IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 12, Issue 8 Ver. I (August. 2018), PP 29-36
www.iosrjournals.org

Morphological and Chemical Composition of Total Particulate Matter in Region of Qena/ Egypt

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Abstract : *This work concerns chemical constituents and morphology of total particulate matter (TPM) using scanning electron microscope SEM, coupled with energy dispersive X-ray (EDX). The samples of TPM are collected in Qena city, upper Egypt during the period from June 2016 to January 2017. Results indicated that the average mass concentration of total suspended particulate matter was 158.3 ± 40.1 μg/m^3, the winter average value was 182.5 μg/ m^3, while the summer average value was 132.5 μg/m^3. In the entire study period TPM particles have irregular, spherical and aggregated shapes. Elemental analysis indicates that C, Si and Ca were the abundant elements in the particles followed by Al, Na and Fe amongst all the elements. Carbon soot particles were the dominants with high percentage in all the TPM samples. With respect to the crustal and mineral dust particles, Si rich particles associated with Al was present in major amount than other elements. The Ca rich particles were the second abundant. This indicates that TPM particles mainly originated from soil crust and anthropogenic activities.*

Keywords - *Total particulate matter, Morphology, Elemental analysis, Qena, Egypt*

Date of Submission: 23-07-2018 Date of acceptance: 10-08-2018

I. Introduction

Particulate Matter (PM) is a widespread air pollutant, consisting of a mixture of solid and liquid particles suspended in the air with particle diameters in the range of about 0.1 to about 100 μm. Despite their small size an excess of PM in the ambient air can have many negative side effects on the climate and the human health. Particulate matter (PM) is one of six criteria air pollutants regulated by the World Health Organization (WHO) and the Environmental Protection Agencies (EPA) [1].

PM interact with the surrounded environment in many ways and can cause environmental effects such as reduction in visibility, influencing the balance of radiation, and changing cloud properties. The interaction of particles can have both direct and indirect effects on solar radiation and climate [6]. particles play a major role in the acidification of clouds, rain and fog [2].

Aerosols in the atmosphere originate either from natural or anthropogenic sources. Natural sources release aerosols into the atmosphere independent on human activity. Examples of aerosols that originates from natural sources are pollen, smoke from forest fires, ash from volcanic eruptions, desert dust from sand storms and sea salt from wind driven sea spray. Anthropogenic sources involve emissions from fossil fuel combustion from both vehicular exhaust and industrial sources, biomass burning, agricultural activities and construction activities. The industries can directly and indirectly emit fine particles into atmosphere.

The chemical composition of PM can determine the type and intensity of toxic responses due to the presence of various metals and organic compounds that affect the impact of particles on the environment and human health. So that, there has been increasing interest in characterizing the morphology (size and shape) and chemical composition of atmospheric aerosol particles by using various techniques [1].

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectrometer (SEM-EDX) is the most useful technique that can give single particle observation and information about its elementary composition without any extraction of filters. Individual particle analysis can be used to derive size information of the composition and morphology of atmospheric aerosol particles which cannot be achieved by bulk chemical analysis alone. The further information such as sources, formation and size distribution of atmospheric PM can also be determined through the techniques [3, 4].

The elements Si, Ca, Al, Mg, Fe, and K tend to be related to crustal sources, such as agricultural activities, construction activities, and unpaved roads. Na tends to be more indicative of salt aerosol. Mg originates probably in marine aerosol due to a strong correlation with chloride. Ca is suggested to have both natural and anthropogenic origins, which is supported by the higher correlation between Ca and the diesel exhaust tracer. Fe can be emitted from industrial steel processes and from Earth's crust, while K can be

produced by biomass burning [5]. Some industrial processes can lead to increases in some metal concentrations such as Cd, Cu, Ni, Zn and Pb. These metals show to be having multiple sources and can be also produced by fuel combustion and vehicular emission [6]. Morphology of soot particles depend on different types of fuels, burning conditions and atmospheric processes [7]. These particles with fine size is considered as greater absorber, they have attracted special attention due to their contribution to climate change (global warming), reduced visibility and adverse health effects. The surface properties of soot particles provide a good adsorption conditions for many semi volatile compounds to form secondary aerosol particles [8].

This work aims at determination of the morphological and chemical composition of Total Particulate Matter (TPM) by using SEM- EDX technique as well as studying the variation of TPM composition over the summer and winter seasons at region of Qena/Egypt.

II. Material and Methods

2.1. Sample Collection and Site Location

Sampling was carried out at the outside balcony of atmospheric physics laboratory (about 10 m above the ground), located at the faculty of science, south valley university, Qena (26.2 N, 32.75 E)/Egypt. The site is represented urban area with moderate traffic due to the student activities inside the university, some colleges are situated around the site, also the campus contains some activities for new building construction. The university is lie in area about 6 km away from the center of Qena city which located in the south -western side of the sampling site. In the north and east sides, the university is surrounding by desert area.

The samples of TPM were collected with high volume air sampler (Model: HV2STE, F&G specialty products, Inc.). Volume sampler is a basic instrument that is widely used all over the world to measure particulate mass concentration. The sampler operated at a flow rate of 10 litter per minute for continuous 24-hour period. TPM samples were collected with an interval of 7 days (once in week) during a period covers summer, autumn and winter seasons. Summer is represented by the period (from June 2016 to July 2016), autumn season by October 2016 and winter season by (December 2016 to January 2017).

The particulate samples were collected on polycarbonate membrane filter (with 47mm diameter, 0.22 µm poor size), it is widely used for particulate collection especially for the SEM analysis. Before the sampling, the polycarbonate filters were dried at 50 °C for one hours. Both blank and loaded filters were conditioned in desiccator at temperature of 30 °C and relative humidity below 40% for at least 24 h to remove the moisture content of the filter and weighed on an electronic balance (sensitivity ± 0.1 mg, A&D company, Tokyo, Japan). Each filter was weighed at least three times before and after sampling. Repeat measurement of the filter weights provide more accuracy and reducing error in the aerosol mass concentration. Filters were handled only with clean tweezers to avoid contamination. After weighing, the samples were kept in storage boxes and stored in freezer until the time of analysis to prevent the degradation of PM components.

2.2. The Used SEM-EDX Instrument

The collected samples of TPM were analysed for morphological and elemental composition using SEM-EDX at National Research Centre, Cairo, Egypt. The analysis of PM samples was carried out by using scanning electron microscope SEM (Model: Quanta 250 FEG, Netherland) coupled with energy dispersive X-ray (EDX). The Quanta FEG250 SEM instrument is an environmental Scanning Electron Microscope used for high-resolution imaging and composition analysis by energy dispersive X-ray microanalysis (EDS).

III. Results and Discussion

3.1. Mass Concentration of Total Particulate Matter

Average mass **concentrations** of total particulate matter were 158.3 ± 40.1 **µg/m^3**, in the entire study period. This value is higher than the limit permitted by the Egyptian ambient air quality Standard, that given in the executive regulation of environmental law (125 **µg/m^3** for annual average). This high concentration of TPM may be due to the vehicular traffic activities, dust from the desert, biomass burning, fossil fuel combustion, and construction activities which is carried out around the sampling site.

Table 1 and **Table 2** show the monthly and seasonal variation of TPM mass concentrations over measurement site at Qena city. Higher concentration was observed during winter period (cold months), while lowest concentrations were in the summer period (hot month). This variation due to meteorological impacts and seasonal emissions of both anthropogenic and natural activities such as combustion process, soil dust particles, dust transportations [9]. Moreover, PM concentration also varied due to the different atmospheric conditions and long-range transportation from neighbouring areas [10]. These results are confirmed with the variation of PM10 concentrations as will be discussed in separate paper. This paper concerns only morphological and chemical composition of TPM in the study region regardless the effect of meteorological parameters.

Table 1. Monthly variation of TPM at Qena city.

Month	Total Particulate Matter Concentration µg/m^3		
	Min.	Max.	Ave.
June 2016	101.3	175.3	135.7
July 2016	105.8	124.4	117.4
October 2016	131.2	208.3	174.5
December 2016	100.3	275.7	186.3
January 2017	138.9	218.3	177.8

Table 2. Seasonal variation of TPM concentrations at Qena city.

Season	Total Particulate Matter Concentration µg/m^3		
	Min.	Max.	Ave.
Summer	101.3	175.3	131.5
Autumn	131.2	208.3	174.5
Winter	100.3	275.7	182.5
Total	100.3	275.7	158.3

3.2. Morphological and Elemental Analysis of TPM

The elemental analysis of the TPM samples was conducted using scanning electron microscope-energy dispersive X – ray (Model: Quanta FEG250). The samples of TPM were analysed for morphology, relative abundance of elements and individual particle analysis. The result displayed variation in size and morphologies. The shapes of particles varied from regular to irregular structures. **Fig. 1** shows the SEM image with EDS spectra for the filter before sampling to indicate the influence of particulate sampling on the morphology of filter surface and to inshore that the present elements are from the loaded particles due to air sampling. **Fig. 2** shows the SEM images along with surface elemental composition of TPM during both winter and summer seasons. As depicted from the figures, the shapes of particles varied from regular to irregular structures.

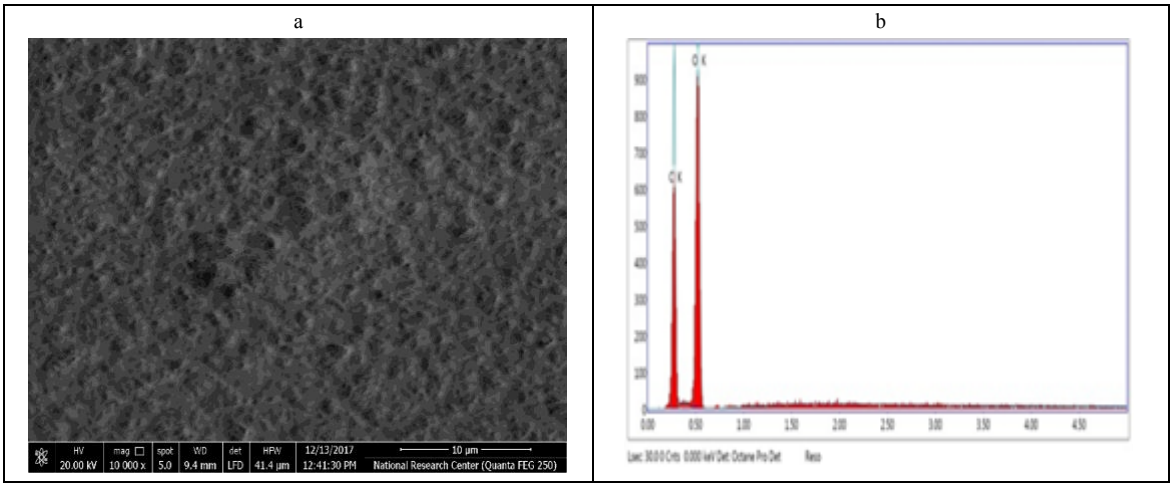

Figure 1. SEM image (a), with EDS spectra (b) for the polycarbonate filter (blank) before sampling.

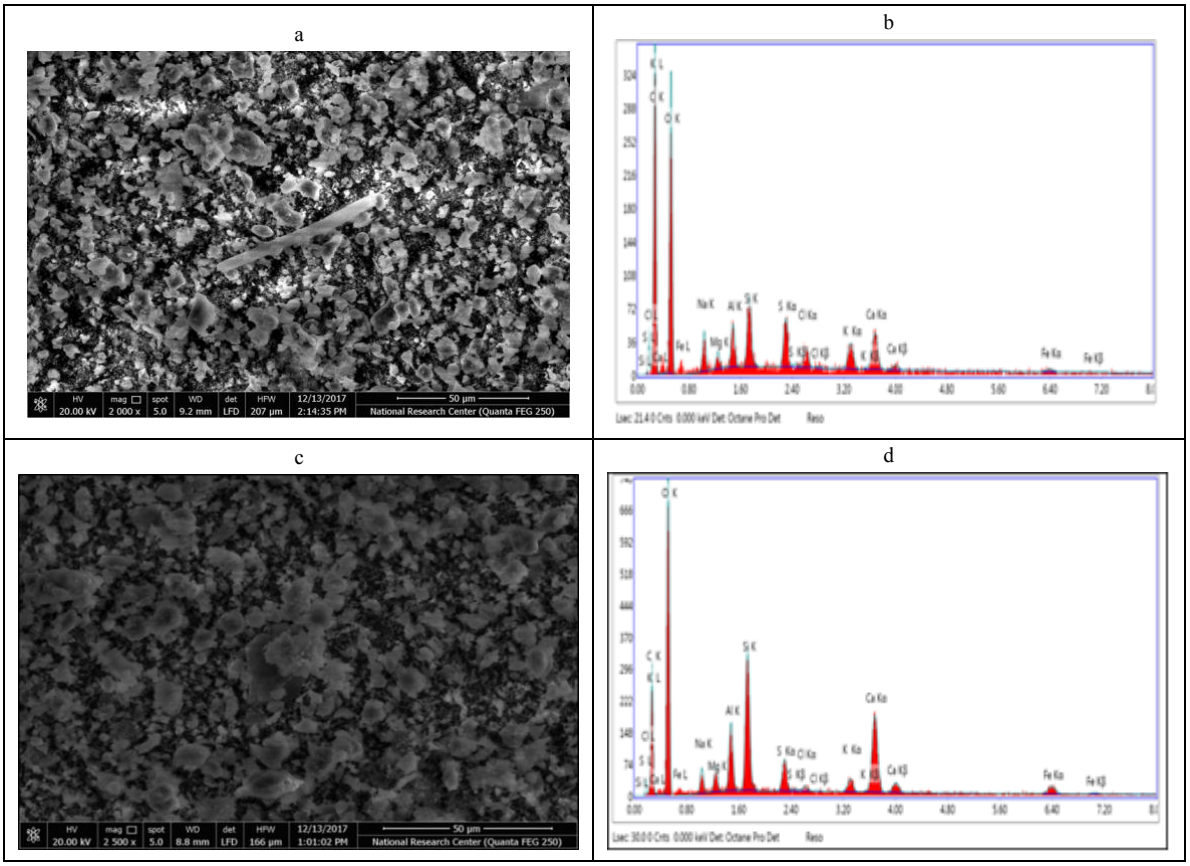

Figure 2. SEM image (a), with EDS spectra (b) of a loaded filter in winter season. Also, SEM image (c), with EDS spectra (d) of a loaded filter in summer.

3.2.1. Relative Abundance of Elements in TPM Samples

Fig. 2 shows the abundance of elements in TPM samples which was estimated by EDX technique. The EDX analysis of all the samples have shown the presence of various elements such as, carbon (C), silicon (Si), calcium (Ca), aluminium (Al), sodium (Na), magnesium (Mg), iron (Fe), sulphur (S), potassium (K) and chlorine (Cl) as indicated in **fig. 3** and **table 3**. It was observed that carbon was found to be abundant element in all TPM samples, followed by Si, Ca, Al, Na and Mg. Other elements like Fe, S, K, Na and Cl were also present in little amount. All the observed particles were associated with the presence of oxygen (O), therefore there is strong probability that these elements are present in the form of oxides or combined with some groups such as carbonates CO_3 and sulphates SO_4. Individual elemental composition during both winter and summer seasons indicates major composition of C therefore, the carbonaceous and Soot particles were found to be the most dominant during the study. The weight percentage of C were varied from 35.4 to 64.7% with average percentage of 44.8%. The crustal element Si was present in major amount than other crustal elements with relative weight percentage varied from 7 to 28.8%. Si mainly originated from soil crust and anthropogenic activities. However, particles with irregular morphology associated with Al, Na, K, and Ca may be originated from burning of agricultural residuals.

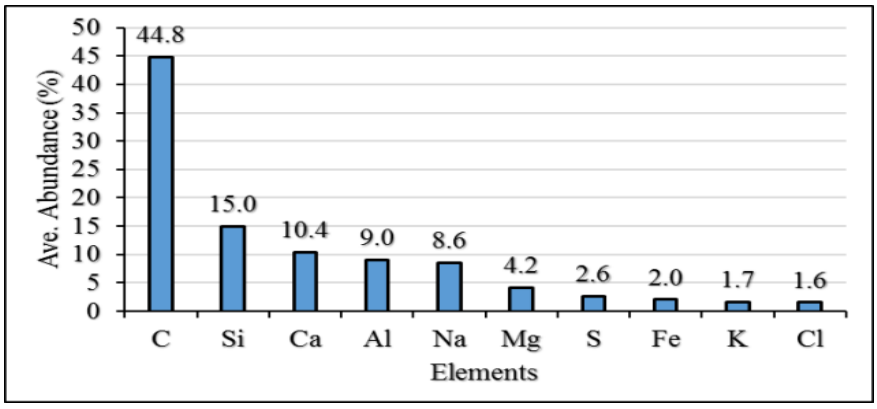

Figure 3. The average relative abundance of elements in TPM samples.

Table 3. The weight percentage of present elements in TPM samples.

Element	Ave.	S. D.	Max.	Min.
C	44.8	8.3	64.7	35.4
Si	15.0	6.9	28.8	7.0
Ca	10.4	4.6	18.3	5.1
Al	9.0	1.9	12.1	6.5
Na	8.6	3.5	15.2	4.3
Mg	4.2	1.3	6.6	2.5
S	2.6	1.0	4.0	1.2
Fe	2.0	0.9	3.5	1.0
K	1.7	0.7	2.9	0.9
Cl	1.6	1.2	3.4	0.4

The PM have different kind of morphology and chemical composition. The PM seasonal variability depend on various sources and weather conditions during different time. Based on morphology and elemental composition, different particles have been determined in various categories such as mineral dust particles which included (Aluminium - Silicates, Ca rich particles, Sodium Chloride (Na Cl) and S rich particles) and carbon soot particles as will be explained in the next section.

3.2.2. Mineral Dust Particles

Aluminium - Silicates

Aluminium-silicates and mineral dust particles which were present in TPM samples were characterized by high fractions and intensities of Si and Al with irregular shapes as seen in **fig. 4**. It was likely to be in the form of Al-silicates, along with other crustal elements including Na, Mg, Fe, and K. The different observed aluminium - silicate particles have basic structure, composed primarily from (Al, Si, O) and (Al, Si, Ca, O) which is named as (Grossular). They were also found to be along with other minerals like, (Fe - Al-Si-O) and (Mg - Al-Si-O). Other elements are present in the aluminium-silicate particles such as Na, and K. These particles are the major components of earth crust and are widely used in construction material. similar observations are found by [11-13]. The origin of silica may to be natural, aluminium-silicates particles make up the largest fraction of global particulate matter mass in the atmosphere, their origin is mainly crustal and can be lifted into the air by wind but, they can also come from anthropogenic activities such as erosion of building construction and road dust. All mineralogical components such as silica particles (SiO2) and Al-silicates (containing Al, Si, Ca and mineral K, Mg and Fe) have irregular forms and were found to be naturally originated. Spherical Al-silicates with small size are anthropogenic fly ash which are originated from combustion process [14].

Calcium-Rich Particles

The average weight percentage of Calcium (Ca) was equal to 10.4% from the mass of total particulate matter, with maximum abundance equal to 18.3% and minimum abundance equal to 5.1%. The EDX analysis of TPM samples indicated that there is high probability of the presence of Ca silicate particle as (CaSiO3), as shown in **fig. 5**, due to large percentages of C, Ca, O, and Si found in the all samples. Clay mineral may be present in the collected samples due to the percentages of C, Ca, O, in the all samples associated with the presence of some minerals elements such as Al, Na, Mg, K and Fe [15].

The presence of Ca rich particles in high percentage of all the samples is may be related to calcium carbonate ($CaCO_3$) which is generally known as (Calcite). These types of particles are mostly originating from building construction, demolition in cement factories, agriculture and natural soil, and vegetative burning [16]. Ca in the particles would be present not only as $CaCO_3$ but also as an internal mixture of $CaCO_3$ and $CaSO_4$[17]. Calcium sulfate particles are originated by acid-base neutralization reactions in atmosphere and by deterioration of building's surface, composed of $CaCO_3$ (marble and limestone) due to reaction with sulfur compounds in the atmosphere. Calcium sulfate is also used to produce cement and it is a secondary product of pollutant gasses [18]. The presence of Ca, C, and O associated with S in all the TPM samples may be attributed to the interaction between atmospheric sulfur and soil materials from the crust. Natural sources may be the probable origin of the particles as indicated by the occurrence of metals in the samples.

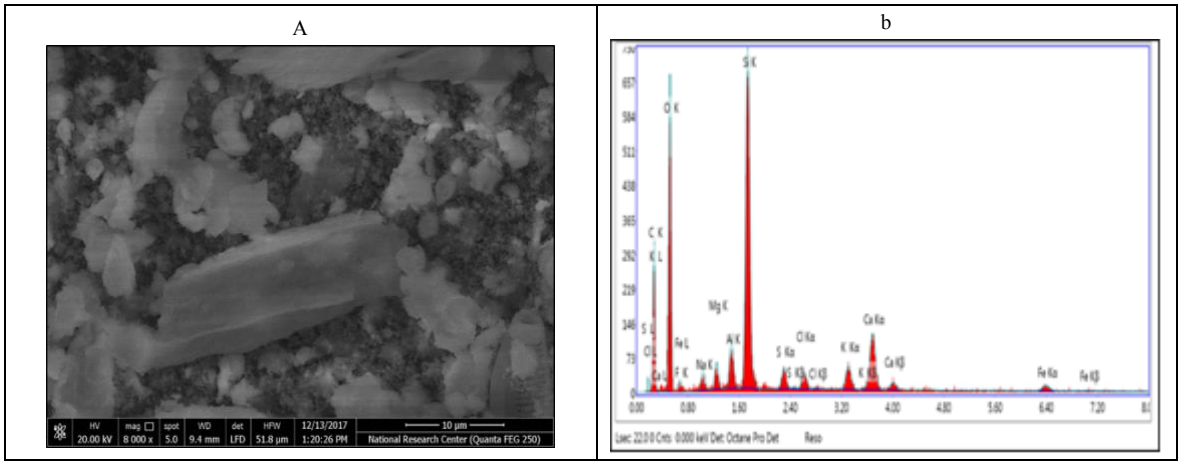

Figure 4. SEM image of Aluminium silicate particles (a) and EDS spectra (b) in TPM samples.

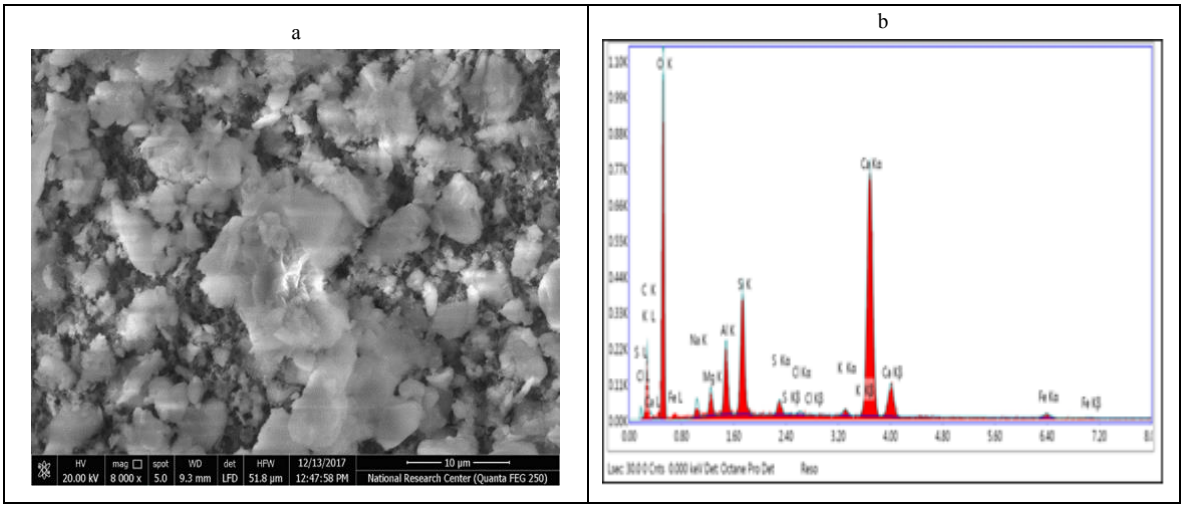

Figure 5. SEM image of calcium rich particles (a) and EDS spectra (b) in TPM samples.

Marine Salts

These particles consist of Na and Cl, sometimes traces of Mg, K, Ca and S are detected. The tabular shape and spectra of these particles is seen in **fig. 6**. Na Cl particles are mainly created from marine aerosols. The group of sodium chloride was observed in coarse particle size which are originated from natural and anthropogenic activities. Moreover, chloride is also converted into sodium chloride and calcium chloride in the atmosphere which may be due to the secondary particles formation [19].

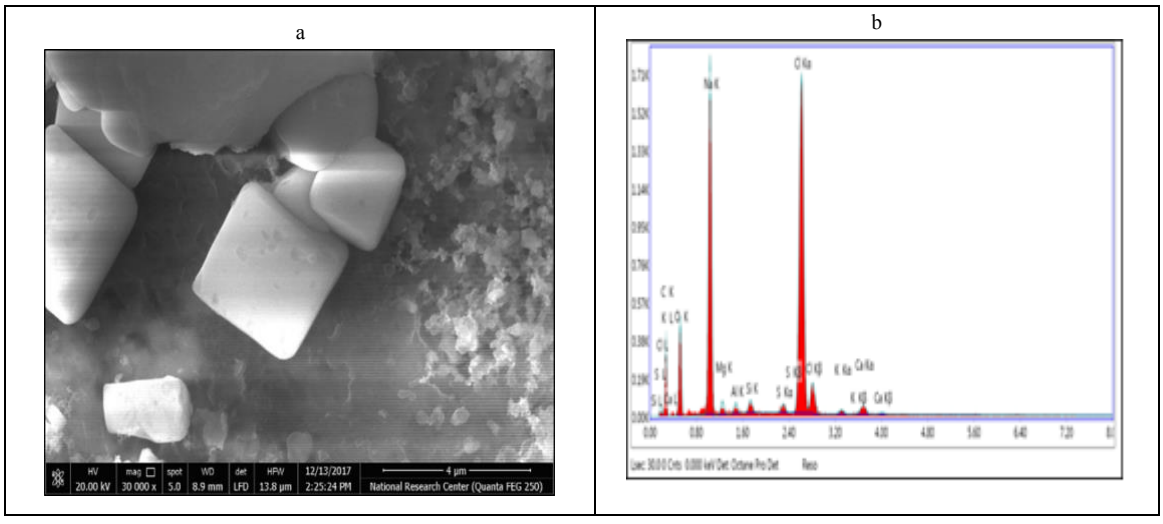

Figure 6. SEM image of sodium chloride particle (a) and its EDX spectra (b) in TPM samples.

Sulfur rich Particles

The average weight percentage of sulfur (S) was equal to 2.6% from the mass of total particulate matter, with maximum abundance equal to 4.0% and minimum abundance equal to 1.2%. The presence of S in the TPM in Qena city may come from the crustal particles which contain sulfur, and this is because the soil and dust itself contains sulfur by coagulation, collision and combination with particles of high sulfur contents or by multiphase reactions with sulfur during transport processes, mainly from homogeneous and heterogeneous reactions. The presence of Sulfur along with a group of Ca-S-O may be attributed to the presence of containing agglomerate (CaSO4). They are responsible for the formation of secondary particles in atmosphere due to photochemical reactions and are considered as scattering type of particles [12].

Fe rich particles

Iron is the only heavy element that is found in the all samples of TPM. The average abundance of iron (Fe) equal to 2.0% from the mass of total particulate matter, with maximum abundance equal to 3.5% and minimum abundance equal to 1.0%. The presence of Fe in the TPM at Qena city is attributed to the natural crust and minerals. Beside that large quantity of dust emitted to the atmosphere resulted from the human activities. The presence of oxygen and other elements such as Si, K and Al along with Fe with irregular shapes suggests that the particle composition includes mainly oxide and sulphate of iron [12].

3.2.3. Carbon and Soot Particles

Carbon was the most abundance elements in all collected samples. The average abundance of carbon was equal to 44.8% from the mass of total particulate matter, with maximum abundance equals to 64.7% and minimum abundance equals to 35.4%. The presence of carbon in particulate matter samples could be in two forms elemental carbon or organic carbon. The elemental carbon may come from the crustal dust which contain carbon in the form of carbonate group (CO_3) associated with some crustal minerals. Another source of carbon is the secondary particles formation due to the processes of gas to particles transformation in the atmosphere, such as CO and CO_2 that can be converted to metals carbonate. The organic carbon come mainly from fuel composition, industrial processes and biomass burning.

As it can be seen in **fig. 7**, soot particles, mainly constituted by carbon particles, are clearly distinguishable from other aerosol types due to its unique aggregated clusters morphology in the form of small spherical aggregates which combined to form chains and large aggregated clusters. These types are originating from Fuel combustion. In some cases, a considerable percentage of soot particles contain trace S which was observed by EDX analysis. S content in soot aggregates may be caused by gas conversion processes to particulates. The spherical, amorphous and typically non-aggregated particles are distinct carbonaceous particles type from soot and these particles is dominated by carbon with amount of S and K [16].

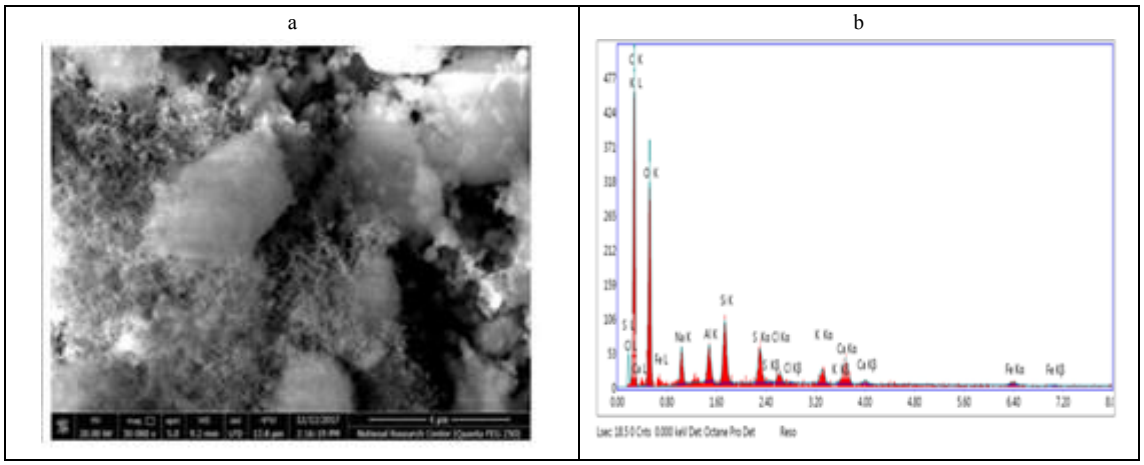

Figure 7. SEM image (a) and EDX- analysis (b) of soot cluster with some traces found in TPM samples at Qena city.

IV. Conclusion

Morphological and elemental composition analysis of TPM by SEM-EDX technique provides useful information for the determination of their chemical properties and sources. TPM particles have irregular, spherical and aggregated shapes. Elemental analysis indicates that C, Si and Ca were the abundant elements in the particles followed by Al, Na and Fe amongst all the elements. Apart from these elements such as S, Mg and other elements like Cl and K was also present in the two seasons. All the observed particles were associated with the presence of oxygen (O), therefore there is strong probability that these elements are present in the form

of oxides or combined with some groups such as carbonates CO_3 and sulphates SO_4. Carbon soot particles were the dominants with high percentage in all the TPM samples. With respect to the crustal and mineral dust particles, Si rich particles associated with Al was present in major amount than other elements. The Ca rich particles were the second abundant. This indicates that TPM particles mainly originated from soil crust and anthropogenic activities. Based on morphology and elemental composition, the particles are classified into following groups such as carbon soot particles, Al-silicates, Ca rich particles and Na-Cl rich particles.

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