

## **Dynamical Characterization and Source Apportionment of Solid Aerosols; an Integrated SEM-TEM Study**

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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  $\mu$ m to 20.4  $\mu$ m the main sources were found to be 57.89% transport and industry, 24.38% biological and anthropogenic, 9.78% natural soil and 7.22% fuel consumption depicted in physico-chemical composition of solid aerosols. TEM micrographs not only provide us important information about global warming and cooling trends but also confirm our experimental findings. No doubt the main objective of the study was not to investigate the human health hazards. However an attempt has been made to correlate health hazard on behalf of their size distribution. It was indicated from the results obtained that the chances of respirable diseases (72.91%), Thoracic diseases (20.89%) and blood stream diseases (6.19%) respectively.*

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

## **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. Physico-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 ( $\mu\text{m}$ ) in terms of diameter. Most of them lie within the size range of 0.1 to 10  $\mu\text{m}$  [1-5].

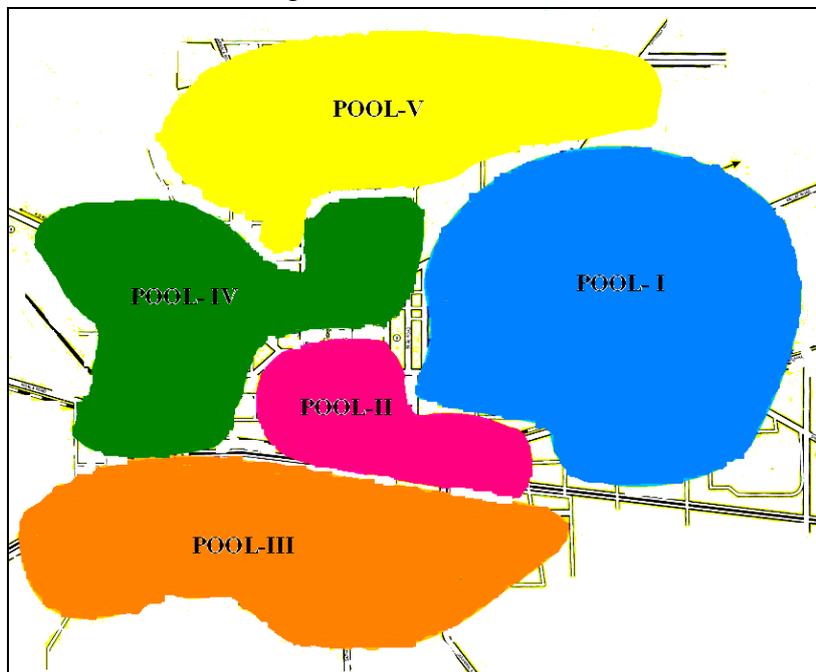
Atmospheric aerosols are composed of chemical compounds of both organic and inorganic nature. Coarse particles are naturally occurring and of primary nature while fine particles are of secondary nature and generated by homogenous and heterogeneous reactions of gaseous precursors such as ammonia, sulfur 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 conducted for characterization, their source origin, their overall contribution towards environmental pollution with special interest in determining the transportational and industrial share.

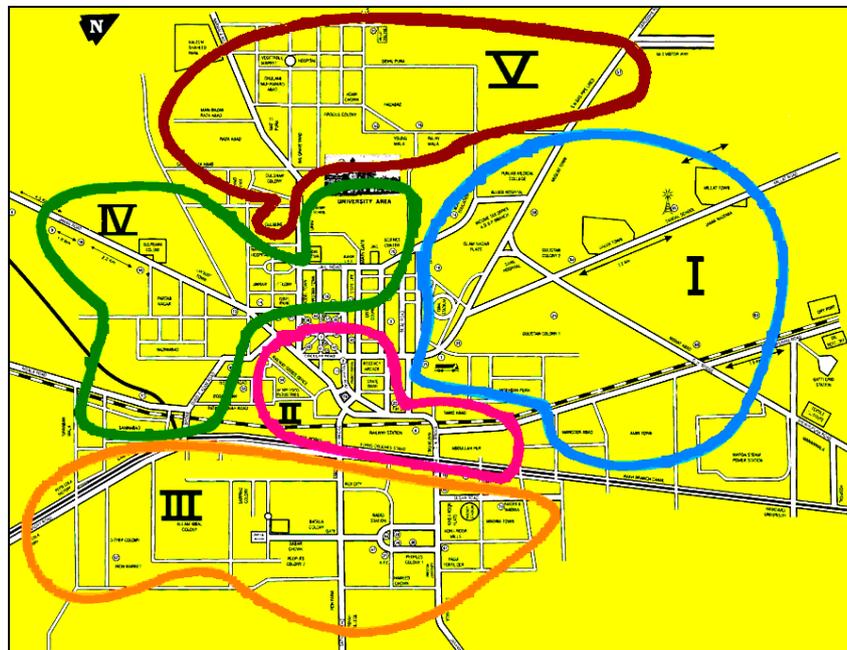
## **2.0 Materials & Methods**

### **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 city of Faisalabad was divided into 5 pools keeping in view the heterogeneity of environment using Space Syntax Map Method, Details are shown in figure 1 and 2.



**Figure 1: Pool classification of Faisalabad city using SRS Technique**



**Figure 2: Detail of sites including in different Pools**

## **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].

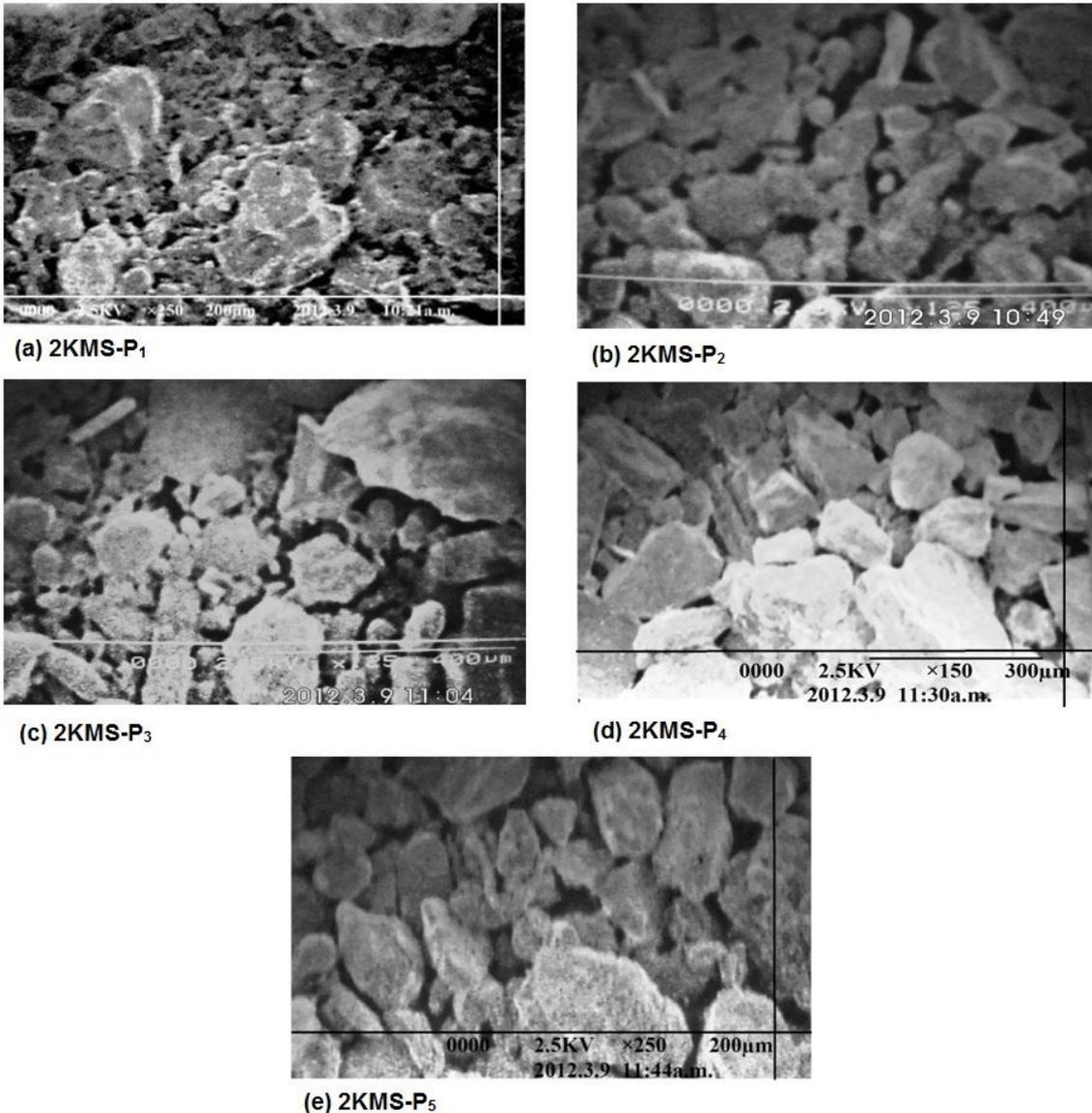
## **Sample Preparation for Transmission Electron Microscopy**

Global cooling and Global warming was determined using Transmission electron microscopy. For this purpose aerosol sample was mixed to 1ml distilled water in epandroff to make suspension of sample. Then sample was sonicated for 3 minutes using sonicator and a drop of this sonicated sample was placed on carbon grid. The carbon grid was subjected to electron beam using Tem after placing it on specimen holder.

### **3.0 Results and Discussion**

#### **3.1 Morphological Structure Study and Source Apportionment of Solid Aerosols using SEM**

For the morphological structure study and source apportionment of solid aerosols related to Faisalabad environment, 5 pool samples, covering all possible sources of solid aerosols, were collected using syntax map method from randomly selected sites from all the pools and were subjected to SEM at 2.5KV. The micrographs obtained at different magnifications revealed a no. of particles in different size ranges and belonging to different sources representing the heterogeneity of Faisalabad environment. Particles were found to be varying in size in the range from 1.2 $\mu$ m to 20.4 $\mu$ m in all the samples. Micrographs of all the samples are shown in figure 3.



**Figure 3: SEM micrograph for different samples**

The size distribution graphs of all the particles detected in each sample are shown in figure 4. In the sample 2KMS-P<sub>1</sub>, a total of 20 particles were detected. The size of these particles ranges from 3.2 $\mu$ m to 15.2 $\mu$ m as shown in figure 4(a). A total of 47 particles were detected in the sample 2KMS-P<sub>2</sub> with the size ranging from 2 $\mu$ m to 10.4 $\mu$ m as shown in figure 4(b). In the sample 2KMS-P<sub>3</sub>, a total of 49 particles were detected in the size range of

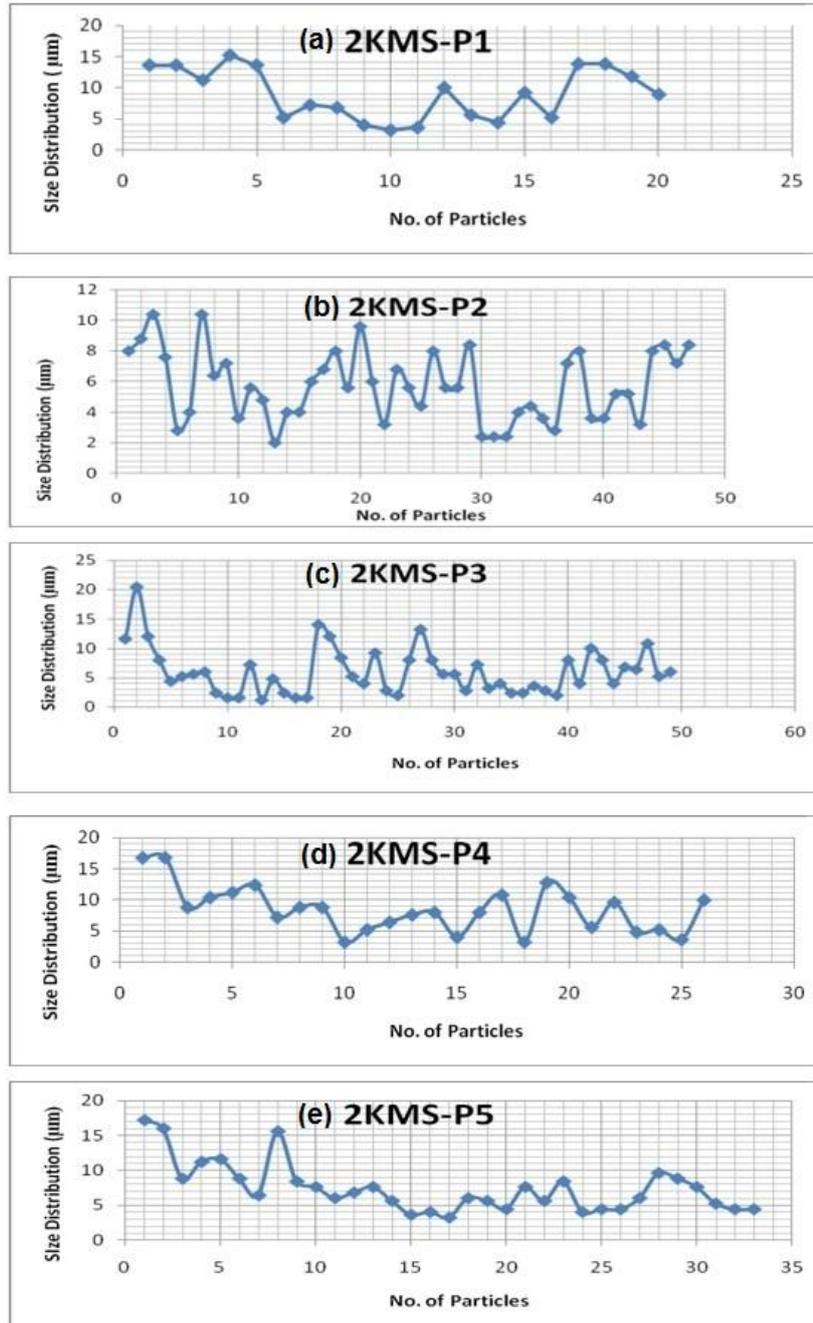
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1.2 $\mu\text{m}$  to 20.4 $\mu\text{m}$  as shown in figure 4(c). A total of 26 particles were detected in the sample 2KMS-P<sub>4</sub> within the size range of 3.2 $\mu\text{m}$  to 16.8 $\mu\text{m}$  as shown in the figure 4(d). The sample 2KMS-P<sub>5</sub> contains a total of 33 particles with their size ranging from 3.2 $\mu\text{m}$  to 17.2 $\mu\text{m}$  as shown in the figure 4(e).

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**Figure 4: Size distribution of Solid Aerosol particles detected in different samples**

SEM micrograph analysis of all the samples revealed the particles with different



morphological structures. On the basis of the morphological structure study, it becomes easier

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to identify the probable sources of solid aerosols. Table 1 shows the weight percentage of different particles with different morphological structures.

**Table 1: Solid Aerosol’s Morphological Structure Study**

Morphological Shape	2KMS-P <sub>1</sub> %	2KMS-P <sub>2</sub> %	2KMS-P <sub>3</sub> %	2KMS-P <sub>4</sub> %	2KMS-P <sub>5</sub> %	Overall average %	Source identification
Angular (Sharp edges)	25	61.07	73.47	65.38	63.64	57.84	Transport and Industry
Round (Spherical, Circular)	25	34.04	24.49	11.11	27.27	24.38	Biological and anthropologic
Coarse Irregular	25	2.13	2.04	11.11	9.09	9.87	Soil derived
Agglomerates	25	ND-	ND-	11.11	-	7.22	Soot agglomerates

Almost 57.84% particles exhibit angular shapes with sharp edges and originated from transport and industries. Usually these particles contain sulphates of Ca, Fe, Pb and K. Mainly sulphate clusters are found to be CaSO<sub>4</sub>. Almost 24.38% of particles appeared to be round (circular + Spherical) in shape having biological and anthropogenic origin. These particles are composed of alumino silicates and oxides of Fe, Zn, Cu, Ni, K, Pb and Ti. Soil derived particles having irregular shapes and composed of Si, Al, C, Ca, Ba, K, Zn, Cu, Te, F and Sr made up 9.87%. Almost 7.22% particles were found to be present with irregular morphology of various shapes containing C, O, Na, Si, Al, Ca, Cd, Zn, Sr, Ti, Ba and Cu as soot agglomerates. The probable source of these particles is fuel combustion. Scanning electron microscope (SEM) with the association of EDX is an effective tool, cheaper and faster than that of chemical analysis because the EDX facility is not available for this study therefore the results presented in this study were compared with national and international data published in scientific literature and journals having impact factor in which the similar shapes were observed and assigned them a specific source on the basis of their chemical composition [21-31].

Colloidal nature of most of the solid aerosols confirms their interaction with reactive organic gasses (ROGs) already found in the environment following the reaction



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Under suitable thermo dynamical conditions which confirms not only the secondary origin of solid aerosols but also occurring of the photochemical reaction and disturbance of radiative environmental budget facing global climatology and photosynthesis phenomena.

Aerosols climate forcing is complex because aerosols both reflect solar radiation to space (a cooling effect) and absorb solar radiation (a warming effect). In addition they can order cloud cover and properties therefore precise composition specific measurements of aerosols and their effect on clouds are needed to access the aerosol role in climate change. Secondly, the rate at which earth's surface temperature approaches into a new equilibrium in response to a climate forcing depends upon how efficiently heat perturbations are mixed in deeper ocean which is also a complex phenomenon and necessary data, empirical relations and theoretical models still suffer a lot of limitations.

Toxicity of atmospheric aerosols depends upon their size, shape and elemental make up as well as the biological sites of deposition. The aerosols with size range from 2.5-10  $\mu$  m proved to be the most dangerous while the particles greater than 10  $\mu$  m were found to be harmless due to their filtration through nose. Health hazards were predicted on the basis of this assumption and the results were shown in table 2 which shows the classification of solid aerosols detected by SEM micrograph analysis in different health hazards generating size fractions [32-47].

**Table 2: Health Hazards on the basis of Size Classification**

<b>Solid Aerosol Size Fraction</b>	<b>2KMS-P<sub>1</sub></b> %	<b>2KMS-P<sub>2</sub></b> %	<b>2KMS-P<sub>3</sub></b> %	<b>2KMS-P<sub>4</sub></b> %	<b>2KMS-P<sub>5</sub></b> %	<b>Overall average</b> %
Fine	-	8.5	22.45	-	-	6.19
Respirable	60	87.23	63.26	69.23	84.85	72.91
Thoracic	40	4.26	14.29	30.77	15.15	20.89

From our experimental findings it has been observed that almost 72.91% of the particles from all the pooling sites are found to be in respirable fraction, almost 20.89% of particles lie within thoracic region and only 6.19% of particles are found to be present in fine fraction. All these particles are generating relevant health hazards among the population of concerned areas [48-62].

Climatic effects of solid aerosols are usually associated with their ability of causing light extinction or visibility reduction and radiative forcing which depends upon size and

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hygroscopic nature of solid aerosols. Ultrafine particles produce global cooling and conversely ultra-coarse particles produce global warming. For this purpose ultrafine and ultra-coarse fractions of solid aerosols were determined as shown in Table 4.3. The results obtained clearly predict that the global warming effect (positive radiative forcing) dominates, contributing towards global cooling effect and increase in albedo phenomena.

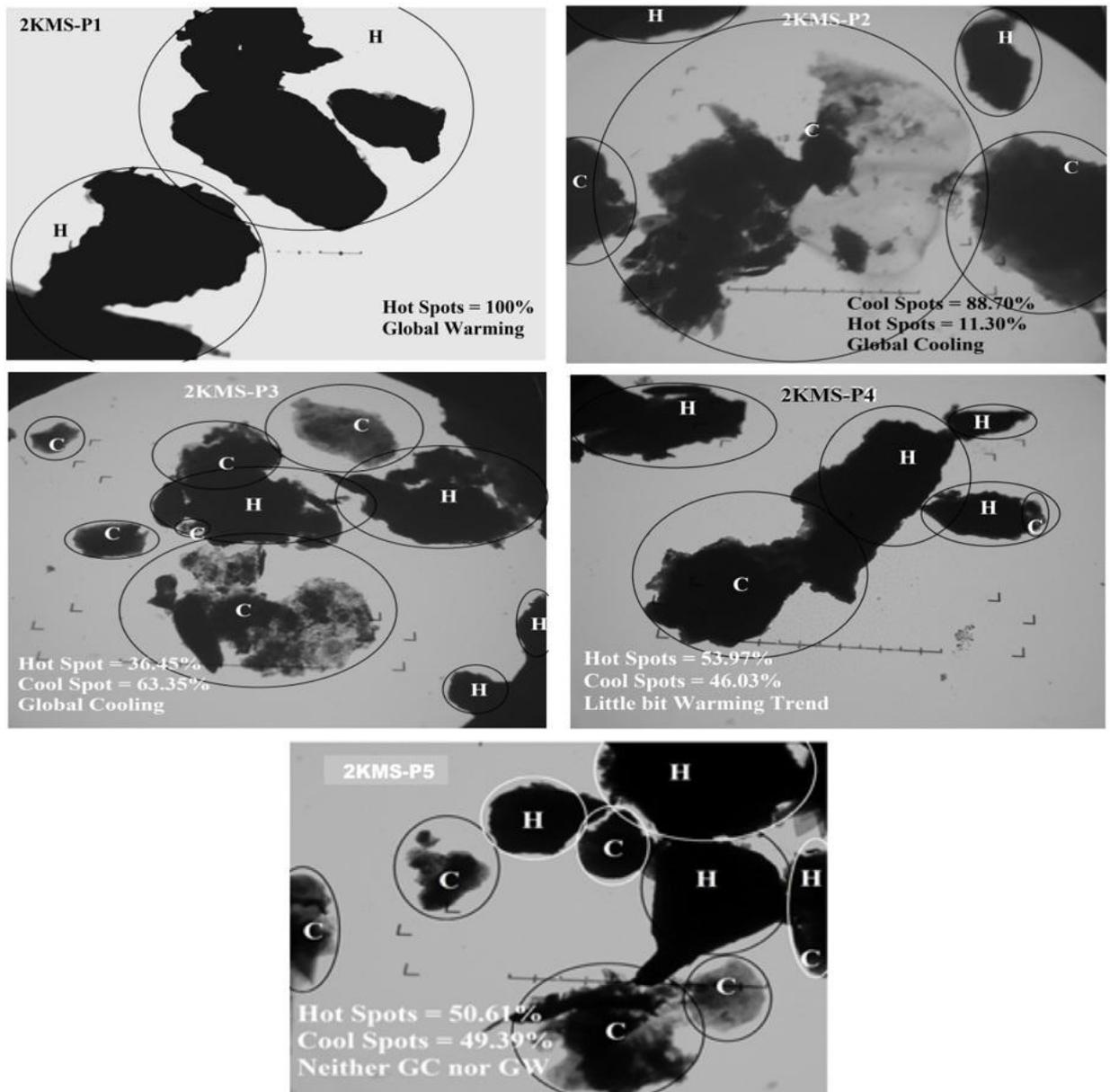
**Table 4.3: Global Warming and Global Cooling trend of Different Pooling Sites of Faisalabad using SEM**

<b>Solid Aerosol Types</b>	<b>2KMS-P<sub>1</sub></b> %	<b>2KMS-P<sub>2</sub></b> %	<b>2KMS-P<sub>3</sub></b> %	<b>2KMS-P<sub>4</sub></b> %	<b>2KMS-P<sub>5</sub></b> %
Ultrafine Scattering	ND	ND	ND	ND	ND
Ultra coarse Absorption	40	4.26	14.29	30.77	15.15
AQI	906	250	380	815	435

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TEM micrographs of some samples also supplement our results as shown in the figure 4.5. The continuous prevailing fog, smog and haze is the clear confirmation of our experimental findings. The categorization of solid aerosol with respect to AQI is also presented in Table 4.3. The AQI analysis showed that the selected sites of Faisalabad environment were found to be very critical, very hazardous, unhealthy and sensitive which indicate not only the complexity but also the high degree of degradation and greater danger to human health, strict actions should be taken to improve the air quality and making it human friendly [63-70].

**Figure 4.5: TEM Micrographs representing different pooling sites**



### **3.2 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 pooling sites were subjected to scanning electron microscope (SEM) at 2.5KV. SEM micrographs revealed a wide range of particles within the size range of 1.2 $\mu$ m to 20.4 $\mu$ m 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 (Table 1).

- Highest amount of particles i.e., 57.84% 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<sub>4</sub>. 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 24.38% 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 9.87% of particles. These particles have irregular shapes and composed of Si, Al, C, Ca, Ba, K, Zn, Cu, Te, F and Sr. Most of 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 7.22%.

Climatic effects of solid aerosols are usually associated with their ability of causing light extinction or visibility reduction and radiative forcing which depends upon size and hygroscopic nature of solid aerosols. Both of these factors play a major role in scattering and

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absorption of sunlight from solid aerosols and light extinction. If size of aerosol particle is smaller than the wavelength of incoming light beam i.e.,  $d_p \ll \lambda_{\text{light}}$ , then the light beam scatters and reflects back to the space giving rise to global cooling. This happens in the case of ultrafine particles with diameters smaller than  $0.1\mu\text{m}$ . For the particles in the fine and coarse mode transmission of light is prominent as wavelength of incoming light beam is equal to particle size which helps in refraction or transmission of light beam from these aerosols. Due to hygroscopic nature, aerosols takes up water and swells up in the conditions when humidity of the environment reaches from (50 to 90)% . So their size increases and becomes greater than the wavelength of incoming light beam i.e.,  $d_p \gg \lambda_{\text{light}}$ . In this case scattering cross section for light decreases while absorption cross section increases giving rise to light absorption and hence global warming. This usually happens in the case of ultra-coarse particles. SEM micrographs of samples taken from different 5 pools of Faisalabad city revealed the concentration of ultra-coarse particles in the decreasing order as  $2\text{KMS-P}_1 > 2\text{KMS-P}_4 > 2\text{KMS-P}_5 > 2\text{KMS-P}_3 > 2\text{KMS-P}_2$  as shown in the table 4.3. No ultrafine particle was detected in any of these samples. This indicates that global warming trend of Faisalabad environment decreases as we move from highly polluted areas to low polluted or clean areas i.e., from industrial to transportational, transportational to residential cum commercial cum industrial, residential cum commercial cum industrial to residential cum commercial and residential cum commercial to residential areas. TEM micrographs of some samples also supplement our results as shown in the figure 4.5. It is also evident from our findings that solid aerosols present in Faisalabad environment exhibit remote nature due to their movement from highly polluted areas to low polluted areas.

### **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 method pooling and double tape method. No doubt it is expected that the findings of this study will be useful far policy makers city managers and environmentalists as morphology and topography of solid aerosols are regarded as an essential components. An attempt has been made to rectify the major discrepancy of the scanning electron microscopy. However, the need of more background data on aerosols physico-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.

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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. For the quality assurance, ensure the safeguard for human health and guaranteed sustainable development of the urban geochemical environment of Faisalabad.

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