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Scanning Electron Microscopical and Physio-Chemical Characterization of Solid Aerosols Related To Pollutant Web Identified At Faisalabad (Pakistan)

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ABSTRACT

Solid aerosol size and shape are the most discussed physical properties considering their behavior, source identification and possible health hazards. Some aerosols not only have a special chemical composition but also a typical shape on behalf of which their method of formation and source of origin is identified. The results obtained in this study using SEM (Hitachi S-2380N at 2.5kV) revealed that the size range of solid aerosols was found to be from 1.2 μm to 20.4 μm the main sources were found to be 70.00% transport and industry, 10.05% biological and anthropogenic, 10.68% natural soil and 9.60% fuel consumption depicted in physio-chemical composition of solid aerosols. pH values of most of the samples lies between 8 and 8.5 while E_C values vary between 2.200 and 6.510 showing the alkaline nature and soil derived origin of most of the solid aerosols. No doubt the main objective of the study was not to investigate the human health hazards. However attempt has been made through empirical relations to find the co-relationship between physio-chemical composition of solid aerosols and related health hazards and it was found that 70.70% had developed headache, 57.82% Giddiness, 16.24% ENT, 11.99% heart disease, 9.15% cancer, and 4.79% skin diseases respectively. Protective measures are strongly recommended.

Keywords: Solid aerosols, syntax map method, scanning electron microscope, particle size distribution, particle shape, morphology, health impact co-relationship, protective measures

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1.0 INTRODUCTION

Knowledge of physical properties like shape for determination of cell wall interaction, the diameter for the determination of chances of inhalation and part of inhalation along with risk of death becomes the crucial part of research nowadays. Aerosols vary in size, shape, elemental composition, morphology and concentration both spatially and temporally depending upon different types of natural and anthropogenic emission sources. Some additional factors such as short range and long range local and remote aerosol dynamics, different climatological and meteorological conditions and the presence of gaseous precursors giving rise to secondary aerosols by heterogeneous reactions are also significant in this regard. Physio-chemical characterization is broadly being used for the determination of elemental make up of aerosols and their source identification. Mainly, the aerosols consist of carbonaceous materials (OC, EC), sulfate, nitrate, ammonium, sea salt (sodium, chloride), and crustal matter (mineral dust) which define different emission sources. Size distribution of atmospheric aerosols along with their chemical characterization plays a key role in source apportionment. The size of aerosols ranges from 1 nanometer (nm) to 100 micrometer (µm) in terms of diameter. Most of them lie within the size range of 0.1 to 10 µm [1-5].

Atmospheric aerosols are composed of chemical compounds of both organic and inorganic nature. Coarse particles are naturally occurring and of primary nature while fine particles are of secondary nature and generated by homogenous and heterogeneous reactions of gaseous precursors such as ammonia, sulfur dioxide etc. with organic and inorganic compound such as sulfates, nitrates, ammonium, organic carbon etc [6-8].

In addition to organic and inorganic compounds, Atmospheric aerosols also contain variable minor amounts of different trace metals (e.g. V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd Ba and Pb). Although the total proportion of these trace/heavy metals in particle mass is only a few percent or less yet they proved to be carcinogenic for human beings and animals. They originate from various man made sources, including the metal industry, fossil energy production, refuse incineration and traffic [9-13]. Research presented in this paper involves the analysis of solid aerosol loading in the urban environment of Faisalabad and was

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conducted for characterization, their source origin, their overall contribution towards environmental pollution with special interest in determining the transportational and industrial share.

2.0 MATERIALS & METHODS

2.1 Site selection pool diagram

Site selection has a prime importance in conducting research relevant to atmospheric solid aerosol characterization and source identification. For this purpose the identified web of Faisalabad was divided into 3 pools keeping in view the heterogeneity of environment using Space Syntax Map Method, Details are shown in figure 1 and 2.

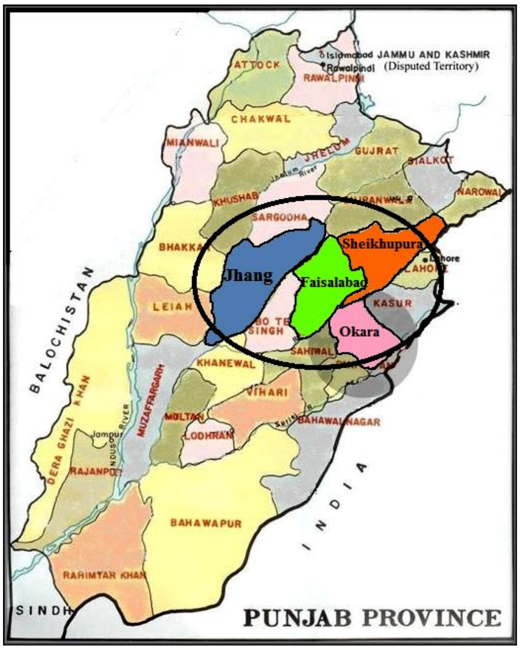

Fig 1: Pool classification of Faisalabad city using SRS Technique

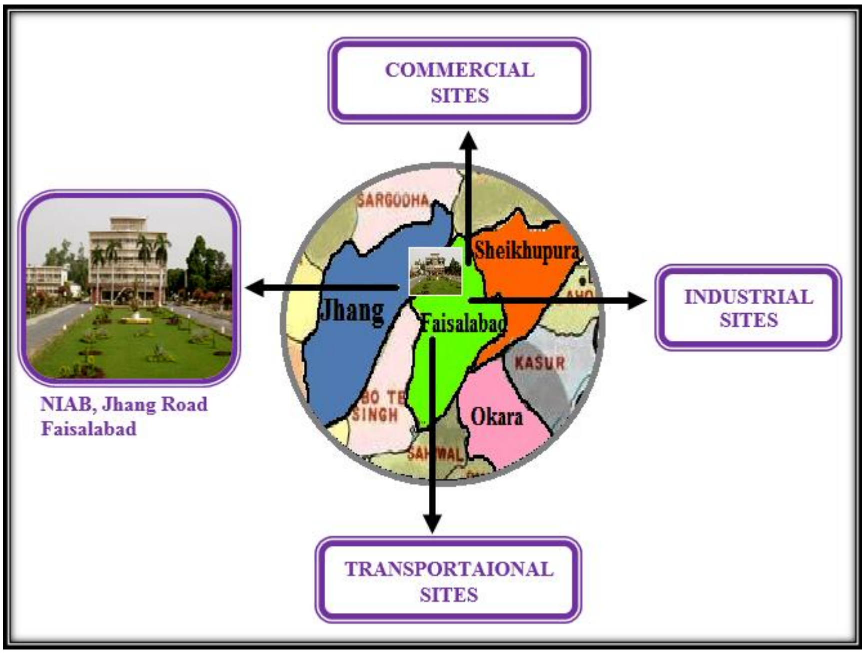

Fig 2: Detail of sites including in different Pools

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2.2 Sample Preparation for Scanning Electron Microscopy

Samples were prepared with very simple and novel technique of using double tape. For this purpose, Aluminium stubs with flat surfaces were cleaned using acetone and then tape was applied gently on them. Stubs were immersed in solid aerosol samples and lifted up. In this way a very thin and fine layer of solid aerosols was deposited on stubs which were ready for sample loading for Scanning Electron Microscope. Sample prepared by this procedure were found to give good results because of no chances of mixing of coating layers and coating material with the original sample. Imaging of solid aerosols was carried out using the scanning electron microscope (Hitachi S-2380N at 2.5kV) [14-20].

3.0 RESULTS AND DISCUSSION

Table 1: Statistical analysis of data related to pH and EC of solid aerosols

Statistics	Industrial Sites		Commercial Sites		Transportational Sites	
Sr. No	**pH**	**EC**	**pH**	**EC**	**pH**	**EC**
1	7.7	3.79	8.07	3.23	7.87	5.97
2	8.04	2.4	7.91	4.58	7.89	4.12
3	8.24	6.15	8.05	4.79	8.12	5.86
4	8.33	5.19	7.19	3.43	8.67	4.45
5	8.11	6.1	7.99	3.46	7.56	3.8
6	8.25	4.95	7.95	5.33	7.91	5.9
7	8.15	2.2	7.8	5.11	8.34	3.29
8	7.99	4.03	7.72	5.87	8.1	5.7
Mean	8.101	4.351	7.835	4.475	8.0575	4.88625
Max	8.330	6.150	8.070	5.870	8.670	5.970
Min	7.700	2.200	7.190	35.80	7.560	3.290
S.D	0.198	1.522	0.287	0.990	0.3366	1.09008
Median	8.130	4.490	7.930	4.685	8.005	5.0750
C.V	0.024	0.350	0.037	0.221263	0.04177	0.22309

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Fig 3: Physical Appearance of Collected Solid Aerosol Samples

Table 2: Colour Differentiation of Solid Aerosol Samples

Sample code	Colour	Sample code	Colour
2KS01	Greenish black	2KS11	Dark brownish gray
2KS02	Light yellowish gray	2KS12	Dark brownish gray
2KS03	Light greenish gray	2KS13	Dark ash gray
2KS04	Light brownish gray	2KS14	Brownish gray
2KS05	Yellowish brown	2KS15	Deep brown amber
2KS06	Brown amber	2KS16	Deep brown amber
2KS07	Dark gray	2KS17	Deep amber
2KS08	Dark grayish bluish cyan	2KS18	Light brownish gray
2KS09	Ash gray	2KS19	Deep brown amber
2KS10	Brownish black	2KS20	Azurish gray

3.1 Morphological and Topographical Analysis of Solid Aerosols Using SEM

In this study, morphology and surface topography of randomly selected solid aerosols were determined using scanning electron microscopy. For this purpose maximum 6 samples(2 from each site) were chosen out of 24 collected samples from three different sites.

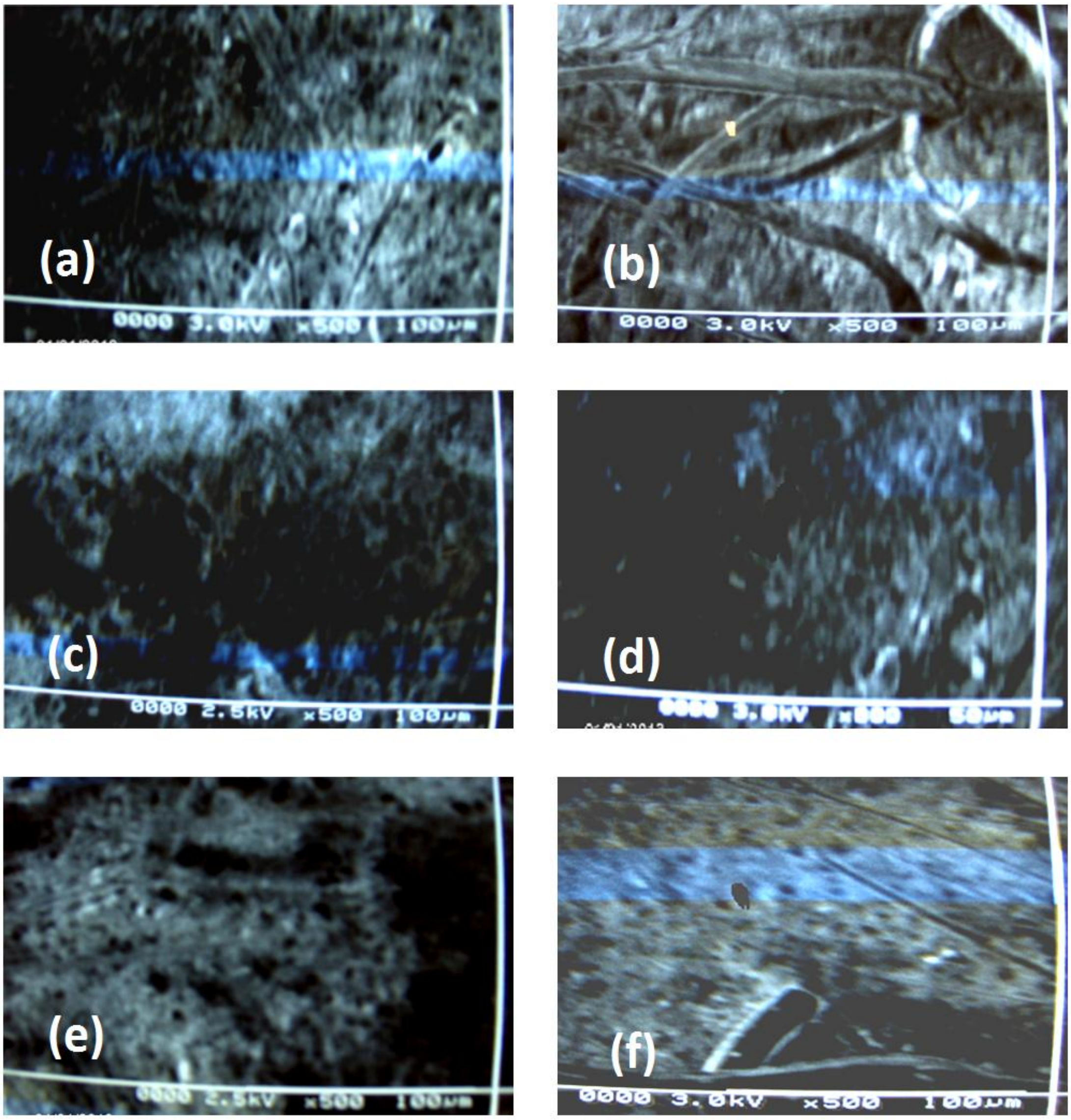

Fig. 4: SEM Micrographs of Solid Aerosol Samples (a) Sample Code 2KS02 (b) Sample Code 2KS07 (c) Sample Code 2KS12 (d) Sample Code 2KS16 (e) Sample Code 2KS20 (f) Sample Code 2KS24

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All the samples were strained to evacuate fiberous material and were stacked them one by one on the stubs of the electron microscope. For each and every sample, the running methodology of electron microscope was kept precisely the same by differentiating the voltage and magnification. SEM micrographs were obtained at a specific voltage and magnification when images become clear. Photographs with different magnifications were taken by using a digital camera. Each and every micrograph was labeled with applied voltage and magnification. Then all micrographs were analyzed by drawing different shapes on them geometrically.

Four shapes were identified which confirms that four phases are present in the 2KS16 SEM micrograph. Total Area calculated for all shapes was 77.87cm^2 as shown in Table 3 and 4 and in the similar lines for Circles, Ellipse, Squares, Rectangles and Triangles are (6.37%, 73.35%, 10.05%, 10.68% and 9.60%) respectively. Five shapes were identified which confirms that five phases are present in the 2KS02 SEM micrograph. Total Area calculated for all shapes is 47.84cm^2 as shown in Table 3 while percentage area of Circles, Ellipse, Squares, Rectangles, Triangles are (13.86%, 32.29%, 10.05%, 0.073%, 36.48%) respectively. Two shapes were identified which confirms that two phases are present in 2KS24 SEM micrograph. Total shapes area calculated was found to be 49.74 cm^2 as shown in Table 5 and 6 while percentage area for circles and ellipses were 40.08% and 59.91% respectively.

Table 3: Size distribution of Solid Aerosol particles on the basis of geometry detected in 2KS02

Sr.No	Circles (Diameter) cm	Area($\pi d^2/4$) cm^2	Length/Width
1	2.6	5.306	1
2	1.3	1.326	1
Total Area	6.632 cm^2		

Sr.No	Ellipse(2a,2b) cm	Area(πab) cm^2	Length/Width
1	0.8,0.6	4.0192	2
2	1.4,2.6	11.429	1.857
Total Area	15.448 cm^2		

Sr.No	Squares(L) cm	Area (L^2) cm^2	Length/Width
1	1.5	2.25	1

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2	1.6	2.56	1
Total Area	4.81		

Sr.No	**Rectangles(L,W) cm**	**Area(L×W) cm^2**	**Length/Width**
1	2.5,1.4	3.5	1.785

Sr.No	**Triangles (a,b,c) cm**	**Area$(s(s-a)(s-b)(s-c))^{1/2}$ cm^2**	**Length/Width**
1	4.5,4.5,6.1	11.745	1.355
2	3.7,3.7,3.5	5.705	1.057
Total Area	17.45		

On behalf of TEM micrographs it can be said that the circles, triangles, rectangles, squares etc. show the mixation of phases and elements with the branches of amorphous particles, interlocked with fibrous materials of different types and shapes after deposition grown in a fractal like structures.

Table 4: Size distribution of Solid Aerosol particles on the basis of geometry detected in 2KS16

Sr.No	**Circles(Diameter) cm**	**Area($\pi d^2/4$) cm^2**	**Length/Width**
1	2.5	4.960	1

Sr.No	**Ellipse(2a,2b) cm**	**Area(πab) cm^2**	**Length/Width**
1	3.4,4	42.704	1.18
2	1.7,2.7	14.413	1.588
Total Area	57.117 cm^2		

Sr.No	**Rectangles(L,W) cm**	**Area(L×W) cm^2**	**Length/Width**
1	3.2,2.6	8.32	1.230

Sr.No	**Triangles(a,b,c)**	**Area$(s(s-a)(s-b)(s-c))^{1/2}$ cm^2**	**Length/Width**
1	4,4.1,4.4	7.478	1.073

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Table 5: Size distribution of Solid Aerosol particles detected in 2KS24

Sr.No	Circles (Diameter) cm	Area($\pi d^2/4$) cm^2	Length/Width
1	2	3.14	1
2	0.4	0.126	1
3	1.6	2.009	1
4	0.9	0.636	1
5	0.8	0.502	1
6	0.7	0.385	1
7	0.9	0.636	1
8	1	0.785	1
9	1.3	1.326	1
10	0.7	0.385	1
11	0.7	0.385	1
12	0.8	0.502	1
13	0.9	0.636	1
14	0.9	0.636	1
15	0.7	0.385	1
16	0.6	0.283	1
17	0.8	0.502	1
18	0.7	0.385	1
19	0.6	0.283	1
20	0.5	0.196	1
21	0.7	0.385	1
22	0.8	0.502	1
23	0.8	0.502	1
24	1	0.785	1
25	1	0.785	1
26	0.7	0.385	1
27	1.1	0.950	1
28	0.7	0.385	1
29	0.8	0.502	1
30	0.9	0.636	1
Total Area		19.94	

Additional agglomeration during and after sampling may also be observed which finally resulted the aerosols to convert into a big particulate mass comprising particles of different chemistry and structure which is in accordance with the other similar international studies found in literature in which it is reported that crystal particles does not grow much even at

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very high relative humidity and low temperature but the soot keep growing and form pollutant web. It is pertinent to mention that during sampling relative humidity and temperature varied between (35 to 71) % and (10 to 34) Cº respectively on behalf of which we have obtained soot aggregate with size much greater than expected. The similar phenomenon may happen inside the body when aerosols are inhaled and coagulate to coarse particles where replenishment and flashing out from the human body is very difficult than that of the fine particles. The degree of impairment is escalated when it is incorporated with some trace metals hazardous for human health. The importance of this study is increased due to the fact that Faisalabad is highly polluted like other big cities of the world having huge population size, expanded industries, transport and urbanization. Hence having a large amount of compound phases and trace metals and a large number of populations are continuously exposed to these hazardous pollutants [21-40].

Table 6: Size distribution of solid aerosils on the basis of geometry for sample 2KS24

Sr.No	Ellipse(2a,2b) cm	Area(πab) cm^2	Length/Width
1	0.7,1.4	3.077	2
2	0.7,1.3	2.857	1.857
3	0.6,0.8	1.507	1.333
4	0.6,0.8	1.507	1.333
5	0.6,0.8	1.507	1.333
6	0.6,0.8	1.507	1.333
7	0.8, 1	2.512	1.25
8	0.8,1.3	3.265	1.625
9	0.7,0.6	1.318	1.167
10	0.5,0.7	1.099	1.4
11	0.6,0.8	1.507	1.333
12	0.7,0.8	1.758	1.14
13	0.7,0.9	1.978	1.285
14	1 , 1.2	3.768	1.2
5	0.4,0.5	0.628	1.25
Total Area (cm^2)		10.455	

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The table 1 gives the statistical analysis of the record for pH and EC values. The table shows that pH values of all the samples were between 7.190 to 8.670 with a majority of them having value 8 or near about 8 showing alkaline nature and less chances of acidic rain in the region while EC values of all the samples were between 2.200 and 6.510 The low values of samples indicate that the major contributor to solid aerosols is the soil derived minerals. The anthropogenic content of the samples appear to be a minor contributor to most of them.

SEM micrographs showed that aerosols related to selected sites were quite diverse having shapes of circles, triangles, rectangles, squares showing the presence of soot particles, spherical particles, cubical, semi-cubical particles, irregular shaped and cumulus inorganic particles confirming the natural and anthropogenic origin both and complexity of the environment.

To check the health hazards due to trace metals empirical relations were developed for identified trace metals trace metals Cr, Mn, Ni, Pb and Zn keeping in view the other trace metals as non-significant for this study. The data obtained indicates that 70.70% had developed headache, 57.82%, Giddiness 16.24, ENT, 11.99% heart attack 9.15%cancer and 4.79% skin diseases. The results were shown in table 7 [41-55].

Table 7: Health Hazard Trend for the population residing in and around pollutant web

Sr. No	Diseases	Average %age of Health Hazards Effects	Health Hazards Trend at NIAB Site
1	ENT	16.2322%	Headache > Giddiness > ENT > Heart Attack > Cancer > Skin Disease
2	Giddiness	57.8187%	
3	Fatigue	BDL	
4	Gastrointestinal	BDL	
5	Urinary	BDL	
6	Cancer	9.1590%	
7	Heart Attack	11.9910%	
8	Headache	70.7034%	
9	Skin Disease	4.7934%	
10	Respiratory Disease	BDL	

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Key: BDL = Below detection limit

4.0 DISCUSSION

Morphological structure study and source apportionment are the important features for the complete characterization of solid aerosols along with their compound phase analysis and elemental make up determination. For this purpose Solid aerosol samples collected from different locations of the identified pollutant web were subjected to scanning electron microscope (SEM) at 2.5KV. SEM micrographs revealed a wide range of particles within the size range of 1.2µm to 20.4µm having varying morphological structure. On the basis of morphological structure study, it becomes easier to identify the probable sources of solid aerosols. So, particles revealed in these micrographs have been divided in to four types with respect to their morphology.

- Highest amount of particles i.e., 70.70% appeared to exhibit angular shapes with sharp edges. The origin of these particles in atmosphere is anthropogenic as evident from the formation of these particles due to the reactions of sulfur compounds and other particles. Usually these particles contain sulphates of Ca, Fe, Pb and K. Mainly sulphate clusters are found to be $CaSo_4$. Identification of gypsum (G) as a major phase in XRPD studies of the same samples also explain this anthropogenic origin as Faisalabad environment do not contain Gypsum naturally. So, the probable sources of these particles are transport and non-ferrous industries.
- Almost 10.05% of particles were found to be round (circular + Spherical) in shape. Usually these particles are composed of alumino silicates and oxides of Fe, Zn, Cu, Ni, K, Pb and Ti. These particles are considered to be of complex nature and mainly of both biological and anthropogenic origin. So apart from biological origin, these particles are mainly originated from industrial emissions.
- Another kind of particles revealed from SEM micrographs is the mixed aggregates of coarse particles. These particles make up almost 10.68% of particles. These particles have irregular shapes and composed of Si, Al, C, Ca, Ba, K, Zn, Cu, Te, F and Sr. Most of

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these elements are of crustal origin thus the probable source of these particles is Natural soil re-suspension and road dust.

- Some particles were found to be present with irregular morphology of various shapes. These particles are usually soot agglomerates and composed of C, O, Na, Si, Al, Ca, Cd, Zn, Sr, Ti, Ba and Cu. The formation of these particles occurs due to high combustion processes such as fuel combustion for vehicles and industries. The weight percentage of these particles is found to be 9.60%. Variation of pH values between 8 and 8.5 and E_C values between 2.2060 and 6.510 conformed the alkaline and soil derived origin of solid aerosols and no occurrence of acid rain for the time being. Positive co-relationship between physio-chemical properties and health hazards suggests the urgent need of the protective measures [56-62].

FUTURE RECOMMENDATIONS

This paper summarizes the study results that will provide the basis for considering of strategies to deal with morphological studies of solid aerosols using novel ideas of syntax map, cooling and double tape method. An attempt has been made to rectify the major discrepancy of the scanning electron microscopy. However, the need of more background data on aerosols physio-chemical characteristics particularly from mix environment like Faisalabad, will lead to scientific community to expand and use the methods developed in this study to conduct further similar studies. Such simple techniques should be useful for environment and health impact of industrial and transport based aerosols, obtained images play a key role in the development of co-relationship between human anatomy and solid aerosol’s pollution.

However, it must be kept in mind that the data provided in this study is only the snapshot for a few sites as well as guidelines for such types of studies. Much more data will be required to characterize the atmospheric aerosols especially the aggregates sufficiently to permit reliable estimate of their large scale effects on climatology, meteorology and ecological balance.

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