

# Cairo University

# Journal of Advanced Research



## **ORIGINAL ARTICLE**

# Mass size distributions of elemental aerosols in industrial area



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## ARTICLE INFO

Article history: Received 9 April 2014 Received in revised form 14 June 2014 Accepted 22 June 2014 Available online 28 June 2014

*Keywords:* Mass concentration Aerosol particles Size distribution Cascade impactor

## ABSTRACT

Outdoor aerosol particles were characterized in industrial area of Samalut city (El-minia/Egypt) using low pressure Berner cascade impactor as an aerosol sampler. The impactor operates at 1.7 m<sup>3</sup>/h flow rate. Seven elements were investigated including Ca, Ba, Fe, K, Cu, Mn and Pb using atomic absorption technique. The mean mass concentrations of the elements ranged from 0.42 ng/m<sup>3</sup> (for Ba) to 89.62 ng/m<sup>3</sup> (for Fe). The mass size distributions of the investigated elements were bi-modal log normal distribution corresponding to the accumulation and coarse modes. The enrichment factors of elements indicate that Ca, Ba, Fe, K, Cu and Mn are mainly emitted into the atmosphere from soil sources while Pb is mostly due to anthropogenic sources. © 2014 Production and hosting by Elsevier B.V. on behalf of Cairo University.

#### Introduction

In the recent years, aerosols have received increasing attention due to the roles they play in many climate and environmental processes. Size and chemical composition of atmospheric particles are important parameters in several processes occurring in the atmosphere [1], for instance, visibility reduction, cloud and fog formation, particle growth and gas-particle interactions [2]. Particles also have adverse health effects depending strongly on their size, specific surface area, number and chemical composition that regulate the toxicity of any specific

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element. In addition to the environmental and health effects of aerosol particles they also can cause corrosion and damage to materials and works of architecture and arts.

Metals are commonly found in atmospheric particles. While they can be present in almost all sizes of atmospheric particulate, in general, fine particulate carries higher concentrations of metals than coarse particulate [3,4]. Metals associated with respirable particles have been shown to increase numerous diseases [5,6]. Metals in the urban atmosphere are frequently associated with specific pollutant sources, and these are often used as tracers in order to identify the source of atmospheric particulate [7–11].

Knowledge of the size distribution of atmospheric particles within which trace elements and metals reside is not only vital in understanding particulate matter effects on human health, but also controls the extent to which metals may be dispersed via atmospheric transport and hence is a prerequisite for the determination of rates of deposition of metals to the Earth's surface [12].

2090-1232 © 2014 Production and hosting by Elsevier B.V. on behalf of Cairo University. http://dx.doi.org/10.1016/j.jare.2014.06.006

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The dispersion and accumulation of particulate matter in any location is mainly affected by the existing sources, meteorological conditions and local topography [11]. Atmospheric aerosol dispersion in industrial zones has received little attention. Therefore, the objectives of this study were to investigate the mass concentration and mass size distribution of elements in the aerosols at industrial area of Samalut in El-minia governorate (upper Egypt).

## Methodology

In the present work a low pressure Berner cascade impactor was used as an aerosol sampler. The impactor contains eight size fractionating stages and operates at a flow rate of  $1.7 \text{ m}^3 \text{ h}^{-1}$ . The cut-off diameters of the impactor stages are 82, 157, 270, 650, 1110, 2350, 4250 and 5960 nm. Cut-off diameter is defined as the particle size that gives 50% of the collection efficiency. An accurate method of the impactor was calibrated in the isotope laboratory Gottingen University, Germany [13]. Measurements were taken from August 2012 to January 2013. Three or four runs were conducted in each month. The sampling time of each run is 6 h. Samples were collected at iron and steel Quarry closed to the cement factory in Samalut/El-minia (latitude: N 28° 18  $\setminus$  30  $\setminus$ , longitude E 30° 42  $\setminus$  28  $\setminus$  ). This site represents an industrial area surrounded from the east by mountains. These mountains are formed with limestone rocks and have elevation of about 20 m (Fig. 1).

The samples collected by low pressure Berner cascade impactor were analyzed by atomic absorption spectroscopy for seven elements including Lead (Pb), Manganese (Mn), Iron (Fe), Copper (Cu), Potassium (K), Calcium (Ca) and Barium (Ba). The sample was prepared for elemental analysis by cutting substrate into small pieces and then 5 mL diluted HCl (1 + 1) was added to the sample and gently heated on hotplate till complete dissolution. Few drops of HNO<sub>3</sub> are added to the solution. The solution is transferred to auto sampler cup and completed to 10 mL deionized water. This elemental analysis was performed at National Institute for Standards, NIS-Egypt.

Meteorological parameters (temperature and relative humidity) were recorded by Hi 8564 thermo hygrometer during the sampling. The temperature varied between 30 to 39 °C with mean value 36 °C while relative humidity varied between 18 to 42% with mean value 32%. Samples collected under abnormal weather conditions were canceled. Gravimetric analysis of the samples was conducted by Mettler analytical AE240 Dual Range Balance to get the collected mass of the aerosol particles on the substrates.

Knowing the mass of the collected particles, the flow rate of the impactor and the sampling time, mass concentrations of aerosol particles were calculated as follows:

$$v = \frac{m}{Q \cdot t} \dots \mu g/m^3$$

where v is the specific mass concentration, m is the total deposited aerosol mass on the impactor stages ( $\mu$ g), Q is the impactor flow rate (m<sup>3</sup>/h) and t is the sampling time (h).

The parameters of the mass size distribution, mass median aerodynamic diameter (MMAD) and geometric standard deviation (GSD) were given by the following equations [14].

$$\ln \text{MMAD} = \frac{\sum n_i \ln d_i}{\sum n_i}$$



Fig. 1 Sampling site on EL-Minia governorate map.

$$\ln(\text{GSD}) = \left[\frac{\sum n_i (\ln d_i - \ln MMAD)^2}{\sum n_i}\right]^{\frac{1}{2}}$$

where MMAD is the Mass Median Diameter,  $n_i$  is the fraction in stage *i*,  $d_i$  is the cutoff diameter of the stage *i* and GSD is the geometric standard deviation. MMAD is defined as the diameter at 50% cumulative fractions. GSD of the size distribution is defined as the diameter at 84% cumulative mass divided by the diameter obtained at 50%.

#### **Results and discussion**

## Elemental mass size distribution of aerosols

Mass size distributions of individual elements are presented in Figs. 2-5a. The distributions of the investigated elements [Pb, Mn, Fe, Cu, K, Ca and Ba] are bi-modal log normal distribution corresponding to the accumulation and coarse modes. Accumulation mode, consisting of long-lived particles of sizes of a few tenths of a micrometer (100 nm < particle diameter)Dp < 2000 nm). Particles in this mode are forming by gas to particle conversion, chemical reactions, condensation and coagulation, while the particles in the coarse mode (Dp > 2000 nm) are generated by mechanical processes such as sea spray, erosion, and resuspension and are removed by sedimentation and washout. This mode contains windblown dust, sea salt spray, and plant materials. The coarse particles are characterized by a high deposition velocity and they have short residence times. The residence time of aerosols depends on their size, chemistry and height in the atmosphere. The modal size and composition of aerosols are varied, depending on the nature of the surface cover and atmospheric condition.



**Fig. 2** Mass size distribution of Pb and Fe at industrial area of Samalut.

Table 1 illustrates the distribution parameters. The lowest mass median aerodynamic diameter of the accumulation mode,  $MMAD_A$  (330 nm) is found for Mn with a geometric standard deviation,  $GSD_A$  of 2.25 while Pb has the highest  $MMAD_A$  (780 nm) with a  $GSD_A$  of 1.75. Cu has the lowest mass median aerodynamic diameter in the coarse mode,  $MMAD_C$  (2422.2 nm) with a  $GSD_C$  of 1.1 while Fe has the highest  $MMAD_C$  (3830.9 nm) with a  $GSD_C$  of 1.4. The bimodal nature of elements size distribution has been reported for different industrial sites [11,15].

The mass size distribution of Pb is mostly concentrated in the accumulation mode (650–1100 nm) and coarse mode (2350 nm). Mn distribution shifts to lower size in the accumulation mode (157–650 nm) and it is concentrated at the same size (2350 nm) of coarse mode.

The mass size distributions of Fe and Cu are mostly concentrated in the accumulation mode (157-1100 nm) and coarse mode (2350-4250 nm) for Fe and shifts to higher size at 5960 nm for Cu.

The mass size distributions of Ca and Ba are mostly concentrated in the accumulation mode (650–1100 nm) and coarse mode (2350–4250 nm). K is mostly concentrated at the coarse mode (2350 nm).

These distributions suggesting that the natural crustal sources i.e. dust mountains contribute the industrial sources for the emission of the elements [16]. It can be seen that the



**Fig. 3** Mass size distribution of Cu and Ca at industrial area of Samalut.

elements in the accumulation mode are more distributed  $(2.25 \ge GSD_A \ge 1.4)$  than the elements in the coarse mode  $(1.14 \ge GSD_C \ge 1.41)$ . This could be attributed to the difference in aerosols origins and the variation of their residence time in the atmosphere.

The enrichment factor (EF) was calculated to differentiate elemental concentrations from various sources. EF was determined to show the degree of enrichment of a given element in the atmosphere compared to the relative abundance of that element in reference material. Usually, Si, or Al or Fe is used as the reference crustal element. In this study Fe was used as a reference element relative to the crustal material. The EF of an element E in an aerosol sample is defined as [1]:

$$EF = \frac{\left(\frac{E}{R}\right)air}{\left(\frac{E}{R}\right)crust}$$

where *R* is the reference element and  $\left(\frac{E}{R}\right)air$  is the concentration ratio of *E* to *R* in aerosol sample and  $\left(\frac{E}{R}\right)crust$  is the concentration ratio of *E* to *R* in the crust. If EF is less than 10, crustal soils are most likely the predominant source of element *E*, the elements with an EF value close to unity show strong influence of a natural component and if EF is higher than 10, the elements would have a significant contribution from non crustal sources. The investigated elements (K, Cu, Mn, Ca and Ba) have EF less than 10 suggesting that they are attributed to soil and dust sources. Fe has a unity EF which



**Fig. 4** Mass size distribution of K and Mn at industrial area of Samalut.



Fig. 5a Mass size distribution of Ba at industrial area of Samalut.

reveals a strong impact of a natural component. Anthropogenic activities is indirectly contributing the re-suspension of these elements in the air even so their natural origin [16]. Pb showed an EF higher than 10 suggesting that Pb is emitted mainly from anthropogenic sources.

 Table 1
 Average mass size distribution parameters of elements at industrial area of Samalut (El-Minia).

Accumula	tion	Coarse		
Element	MMAD <sub>A</sub> (nm)	GSD <sub>A</sub>	MMAD <sub>C</sub> (nm)	GSD <sub>C</sub>
Pb	780	1.75	3059.5	1.40
Mn	330	2.25	3053.3	1.41
Fe	380.6	2.3	3830.9	1.40
Cu	654.8	1.4	2422.2	1.10
Κ	370.5	2.3	3136.1	1.30
Ca	598.5	2.1	3456.8	1.40
Ba	630	1.9	3312.3	1.40

The average mass size distribution of particulate matter (PM) at industrial area of Samalot is shown in Fig. 5b. The obtained mass size distributions are found as bi-modal log normal distribution which is corresponding to accumulation and coarse mode. The mean value of the mass median aerodynamic diameter for accumulation mode, MMAD<sub>A</sub> is 392.8 nm varied between 343.5 nm (in November 2012) to 471.7 nm (in January 2013) with mean geometric standard deviation (GSD<sub>A</sub>) 2.43 ranged from 2.29 (in January 2013) to 2.6 (in December 2012). Mass median aerodynamic diameter for coarse mode, MMAD<sub>C</sub> varied between 3271 nm (in January 2013) to 3895.8 nm (in October 2012) with mean value 3676.2 nm which has GSD<sub>C</sub> varied between 1.43 (in December 2012) to 1.48 (in September 2012) with mean value 1.46.

The particles in the accumulation mode are more distributed ( $2.6 \ge \text{GSD}_A \ge 2.3$ ) than the particles in the coarse mode ( $1.5 \ge \text{GSD}_C \ge 1.4$ ). This can be attributed to the difference in aerosols origins and their residence time. The accumulation mode is formed by gas to particle conversion through chemical reactions. This process is affected strongly by the concentration of some impurities in the atmosphere such as sulfur and nitrogen oxide. The particles of this type grow faster than particles in the coarse mode. On the other hand the residence time of the particles in coarse mode is short (high deposition velocity), where there is no chance for these particles to grow by coagulation to produce abroad size distribution.



**Fig. 5b** Average mass size distribution of particulate matter (PM) at industrial area of Samalut.



Fig. 6a Mass concentration of elements at industrial area of Samalut.

#### Elemental mass concentration of aerosols

Average mass concentrations of the elements are shown in Fig. 6a. The mean concentration ranged from  $0.42 \text{ ng/m}^3$  to  $89.62 \text{ ng/m}^3$ . Aerosol concentrations varied depending on local sources and meteorological conditions. The highest concentration is obtained for Fe (89.62 ng/m<sup>3</sup>) followed by K (25.65 ng/ m<sup>3</sup>), Cu (2.99 ng/m<sup>3</sup>), Mn (2.09 ng/m<sup>3</sup>), Pb (1.68 ng/m<sup>3</sup>) followed by Ca  $(0.52 \text{ ng/m}^3)$  and the lowest is Ba  $(0.42 \text{ ng/m}^3)$ . The high concentration of Fe is probable due to re-suspension of mountains local dust [1] where sampling area is characterized by an industrial nature as it is surrounded by the quarries and the cement plant. The low concentration of Ba is due the absence of the main source responsible for the emission of Ba in the sampling area as the main source of barium in aerosols is the painting works of motor vehicles [17].

In general, Fe, Mn and Pb were associated with natural and industrial-related elements suggesting both origins. The possible industrial sources of Fe and Mn are ferromanganese production plants, steel and cement industries [18,19]. Another possible source of Fe is motor vehicle emissions, Re-suspended soil, traffic and Heavy oil combustion [20,21].

Correlation analyses have been conducted and they are presented in Table 2. The correlations indicate a potential common origin, especially for Cu/Fe, Cu/Pb and Fe/Pb having correlation coefficient values higher than 0.9. A strong positive correlation between two elements indicates that the characteristics and origin of emission for both elements may be similar.

Fig. 6b shows the variation of mass concentration of aerosol particles with average metrological observations of ambient temperature and relative humidity from August 2012 to

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Variation of particle mass concentration, temperature Fig. 6b and relative humidity at industrial area of Samalut.

January 2013 at industrial area of Samalot (El-Minia). In the size range of Berner impactor the mean mass concentration of aerosols is ranged from  $215 \pm 14.6 \,\mu\text{g/m}^3$  (in August 2012) up to 550  $\pm$  24 µg/m<sup>3</sup> (in December 2012) with mean value  $315 \pm 17.4 \,\mu\text{g/m}^3$ . This value is nearly close to the results obtained by EL-Saied [16]; 275 µg/m<sup>3</sup> (in Cairo) and 288  $\mu$ g/m<sup>3</sup>(in Tanta).

The mass concentrations are nearly changed inversely to the air temperature. At high temperature, especially when the weather is calm, air stratus near the surface of the earth move upward convection currents, and then the dust will distribute vertically at large area. The humidity plays an important role in the particle growth that affects on the particle deposition.

#### Conclusions

In this study, characteristics of aerosol particles were reported in industrial area of Samalut city (El-minia/Egypt) using low

Table 2	Matrix of corr	elation coefficients	among different	elements.	
	P	G	TZ.	G	

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	Ba	Ca	К	Cu	Fe	Mn	Pb
Ва	1						
Ca	-0.72118	1					
K	-0.65456	0.238743	1				
Cu	0.033387	0.658145	-0.23821	1			
Fe	0.010859	0.661361	-0.50729	0.907677	1		
Mn	-0.90521	0.358443	0.731935	-0.44964	-0.41891	1	
Pb	0.01526	0.661321	-0.49965	0.91531	0.999822	-0.42491	1

pressure Berner cascade impactor as an aerosol sampler. Seven elements were investigated including Ca, Ba, Fe, K, Cu, Mn and Pb using atomic absorption technique. The mean mass concentrations of the elements ranged from  $0.42 \text{ ng/m}^3$  to  $89.62 \text{ ng/m}^3$ . The highest concentration is obtained for Fe ( $89.62 \text{ ng/m}^3$ ) followed by K ( $25.65 \text{ ng/m}^3$ ), Cu ( $2.99 \text{ ng/m}^3$ ), Mn ( $2.09 \text{ ng/m}^3$ ), Pb ( $1.68 \text{ ng/m}^3$ ) followed by Ca ( $0.52 \text{ ng/m}^3$ ) and the lowest is Ba ( $0.42 \text{ ng/m}^3$ ). The mass size distributions of the investigated elements were bi-modal log normal distribution corresponding to the accumulation and coarse modes.

The enrichment factors indicate the influence of the significant sources in the investigated area. The investigated elements (K, Cu, Mn, Ca and Ba) have EF less than 10 suggesting that they are attributed to soil and dust sources. Fe has a unity EF which reveals a strong impact of a natural component. Pb showed an EF higher than 10 suggesting that Pb is emitted mainly from anthropogenic sources.

#### **Conflict of Interest**

The authors have declared no conflict of interest.

#### **Compliance with Ethics Requirements**

This article does not contain any studies with human or animal subjects.

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