Effect of Cyclone on the Composition of Rainfall at Karachi City

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Abstract: A rapid urbanization results in increased levels of atmospheric pollutants and magnitude of this increase is much higher in the cities of developing world. Speciation of chemicals in rainwater is one way to assess the degree and nature of atmospheric contaminant accumulation and sources of these contaminants. In June 2010 an episode of heavy rain in the megacity of Karachi occurred due to the impact of Cyclone PHET, which was expected to hit Karachi city along the Arabian Sea. Cyclone impacted rainwater samples were collected from all over Karachi city and analyzed by chromatographic and spectroscopic techniques. A wide range of concentrations were observed among different sites i.e. pH (range 6.13 - 7.92, average 7.31), conductivity (range 9µS/cm - 154µS/cm), major anions F^- (0 - 9.22µeq/L), Cl^- (31.7 - 184.7µeq/L), NO_3^- (2.2 - 13.7µeq/L), SO_4^{2-} (9.3 - 614µeq/L) and cations Ca^{2+} (13.1 - 364.3µeq/L), Mg^{2+} (5.83 - 72.65µeq/L), Na^+ (49.1 - 344.7µeq/L), NH_4^+ (0.86 - 58.59µeq/L) and K^+ (0 - 61.44µeq/L). This wide variation of distribution was attributed to the long range transportation and climatic conditions due to cyclone effect. Industrial area samples showed a dominating character of industrial influence whereas residential areas were influenced more with the coastal impact. Spatial interpolations were used to interpret the chemical data on geographical maps using ArcGIS® .

Keywords: Rainwater, cyclone, urbanization, industrialization, contaminants.

INTRODUCTION

Cyclone, a type of tropical storm system, is created due to the strong wind with closed circulation of moving fluids in low pressure and warm temperature near the South Pacific and Indian Ocean. Tropical cyclones are natural disasters cause immense damage along its track allied with thunder storms and heavy rainfall. The intensity of tropical cyclones is categorized into different degrees depending on its wind speed and amount of resulting precipitation occurred [1]. The study of chemical composition of dissolved species in cyclonic precipitation can provide effective information on the rapid environmental changes and contamination sources [1, 2], however very less data is available regarding the chemical speciation of cyclonic precipitation. Major ions in rainwater have strong impacts on the distribution of chemical species near coastal area which are then deposited on earth surface through the wet and dry deposition events. The chemical composition of rain water varies from site to site and region to region due to influence of local sources. If the source is influenced by human impact on environment, the nature of rainwater becomes acidic because of anthropogenic activities which contribute acidic ions like SO_4^{2-} and NO_3^- and a basic

ion NH_4^+. Despite relatively large emissions of man-made acidic ions being entered in atmosphere, the alkaline nature of rainwater suggests dominance of neutralizing compounds like calcium, magnesium and ammonium ion [3]. The concentration of major ions in precipitation are influenced strongly by several physical factors, including air–mass origins, pollutant sources, transportation media, migration pathways and types of aerosol particles [4-6]. Cyclones are an important climatic and environmental feature in the region of Arabian Sea [7]. However, there is limited baseline information on concentrations of dissolved species associated with cyclone events in this region, particularly for concentrations of major ions.

Rainwater chemistry is a complicated interaction of natural and anthropogenic sources, their atmospheric transport and chemical transformation processes depending on the region [8]. In general, water available in natural state includes several inorganic and organic constituents which are beneficial for proper growth and biological functions of the biota. But due to ever growing industrial and human activities in different forms, the chemical composition of water is very much affected [9]. The study of chemical elements in wet precipitation is of great importance because of their adverse environmental and human health effects. Rainwater composition plays an important role in scavenging soluble components from the atmosphere and helps to understand the contribution of different

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sources of atmospheric pollutant. These scavenged pollutants affects the chemical composition, pH of rain water, which leads to the damage of trees, plants, crops, acidification of lakes and rivers, respiratory disorders in human, poisoning in wild life and damage of most treasured monuments [10]. The chemical analysis of rain and aerosol samples gives the first level of necessary information to identify not only the sample composition but possible sources of pollution of chemical constituents' origin [11].

A super cyclone named as Cyclone PHET agitated the Arabian Sea in June 2010 and hit the coastal line of Oman and then directed towards India and Karachi in Pakistan [12-14]. Cyclone "PHET" (a Thai word pronounced as Pet meaning "diamond") was initiated due the depression formed in central Arabian Sea near 15°N and 64°E. It was intensified into a very severe tropical cyclone (with maximum sustained wind 64-119 Knots near the centre) and was expected to hit land areas of south Karachi. Under the influence of this system fairly wide spread rainfall with scattered heavy to very heavy falls accompanied by strong gusty winds were expected to occur [15]. Karachi city received thunder showers accompanied by strong dust storm during first week of June 2010 as a result of being expected landfall for PHET [16-18].

MATERIALS AND METHODS

Site Specifications

Karachi is a coastal mega city situated along the Arabian Sea in south-west of Pakistan. It is one of the largest city of Asia with a population of about 20 million and comprises of industrial areas, harbors, oil refineries, railway stations, airports, and an enormous number of vehicles participating in gaseous emissions. The coastal meteorology and hydrography of Karachi is controlled by the seasonal change in the north Arabian Sea. i.e. monsoonal system. The Arabian Sea is known to be frequented by general cyclonic storms and some of these had been among the worst cyclonic storms of the world from their severity point of view, resulting in huge losses to life and property in the coastal area. A significant number of the cyclonic storms produced in the Arabian Sea move towards north and northeast and some of them land in coastal area of Pakistan. The available data on cyclones and storm reveals that Pakistan coast is vulnerable mostly during the period from April through June while no storm have ever been observed during January to March [18].

In this study, Karachi city was distributed into three main zones Residential, Industrial and Commercial depending upon the demographic development and rapid urbanization (Figure **1**).
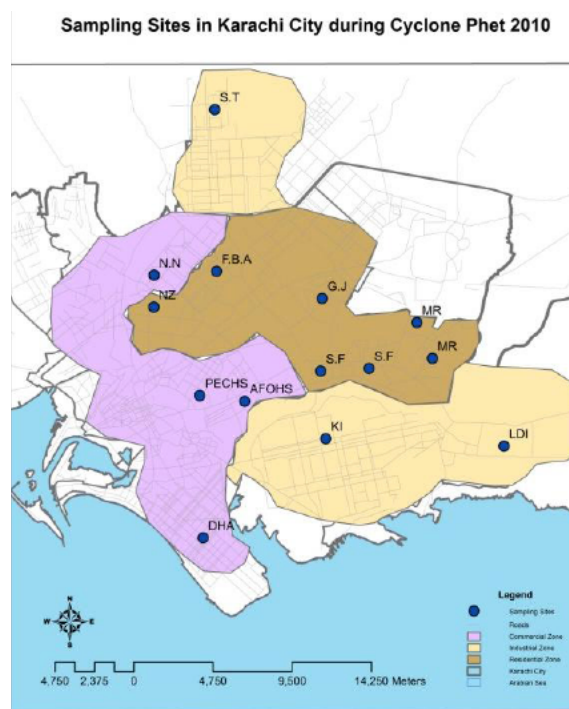

Figure 1: Map of Karachi city showing different zones and the sampling sites.

Representative samples were collected from all the zones to assess the impact of anthropogenic, terrogenic and other natural sources of contamination. Three sites were selected to cover the industrial zone of Karachi namely Korangi Industrial (KI), Landhi Industial (LI) and Surjani Town (ST). Residential Zone was covered through seven sampling sites Shah Faisal Colony (SF), Malir Colony (MR), Fedral B Area (FBA), Gulistan - e - Johar (GJ) and Nazimabad (NZ) whereas four sites selected to represent the Commercial zone; North Nazimabad (NN), PECHS, AFOHS and DHA. The industrial areas comprise different nature of industries from cottage to heavy manufacturing industries, Residential Zone is thickly populated area, some of the areas are well planned and most of the areas are with congested housing schemes and unplanned garbage dumping and burning areas, Commercial Zone - mainly represent the centralized shopping activity areas that resulting in heavy vehicular density and traffic jam in peak timings.

Sample Collection and Analysis

Rainwater samples were collected from different localities of Karachi city. Wet-only samples were

collected in pre-cleaned inert plastic (nature) buckets followed by transfer to PTFE Teflon screw capped wide mouth sample bottles of approx - 500 mL volume capacity. All buckets and sample vials were soaked with Nitric Acid (approx. 0.1N) and were rinsed several times (at least triplet) with double de-ionized water in laboratory and air dried without sunlight, prior to the shifting to sampling sites. While sample collection, all buckets were placed at roofs or at open ground to avoid other sources of contamination. After the cyclonic event, all the samples were measured volumetrically and then transferred to the pre cleaned and properly coded sample bottles. All samples then transported to laboratory for the measurements of physical parameters such as pH, Electrical Conductivity, TDS, Salinity, Temperature etc. After the preliminary analysis all the samples were filtered with whatman 40, followed by the microfiltration of all samples using Millipore 0.45 µm to avoid microbial and fungal growth in water samples. Samples were preserved in refrigerator at 4^0C for the analyses of anions and cations through Ion Chromatography using ICS-2500. Ammonium ions were analyzed through Indophenol Method using UV/Visible spectrophotometer. All solutions and standards were prepared in triple deionized water with a conductivity < 0.8 µS/cm (I. Lekouch. 2010).

GPS locations of all sampling sites were noted for the Geo-spatial analysis of data. All primary and secondary data were transferred to GIS database and the variations in concentration of ions were developed in the form of maps using Kriging Interpolation Technique in ArcGIS®. Statistical Analyses was performed using statistical software SPSS® 20.

All samples were assessed on the basis of electroneutrality to maintain the quality of data. The samples were discarded in which the equivalent ratio of sum of cations to sum of anions deviate from the range 0.8-1.2.

RESULTS AND DISCUSSION

Chemical analysis was performed in order to assess the dissolved ions in rainwater samples collected during cyclone PHET in Karachi city on 6th June 2010. The amount of precipitation recorded on the sampling sites was 77.4 mm. The corresponding parameters of rainwater samples were measured: pH, electrical conductivity (EC), major anions (Cl^-, SO_4^{2-}, NO_3^-), and major cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) (Figures **4** and **5**).

The values of pH were (range 6.13 - 7.92, average 7.43) and EC were (range 9µS/cm - 154µS/cm). A perfect correlation has been observed between the sum of anions to the sum of cations (R^2=0.92) (Figure **2**). The concentration and sequence of ions present in rainwater indicates their origin and sources of contamination. The overall pattern of major ions in rain episode is: Ca^{2+} > SO_4^{2-} = Na^+ > Cl^- > Mg^{2+} = K^+ > NO_3^- > NH_4^+ > F^- (Table **1** and Figure **3**). Heavy rains during the period of cyclone PHET not only included sea salt ions in the atmosphere but strong gusty winds also included the dusty, crustal components in rain. Due to which high concentrations of Ca^{2+} and SO_4^{2-} ions were observed along with comparative high concentrations of Cl^-, Mg^{2+} and Na^+. Concentration of NH_4^+ was higher only in the regions of vegetations but not higher enough to consider it as the neutralizing component of atmosphere. High concentrations of cations reveal the alkalinity of rain water samples. Minor ions such as F^-, Br^-, NO_2^- and HCO_3^- were also measured but in negligible concentration except that of fluoride. Normally fluoride ions are not found in rainwater, but due to the accumulation of fluorides in atmosphere of Karachi city in the form of organofluorides or as a result of garbage incineration processes, are washed out in rainwater.
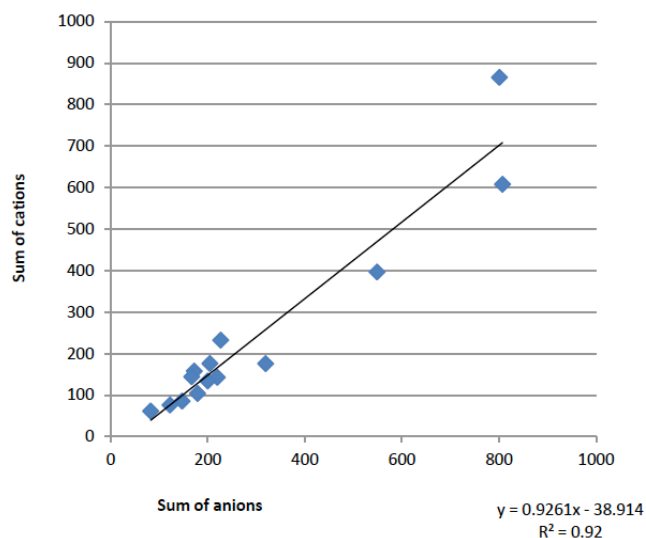

Figure 2: Correlation between Sum of anions to Sum of cations.

In commercial zone, the sequence of ions present in rainwater samples was: Na^+ > Cl^- = Ca^{2+} > SO_4^{2-} > NH_4^+ > Mg^{2+} > K^+ > NO_3^- = F^-. It was observed that the commercial zone is rich in sodium, chloride and calcium ions indicating their marine origin as the commercial region is nearer to the Arabian coast of Karachi and located on the track of wind direction and

Table 1:   Minimum, Maximum and Standard Average of pH, Electrical Conductivity (EC) and Major Ions (µeq/L) in Rainwater Samples

Analyzed Parameters	Mean	Min	Max
pH	7.43±0.34	6.83	7.92
Conductivity (µS/cm)	55.5±49.9	9	154
HCO_3^- (µeq/L)	0.31±0.22	0.06	0.74
Na^+ (µeq/L)	116.8±100.8	49.1	344.7
NH_4^+ (µeq/L)	14.22±15.18	0.86	58.59
K^+ (µeq/L)	19.1±18.98	0	61.44
Mg^{2+} (µeq/L)	23.88±19.6	5.83	72.65
Ca^{2+} (µeq/L)	125.9±112.5	13.1	364.3
F^- (µeq/L)	7.394±2.19	0	9.22
Cl^- (µeq/L)	85±48.6	31.7	184.7
Br^- (µeq/L)	0.1429±0.28	0	0.72
NO_3^- (µeq/L)	25.8±42.3	2.2	137.7
NO_2^- (µeq/L)	0.0907±0.15	0	0.34
SO_4^{2-} (µeq/L)	120.1±172.7	9.3	614
Cations (µeq/L)	299.9±240.6	82.5	807.5
Anions (µeq/L)	238.8±232.5	51.8	865.6
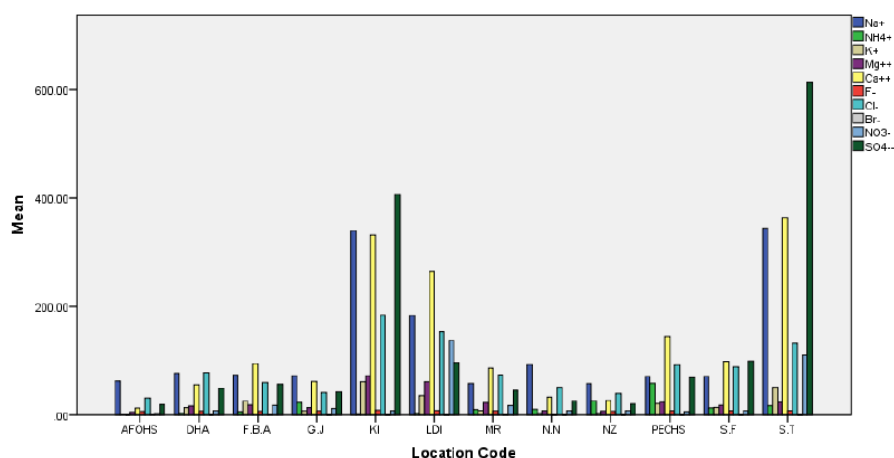
Figure 3: Site wise distribution of major ions (µeq/L) in Rainwater of Karachi city during cyclone PHET 2010.

greatly influenced by the cyclonic event (Figures **1** and **6**).

The sequence pattern of ions in industrial zone of Karachi city was $SO_4^{2-} > Ca^{2+} > Na^+ > Cl^- > NO_3^- > Mg^{2+} = K^+ > F^-$. Highest concentrations of sulfates points towards the anthropogenic origin through the industrial emissions in atmosphere. Higher sulfates indicated the acidic nature of atmosphere which is then concealed by the neutralizing agents such as calcium and sodium having crustal and marine sources. Sample with very high values of SO_4^{2-}, Mg^{2+}, K^+, Cl^- and Na^+ were collected from the area where cement industry and other cottage industries are present and contributing in atmospheric pollution (Figure **7**).
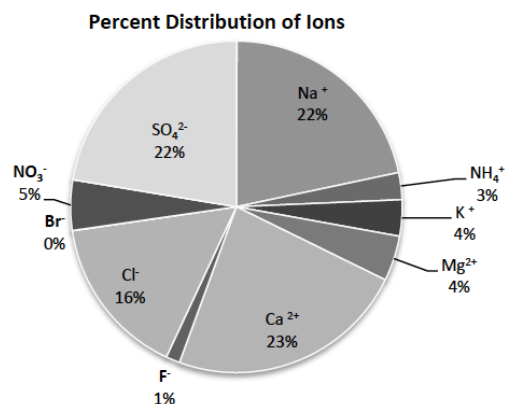
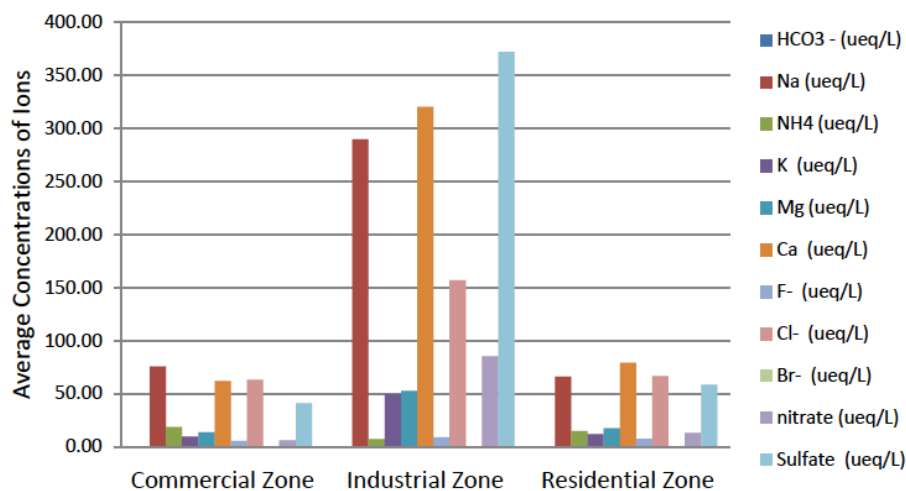**Figure 4:** Percent Distribution of Major ions in Rainwater Samples of Karachi city .

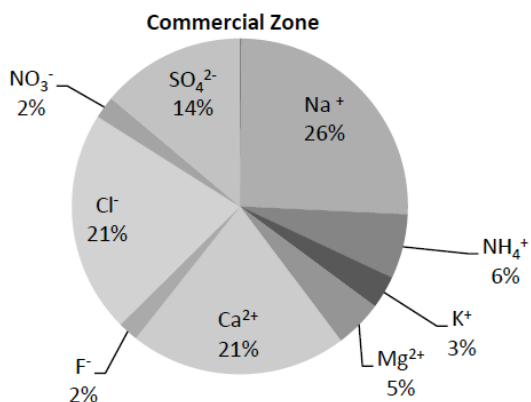**Figure 5:** Zone wise distribution of major ions in Karachi City during cyclone PHET 2010.

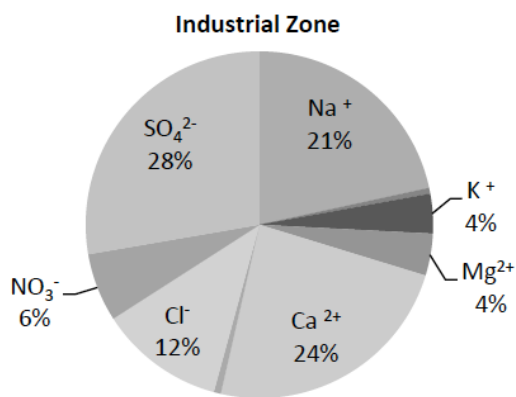**Figure 6:** Distribution of Ions in Commercial Zone of Karachi.

Figure 7: Distribution of Ions in the Industrial Zone of Karachi city.

Residential Zone is located in the center of city, higher concentrations of all the components in this zone points towards the high speed and random wind direction which transported all types of contaminants to the centre of city whether marine, crustal or anthropogenic (Figures **1**, **6** and **11**). The pattern of availability of ions in this zone is $Ca^{2+} > Na^+ = Cl^- >$

$SO_4^{2-} > Mg^{2+} > NH_4^+ = NO_3^- = K^+$ (Figure **8**) The congested construction of buildings supported the deposition of contaminants in this area through rainfall. Calcium is rich as construction process are very common along with fossil fuel and garbage burning contributing to the higher values of chloride, sulfates etc.
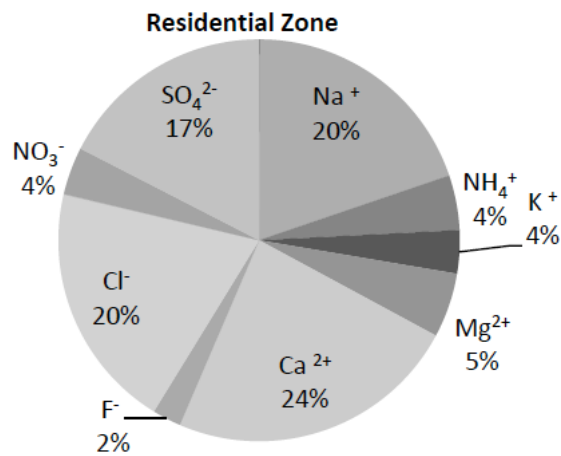

Figure 8: Percent Distribution of Ions in the Residential Zone of Karachi city.

Correlation Matrix

Strong correlation between Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} represent the cyclonic impact on the rainwater samples in which overall ionic load is high and all contaminants from all origins (coastal, anthropogenic and crustal) are present (Table **2**, Figures **9**, **10** and **11**). Contribution of garbage burning, which are frequent in center of city in addition to coastal influenced air masses could be a reason for high loading of ions. Sodium, magnesium and chloride are mainly originated from the sea and potassium most

Table 2:   Matrix Correlation of Major Ions in Rainwater Correlations (Pearson)

	HCO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	Br^-	NO_3^-	NO_2^-	SO_4^{2-}	Cations
Na^+	-0.099												
NH_4^+	-0.335	-0.209											
K^+	-0.325	0.904	-0.145										
Mg^{2+}	-0.286	0.681	-0.262	0.806									
Ca^{2+}	-0.24	0.928	-0.048	0.929	0.763								
F^-	-0.157	0.252	0.036	0.433	0.429	0.429							
Cl^-	-0.292	0.768	-0.214	0.895	0.892	0.827	0.398						
Br^-	-0.015	-0.297	-0.243	-0.205	-0.232	-0.301	0.033	-0.326					
NO_3^-	-0.004	0.558	-0.13	0.511	0.45	0.675	0.222	0.508	-0.162				
NO_2^-	-0.044	0.076	0.215	-0.059	-0.265	0.116	0.166	-0.18	0.115	0.204			
SO_4^{2-}	-0.121	0.929	-0.061	0.821	0.449	0.881	0.307	0.626	-0.254	*0.49*	0.311		
Cations	-0.224	0.966	-0.08	0.949	0.77	0.989	0.378	0.838	-0.316	0.618	0.073	0.899	
Anions	-0.153	0.954	-0.113	0.894	0.605	0.954	0.361	0.769	-0.285	0.654	0.233	0.965	0.959

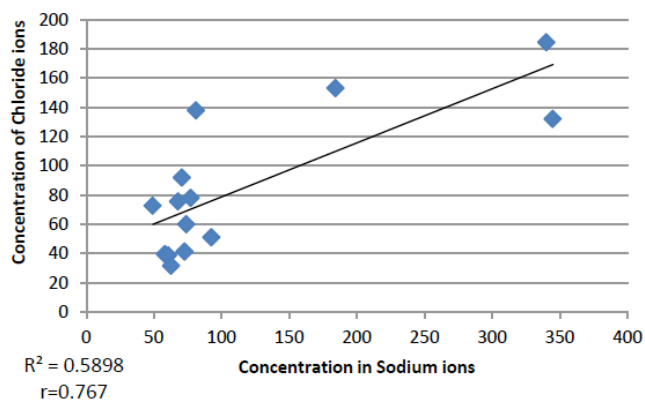likely from mineral formation, biomass burning, biotic sources and fertilizers [19].

$R^2 = 0.5898$
r=0.767

Figure 9: Correlation between Sodium and Chloride ions.

$R^2 = 0.7727$
r=0.88
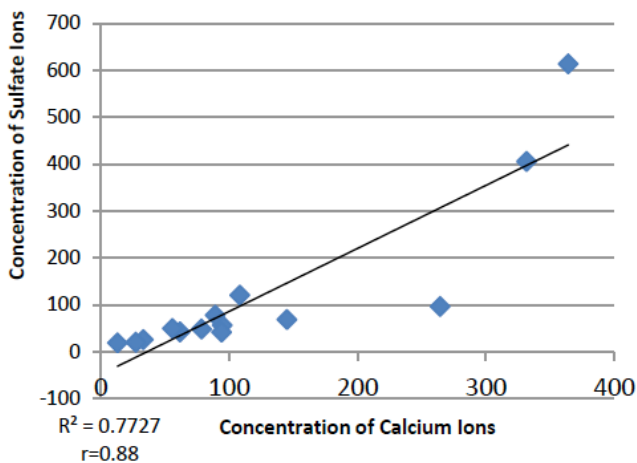
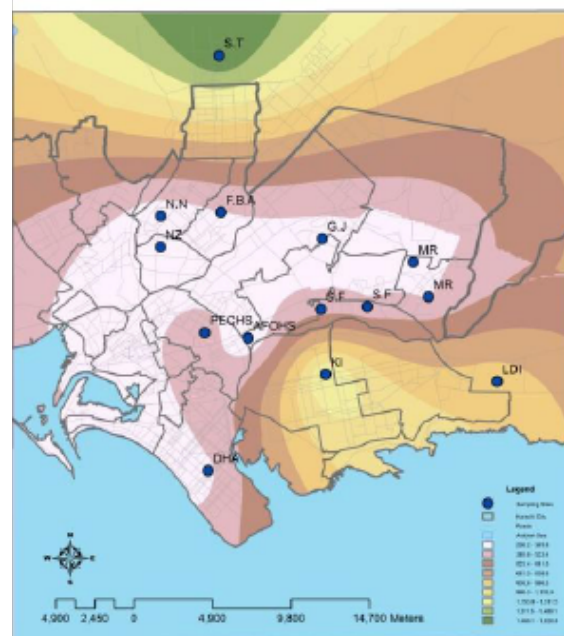**Figure 10:** Correlation between Calcium and Sulfate ions.

Figure 11: Air mass HYSPLIT Backward Trajectory.

The other major source of chloride ions in atmosphere is incineration of organohalide polymer waste [20]. Sulfates entered in atmosphere by sea-salts from wind and wave action, biogenic fossil fuel and vehicular smoke. Sources of nitrates are industries, traffic smoke, fertilizers. Good correlation between chlorides and sulfates indicated the acidic nature and presence of hydrochloric acid and sulfuric acid in atmosphere which are then neutralized by the alkaline components when interacted with rainwater.

A better correlation between Ca^{2+} and SO_4^{2-} represents the contribution of different anthropogenic sources such as cement industries, vehicle smoke, construction debris etc.

The analysis of the major ions showed that the concentration of cations is high as compared to that of anions with Ca^{2+}, Na^+ and Mg^{2+} as the main ions. Collectively it is observed in current study that all ions are distributed all over Karachi city with spikes on industrial zone (Figures **12-15**).
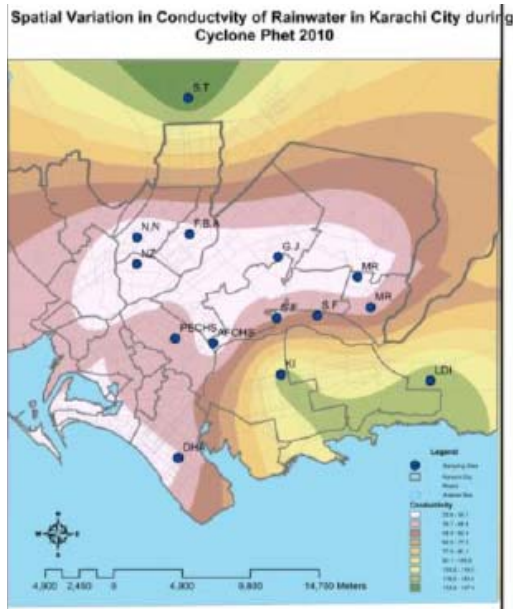

Figure 12: Spatial variation of ions over Karachi city.
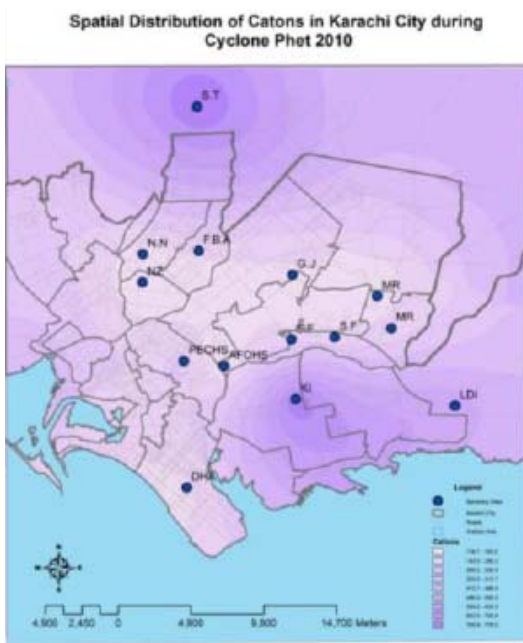
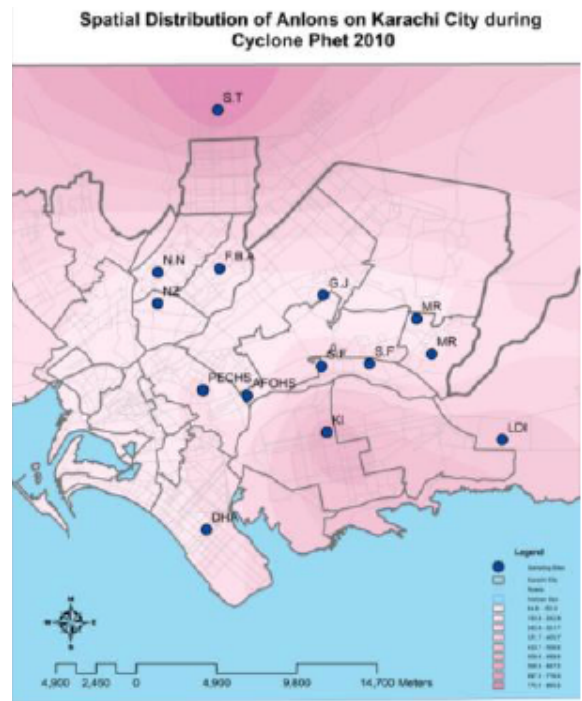**Figure 13:** Spatial variation in conductivity of rainwater samples.

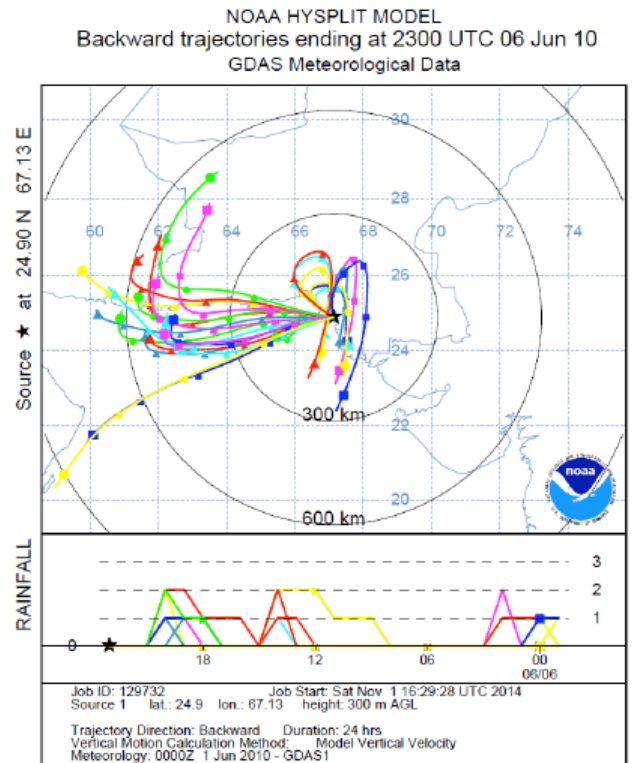**Figure 14:** Spatial Variation of cations over Karachi city.

Figure 15: Spatial variation of anions over Karachi city.

Air Mass HYSPLIT Backward Trajectory Model

HYSPLIT backward trajectory was plotted for the cyclonic event, describing the remarkable difference in track of air of Karachi city. Cyclonic influence resulted

in heavy rain with random air mass trajectory (Figures **11**) and different wind directions [21].

CONCLUSION

The study of cyclonic effect on the composition of rainwater of Karachi city was carried out to evaluate the ionic origin and distribution over the city. Major conclusions are discussed as below:

- Rainwater of Karachi city contained high doses of sulfates and chlorides but higher concentrations of sodium, calcium and magnesium changed its acidic nature to alkaline even during cyclonic event.

- Coastal impact is not quite obvious in industrial zone, as it is already heavily loaded with pollutants of anthropogenic emissions.

- Random wind directions distributed the ions in residential zones and clear coastal influence is observed in commercial zone which is located comparatively closer to the Karachi coast.

- High concentrations of sodium defined the marine influence on environment, whereas high values of calcium show the crustal impact.

- The contamination level of ions is higher in rainwater of Karachi city because of the long range transport of wind, distributing the contaminants all over the city atmosphere.

ACKNOWLEDGEMENT

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