STUDY OF ANIONS AND CATIONS IN AEROSOLS PARTICULATES AT MASTUNG REGION OF BALOCHISTAN

Nida Kazmi[1], .Manzoor Iqbal Khattak[2], Anwar Khan Panezai[3] & Maqbool Ahmad[4]
[1-]Environmental Protection Agency Balochistan.
[2&4]-Chemistry Department Balochistan University, Quetta.
[3-] Institute of Bio-Chemistry Balochistan University, Quetta.
Email:manzoor_iqbal@yahoo.com

ABSTRACT: *The main objective of this work presents to point out anions an cations analysis of aerosols, the tiny soil particles suspended in the atmosphere at the area of Mastung, Quetta. The anions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$,) and cations (Na^+, $K,^+$ Mg^{2+}, Ca^{2+}) were determined through Ions-Chromatographic technique and also, physical characteristics of the aerosols particulates were analyzed be pH meter, Conductivity meter and turbidity meter. The results show that the atmospheric pollution of the Chaman is increasing and is not according to the standard of WHO.*

Keywords: Aerosols Particulates, Environmental Pollution & Ion-Chromatographic Technique.

1. INTRODUCTION

Balochistan is one of the four provinces of Pakistan. Though, it is the largest province in terms of land area but with lowest population, forming the southwestern region of the country. Balochistan shares borders with Punjab and the Khyber Pakhtunkhwa to the northeast, Sindh to the east and southeast, the Arabian Sea to the south, Iran to the west and Afghanistan to the north and northwest. Its provincial capital and largest city is Quetta.

Rich in mineral resources, yet, largely underdeveloped. its provincial economy is mainly dominated by natural resources, especially its natural gas fields, estimated to have sufficient capacity to supply Pakistan's demands over the medium to long term. Aside from Quetta, a further area of major economic importance is Gwadar Port adjacent to the Arabian Sea. A port developed under CEPAC program. Balochistan is noted for its unique culture and extremely dry desert climate

Mastung District is one of its districts situated in the northwest of Balochistan, previously included in Kalat district. Mastung district is depicted in Figure 1 below.

Figure-1. Map of Mastung.

In the global perspective, our planet is suffering from air pollution particularly the regions having dense population are greatly victimized. This situation is grave in developing countries like Pakistan owing to lack of implementation of environmental regulations and laws.

Aerosols play a major role in air pollution. The chemical composition of these particulates is dependent upon the source of origin. Therefore, identification of points of origin is essential to find out the actual composition of the particulates under observation [1-2]. Particulates in the atmosphere are either released naturally or artificially. Natural sources include air and wind-borne dust, emissions from volcanoes, sea sprays, etc. whereas, artificial sources include all the anthropogenic activities such as emissions from burning of fossil fuels, smelting and mining activities, vehicular emissions, construction related operations, emissions from factories and processing of raw materials.

Aerosol particulates have unique behavior and important characteristics. It is because of their complexity in physical and chemical composition [3]. They have been broadly studied in the last decade for their potential health impact [4-6].

Aerosols found in the atmosphere have different size, they have a different chemical composition and vary in quantity and distribution [7]. Studies conducted on aerosol particles have great importance. Aerosols can lead to climate forcing by affecting atmospheric radiations [8]. Global climate change is associated with aerosols as they have the potential to alter photochemical reactions and cloud formation. Light extinction is also influenced by them [9-10]. In addition, these aerosols reduce the visibility of the atmosphere in an urban area and promote fogginess [11]. So, to have better knowhow of these materials, knowing their chemical composition is essential. The troposphere contains dry particulates which are water-soluble because of their ionic nature. Ionic composition of aerosol determines its acidity which helps in the partitioning of semivolatile water-soluble compounds between aerosol particulates and gas phase [12].

Water-soluble inorganic species (WSIS) constitute important components of atmospheric particulates. Climatic factors, geographical conditions, and emissions from industries, vehicles, agricultural practices, and natural sources cast an influence on composition and types of aerosols. Major properties of aerosols are linked with their solubility in water. It is because of water-soluble components in them, e.g. Mg, K, Na, Ca, Cl, Ammonium, Nitrate [13] , Metals, elemental C and Organic compounds [14] which are produced from a chain of sources under complex chemical reactions. Unfortunately, these atmospheric particles are released into the atmospheric layers to pollute it [15-18].

Water-soluble ions having particular concentration and distribution in the aerosols help to identify their sources. It is important in evaluating their chemical transformation and resultant repercussions. Several researchers have attempted to study the chemical composition and mass size distribution of aerosols at different places [19-24] Also, studies on chemical characterization and mass size distribution of aerosols have been done [25-37].

Anions and Cations determination can lead to the identification of various sources of pollution in the atmosphere. It can also indicate the probability of long-range transfer of suspended particles and can prove to be beneficial in finding out the effects of aerosols on human health [38-39]. Human beings are affected by aerosols in one way or another. Presence of high concentration of Pb, for instance, can alter Pb level in blood. It also causes damages to the brain, affects intelligence and behavior of affected masses [40]. Children can ingest dust and heavy metals when these come in contact with their hands or mouths [41].

This study is conducted to determine chemical concentrations of certain pollutants in particulate matter taken from Mastung, Balochistan. Research has not been conducted in this region previously in detail as shown in Figure- 2.

Fgure-2 Almond tree in killi Karez Kark, Mastung, Balochistan.

2. EXPERIMENTAL

The samples were collected at Mastung (killi Karez Kark) at the region of Balochistan by November-December, 2014 and January 2015. All the sampling sites were determined by Field Blanks. Millipore Petri was used for storage of the filters. Refrigeration was ensured during the process to minimize losses because of evaporation and volatilization. Following materials were used during the experiment; HNO_3. pH meter, plastic containers, turbidity meter, carbon analyzer, ion chromatography instrument, turbidity meter etc.

Ion Analysis

Quartz fiber filter aliquots (3 punches of 10 mm∅) were extracted for 20 min ultrasonically in 3.5 ml ultra-pure water. Anions (F^- , Cl^- , NO_2^- , NO_3^- SO_4^{2-} and $C_2O_4^{2-}$) and cations (Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+},) were analyzed with ion chromatography. Details of the analytical method were given by [42] there was an exception that trace columns were not used to deliver the samples, it was done by using autosampler (Spark Holland Marathon) Each sampling site was determined by Field Blanks for calculation purpose.

Carbon Analyzer was used to determine total Carbon. Turbidity meter found turbidity of the samples. Similarly, pH meter and conductivity meter calculated pH and conductivity of the samples. The findings are shown in Table 1 .

3. RESULTS AND DISCUSSION

Table 1 depicts low alkalinity levels owing to high humidity and low temperature. High-level turbidity at higher temperatures is also noticed as shown below.

Table-1. Physical parameters of aerosols particulates of rain waters of Mastung (killi Karez Kark)

No.	Acc #	Sample Collected	# of Events	TOC (mg/l)	Cond. (us/cm)	pH (lab)	Turbidity (NTU)
1	1	6/11/2014	1	0.7664	51.6	6.89	1.91
2	2	25/12/2014	1	0.7653	42.6	6.96	0.81
3	3	12/1/2015	1	0.7543	21.5	5.97	0.71
4	4	13/1/2015	1	0.447	38.3	6.1	0.93

Large TOC concentrations result from the use of old designed engines in vehicles. Iron is produced from brake ware whereas Calcium is produced from lubricating oil combustion.

So, in this case, the high Sulphur content in diesel oil used in vehicles is responsible for high levels of Sulphates in the aerosols as expected. Presently, fuel containing high Sulphur is in use in the region which directly forms SO_3.

Table-2.Anions and Cations of aerosols particulates of rain waters of Mastung (killi Karez Kark) through Technique of Ion-Chromatography.

No.	Acc #	Sample Collected	# of Events	NH_4^+ (ug/l)	F^- (mg/l)	Cl^- (mg/l)	NO_2^- (mg/l)	NO_3^- (mg/l)	SO_4^{2-} (mg/l)	$C_2O_4^2$ (mg/l)	Ca^{2+} (ug/l)	Mg^{2+} (ug/l)	Na^+ (ug/l)	K^+ (ug/l)	TSP
1	001	06/11/14	1	2.7	0.3	4.6	<.01	6.7	5.9	<.10	6.7	1.4	4	3.5	213
2	002	25/12/2014	1	0.3	0.1	1	<.01	6.7	1.7	<.10	1.3	0.1	0.6	0.8	67.7
3	003	12/ 1/14	1	9.2	0.9	14.1	<.01	1.1	15.9	<.10	21	4.8	11.6	11.3	396
4	004	13/1/14	1	2.3	0.2	3.1	<.01	22.3	3.6	<.10	4.2	1	2.7	2.2	91.4

Table -2 and Figure-3 show that Highest TSP concentrations during winter may be attributed to a low temperature of about 2°C and increased heating activities (to keep themselves safe from severe cold people burn vegetable debris, coal and waste material). Low wind velocity and low mixing altitude result in stagnation of the contaminants. In summer, TSP concentrations are low as compared to other seasons. It is because of higher temperature which is a product of direct solar radiations, high velocity of wind, higher mixing heights which support greater dispersion of pollutants in warmer seasons. This season also experiences the influence of dust events. These dust events originate from the Thar Desert and may lead to high TSP concentrations of over 350 µg/m3. Such high TSP concentrations have been excluded from the summer average concentrations. Earlier studies by Dey *et al.* [43], Jethva *et al.* [46] , Badrinath *et al.* [45] and Ram *et al.* [46] show the movement of dust from Pakistan to Afghanistan and India through the Thar Desert from March to June. Chinnam *et al.* [47] have also elucidated transfer of pollutants from dust storms. This is probably due to the scavenging of aerosol particles by rainfall under the influence of southwest monsoon. Winds flow from the Himalayas to southwest across the country. This results in clear and sunny days due to the rise in temperature. This period marks the transition from wet to dry seasonal conditions. This season also experiences the flow of air masses from the northwest region in addition to the local emissions as seen from the back trajectories of post-monsoon season.

Ion Balance

Quality of analysis was checked by means of Ion balance check. Major cations (Na^+, K^+, Mg_2^+, Ca^{2+}, and NH_4^+) and anions (Cl^-, NO_2^- , NO_3^- $C_2O_4^{2-}$ and SO_4 $^{2-}$) make a major portion of solution Principle of Electroneutrality states that Anions must be equal to Cations represented by AE and CE respectively. CE is determined as the sum of all cation concentration divided by equivalent weight.

The concentration of Water Soluble Ions

Water-soluble ions are found in excessive concentration in the atmosphere and make a larger proportion of aerosols. In this study, these water soluble ions were found (F^-, Cl^-, NO_2^-, NO_3^-,$C_2O_4^{2-}$ SO_4^{2-},Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}), their mass concentrations are presented in Table 2. The sum of the water-soluble ionic species (WSIS) ranged from 12.4 to 98.4 µg/m3 with an average of 40.5 ± 34.7 µg/m3 and constituted about 20% of the TSP concentration. Among the ionic species, NO_3^- and Ca^{2+} were the most abundant chemical components (6.7 µg/m3) and each accounted for 18.7% of the total mass of ions and 3.1% of TSP mass. Of all the other non- organic species, SO_4^{2-} had the highest concentration of 5.9 µg/m3 , followed by 4.6 µg/m3for Cl^-, 4.0 µg/m3 for Na^+ , 3.5 µg/m3 for K^+, 2.7 for NH_4^+, 1.4 µg/m3 for Mg^{2+} and 0.3 µg/m3 for F^-.

Sources and Formation of Sulphate and Nitrate

[NO_3^-] / [SO_4^{2-}] ratio may provide some data about the contribution of human activities. If this ratio is > 1 it indicates the greater contribution of NO_3^- that is emissions vehicles whereas if this ratio is < 1, it shows the greater contribution of SO_4^{2-} which shows the dominance of stationary sources (industrial activities) over vehicular activity [48]. At the present site, concentrations of NO_3^- and SO_4^{2-} are comparable in most of the samples. Average [NO_3^-]/[SO_4^{2-}] ratio at the present sampling site was 1.1 ± 0.4 which indicates that although slight dominance of NO_3^- is seen, stationary source emissions and vehicle emissions contribute equally in the area and both kinds of sources may be equally dispersed around the sampling site. Earlier studies at this site indicate that NO_3^- and SO_4^{2-} occur both in coarse and fine mode [36 and 38] . The excess NO_3^- and

SO_4^{2-} over the soil contribution were evaluated. The NO_3^- /SO_4^{2-} ratio for this anthropogenic contribution was found to be a greater contribution of mobile sources over stationary sources. It is possible that during the winter time most of the sulfate is in the fine mode while during the summer time it is mostly in the coarse mode (dust storms). Further evaluation of SO_4/Ca ratio in winter and summer indicates a greater ratio in winter (1.6) as compared to summer (0.7) suggesting an enhanced contribution of SO_4 in the fine mode in winter.

Speciation of Water Soluble Ions

Aerosols show acidic nature mainly due to the presence of SO_4^{2-} and NO_3^- anions. SO_4^{2-} and NO_3^- (SO_2 and NO_x) in the atmosphere and are neutralized by mineral aerosols and ammonia. The correlation between NO_3^- and SO_4^{2-} with Ca^{2+}, Mg^{2+} and NH_4^+ suggest that the acidity in aerosols is neutralized by the alkaline species (Ca^{2+}, Mg^{2+} and NH_4^+) which act as neutralizing agent or buffer. Ca^{2+}, Mg^{2+}, and NH_4^+ react with H_2SO_4 and HNO_3 to form their salts of NO_3^- and SO_4^{2-}. The correlation coefficient was 0.71. Earlier studies at the present site also report Ca^{2+} to be the major neutralizing agent. The studies reveal that Ca^{2+} and Mg^{2+} are coarse particles and NH_4^+ exists in fine mode.The Neutralization Factor (Nf) can help determine the neutralization capacity of various cations with respect to the particular cation. The neutralization factor may be calculated as:

$Nf(Ca^{2+}) = [Ca^{2+}]/[SO_4^{2-}] + 2[NO_3^-]$ (2)

$Nf(Mg^{2+}) = [Mg^{2+}]/[^+]/[SO_4^{2-}] + 2[NO_3^-]$ (3)

$Nf(NH_4^+) = [NH_4^+]/2[SO_4^{2-}] + [NO_3^-]$ (4)

The role of Cl^- in acidity and that of Na^+ in alkalinity is negligible as it is assumed that these ions originate solely

Source Characterization of Water-Soluble Ions

Ionic Correlation

The interrelationship between ions show the sources of pollutants and indicates various gaseous reactions taking place in the atmosphere. Bivariate correlations have been identified to specify the chemical forms of the major ions, F^-, Cl^- , NO_2^- , NO_3^-, $C_2O_4^{2-}$, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} in the atmospheric aerosols of Mustang. Table- 3 shows the correlation coefficients among these major ions. Aerosol samples show good correlation (r = 0.71) between NO_3^-, and SO_4^{2-} that indicates that a portion of these may have originated from a similar source. It may also be possible that a fraction of NO_3 and SO_4 could be associated with Ca, Mg and NH_4 after the neutralization process. Ca and Mg which are vital components of soil show good correlation between each other (r = 0.74) which suggests that they possess a common source. The important molecular species of Ca and Mg could be $Ca(NO_3)_2$, $CaSO_4$, $Mg(NO_3)_2$ and $MgSO_4$.NH_4 was closely correlated with SO_4^{2-} (r = 0.63). The correlation in Table-3, between $NH_4^+$and NO_3^- (r = 0.74) revealed the existence of NH_4NO_3 which is probably formed by the reaction of HNO_3 with NH_3 on moist soil surfaces. Significant correlation of NH_4^+ with Ca, Mg, Na, and K (r = 0.68, 0.62, 0.53 and 0.65, respectively) depicts the outcome of agricultural practices taking place in the regions adjacent to the sampling site.

Crustal Source Identification

The water-soluble ions may originate from mineral dust, anthropogenic activities or may be derived from local soil. Ca and Mg are considered to be of terrigenous origin. Ca was chosen as a reference element to investigate the effect of local terrestrial sources. This is based on the assumption that all Ca in TSP mass be soil derived. The ratios of various ions with respect to Ca in the soil are presented in Table 4. A comparison of these ratios with aerosol values indicates that about 37 to 66 percentile of aerosol constituents correspond to ratios in soil. On the other hand, only a small portion of NO_3 may have originated from soil as NO_3/Ca ratios are close to soil ratios only in about 37% aerosol samples and rest of it may be contributed from other sources.

Table 3. Major ions correlation of aerosols particulates of Mustung, Quetta.

Species	TSP	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
TSP	1									
NH_4^+	0.39	1								
Na^+	0.58**	0.53**	1							
K^+	0.46	0.65**	0.48	1						
Mg^{2+}	0.53**	0.62**	0.71**	0.70**	1					
Ca^{2+}	0.5	0.68**	0.39	0.85**	0.74**	1				
F^-	0.49	0.62**	0.31	0.60**	0.47	0.65**	1			
Cl^-	0.64**	0.65**	0.45	0.79**	0.66**	0.87**	0.64**	1		
NO_3^-	0.61**	0.74**	0.58**	0.89**	0.76**	0.91**	0.72**	0.88**	1	
SO_4^{2-}	0.5	0.63**	0.28	0.67**	0.53	0.76**	0.5	0.74**	0.71**	1

** Correlation is significant ($p < 0.01$).

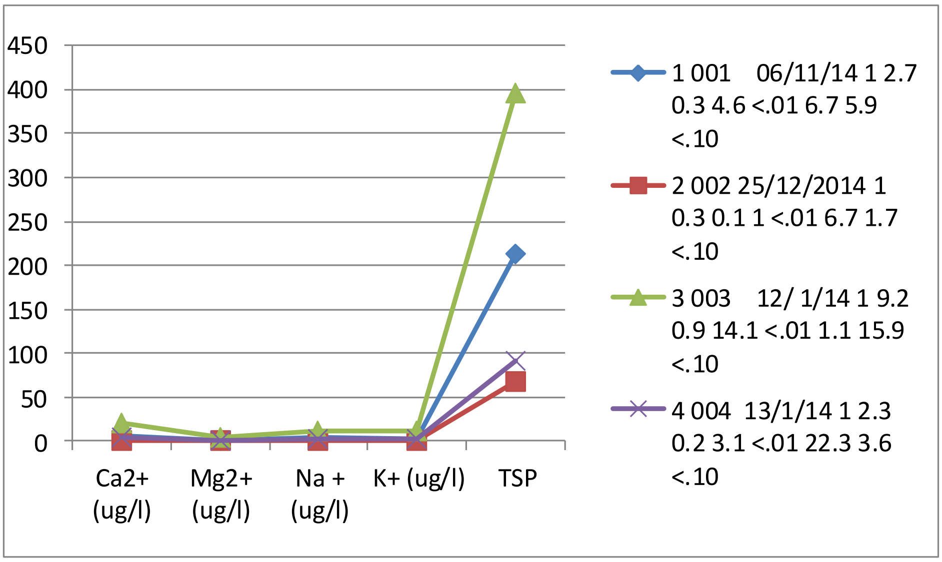

Figure-3. Ionic components of aerosols particulates.

4. CONCLUSION

The present study conducted on water-soluble ions at Mastung (killi Karez Kark) Balochistan, Pakistan, revealed that the average annual TSP concentration at Mustang is 213.2 ± 91.4 μg/m3. TSP increased by about 1.4 times in winter and decreased in monsoon as compared to the annual average concentration. Ca was the major neutralizing agent followed by Mg and NH_4. All the water-soluble ionic species show seasonal variation. High concentrations of most of the ions were observed during the winter season which is a combined effect of biomass burning and meteorological conditions (low temperature, low wind speed, and low mixing height) whereas lowest concentrations were observed in monsoon due to the scavenging of aerosol particles by rainfall. In summer, long range transport contributes for some of the ionic constituents. The influence of monsoon is evident from the strong correlation between the sea salt ions associated with other sources. It may be concluded that the main sources of soluble ions in water at Mastung are probably biomass combustion and local soil and as well as in the emission of traffic. Findings show that rainwater is majorly alkaline and has Ca which shows the neutralization of acidity by soil having Mg, Ca and NH_4. Moreover, these ions are of non-sea salt origin. Ca makes the highest concentration, SO_4 comes second followed by Mg. This depicts incorporation of materials from soil into rainwater. The data and experiment from this research and from the previously published works show major contribution of dust from soil into the formation of particulates. Moreover, it is also observed that composition of rainwater is altered by territorial sources and not human activities or marine sources.

5. RECOMMENDATIONS

● It is alarming that coal consumption in Mastung is in very huge amount in the winter season, therefore the masses should be aware of its negative impacts.

● Also, emission of vehicle diesel and brick kilns can create problem to the environment, therefore the Government should take serious precautionary measures particularly reference to plantation and forestry.

● Govt. of Pakistan should stress on promoting educational standard in the province of Balochistan to make it prosperous.

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