions, apart contributions from other possible sources. Both BC and elemental component contributed merely 16.7% of the total particulate mass concentration, while 83.3% is yet to be accounted for. Most of the elements were enriched relative to soil origin illustrating of their possible associations with other sources such as marine and anthropogenic derived aerosols, particularly Cr, Ni, Pb, and Zn, which are known to originate from man-made activities.

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