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ASSESSMENT OF PHYSICO-CHEMICAL CHARACTERIZATION AND TOXICOLOGICAL EFFECTS OF RAINWATER AEROSOLS PARTICULATE MATTER ON HUMAN HEALTH AND PLANTS IN BALOCHISTAN

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Abstract

The purpose of this study was to evaluate the health effects of exposure to air pollution, with special emphasis on rainwater particulate matter. This is a significant health risk due to this exposure and it is also most prevalent in developing countries. The two industrial areas of Balochistan, Hub, and Quetta, are both affected by diverse types of industrial, urban, and human-made pollution and in this research, we have examined the makeup and health/growth impacts of air particles. The physicochemical characteristics and toxicological outcomes were investigated for these locations. Rainwater samples were used for assessing the air quality of the selected industrial zones. Physicochemical and toxicological analyses of fine particles were performed concurrently with an epidemiological study. These physicochemical investigations revealed that the samples of collected particles shared several key properties. Notably, there were dioxin concentrations up to 125 times higher close to the businesses and marginally elevated levels of trace metals. The results confirmed the need for a toxicological study in this area. These studies highlight the major effects of different combustion sources, such as burning coal, diesel, and biomass. Other industrial activities and the burning of waste are also potential contributing factors. The maximum amount of ion species of Ca^{2+} was found 3.521 µeq/L in Quetta and113 µeq/L in Hub. Also, the second maximum amount was of Mg^{2+} ion species with a value of 142 µeq/L in Quetta. These findings suggest that particulate matter may be hazardous to the lungs and point to the processes at play in the carcinogenicity of aerosol particles which are directly affecting human health. The effects of particulate matter not only cause serious diseases of health but also damages the greenhouse and increases global warming because of its contribution to the formation of cloud. The accumulation of such particulate matter on the surfaces of vegetation leads to the reduction in light as per required for photosynthesis and ultimately increase the temperature of leaves of the plants due to changes in optical properties of leaf surface.

Key words: Air pollution; Aerosol particulate matter; Metabolic activation; Toxicity effects on plants.

Introduction

Airborne particulates, often known as "particulate matter" (PM), are a complex mixture of solid and liquid droplets floating in the atmosphere (Jiang *et al*., 2021). Impacts of varied type of PM have been studied for their impact on health in the light of scale suggested by World Health Organization (WHO) and other concerned departments. For example, according to a report, the levels of $PM_{2.5}$ and PM_{10} in 5 construction areas of Kanpur, India increased by 18-20 time more than National Ambient Air Quality Standard (NAAQS) (Rathi *et al*., 2024). In another study $PM_{2.5}$ in temple areas and crematoriums of Kanpur, India showed extremely elevated level as compared to the allowable limit (Bhadauria *et al*., 2022). These findings reflected deep concern of the adverse health impacts of these pollutants in environment.

Based on their aerodynamic characteristics and production methods, the aerosols are classified into two types. The primary aerosols are particles released into the atmosphere directly from sources, while secondary aerosols are particles that are produced in the atmosphere either via the transformation of a primary particle or by the conversion of gas into particles as a result of the condensation of natural and artificial vapors.

The diameters of the aerosol particles can also be categorized on the basis of their size (Bhadauria *et al*., 2022; Harrison & Yin, 2000). The equivalent aerodynamic diameter (D_{ae}), which is the diameter of a sphere with a unit density (1 g/cm^3) and the same aerodynamic properties as the particle in question, effectively summarizes these attributes (Hinds & Zhu, 2022). Equation (1.1) may be used to calculate the aerodynamic diameter of a particle, where D_g is the geometric diameter, ρ_p is the density of the particle, ρ_o is the reference density (1 g/cm^3), and k is the form factor, which is 1.0 for a sphere. There is no single method for determining the size of aerosol particles; hence, particle diameters will be used in this definition (Moller *et al*., 2008).

$$D_{ae} = D_g\, k \sqrt{\frac{\rho_p}{\rho_o}} \qquad (1.1)$$

The range in the size of particulates in air, starts from a few nanometers to ten micrometres and is quite large and spans four orders of magnitude, as given in (Fig. 1) (Anon., 2012). The large-size particles (2.5 µm< D_{ae}<10 µm) are called coarse particles, and particles having a diameter greater than 10 µm are termed large coarse particles.

In contrast, smaller particles (Dae < 2.5um) are produced by industrial, urban, and biogenic activities and are classified as fine particles. These fine particles may be further separated into an Aitken mode (D_{ae}<0.1 µm) and an accumulation mode (0.1 µm <D_{ae}<2.5 µm). All suspended particles, regardless of their size, are referred to as total suspended particulates (TSP) in ambient air.

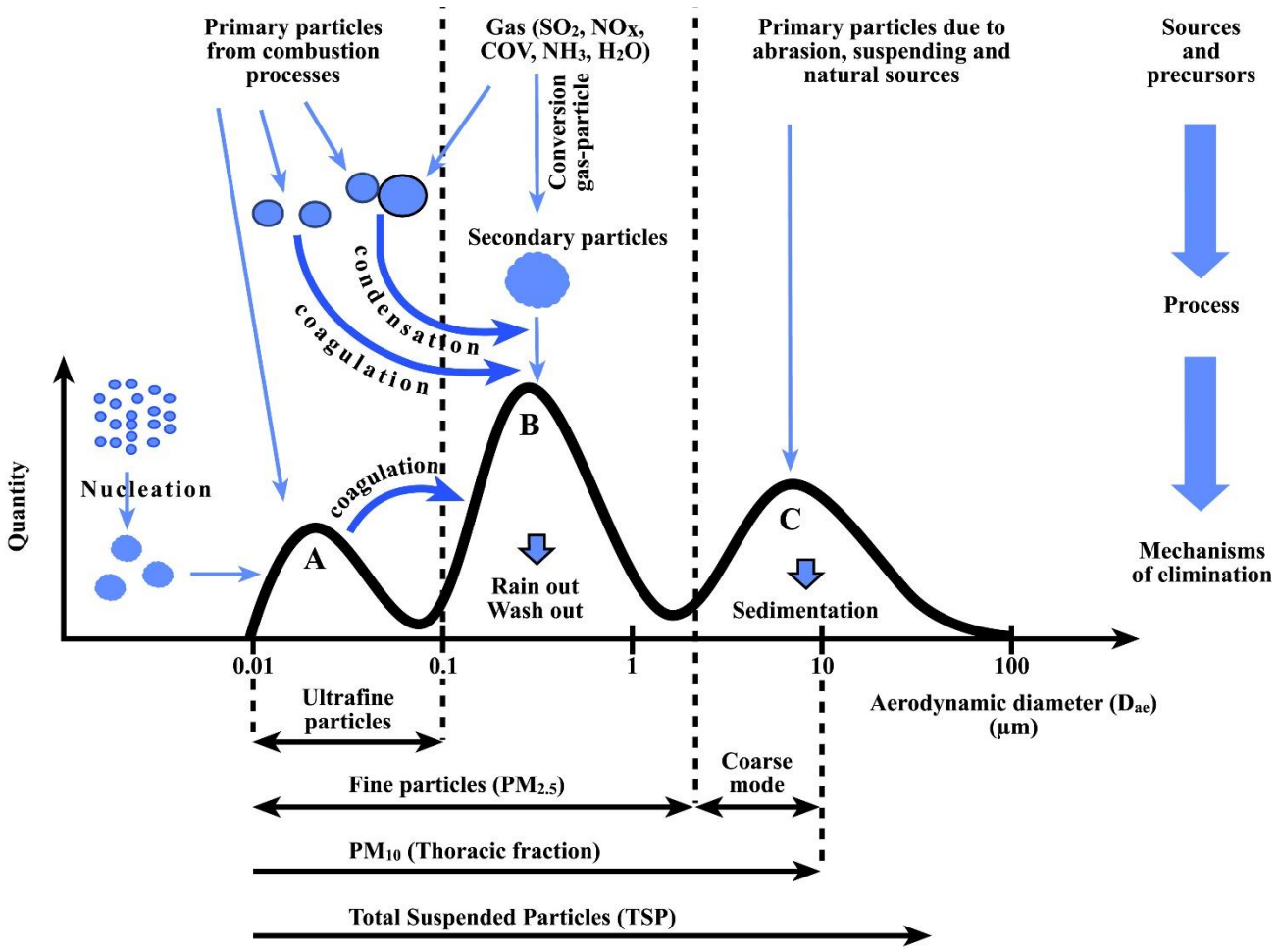

Fig. 1. Schematic representation of the particle size distribution of aerosols and their mechanisms of formation.

When these pollutants i.e., particulate matter are released into the atmosphere then temperature, humidity, photochemistry and other environmental conditions impact their complex interactions with the environment and one another. These pollutants may be divided into two categories: those that originate from primary pollutants and those that result from interactions between primary pollutants. The physicochemical properties of the atmosphere are altered by their presence.

Studies have revealed that a number of meteorological variables, such as wind direction and its speed, topography, heating etc., have an impact on how air pollution dissipates in the atmosphere (Kondratyev *et al*., 2006). The air pollution is not confined to any specified borders (Anon., 2015). Local, regional, and global air pollution are divided into three categories depending on the study size (Cote *et al*., 2008; Ramanathan & Feng, 2009).

Rainwater plays a crucial role in capturing atmospheric airborne particles through two distinct processes according to studies by Kajino & Aikawa, 2015 and Gong *et al*., 2011. The composition of rainwater (RW) is influenced by various atmospheric components, including particulate matter and gases, originating from both nearby and distant natural or human-made sources of pollution. The characteristics of these sources, such as their intensity, physical and chemical properties, and integration of particulate matter into precipitation during cloud formation and transport beneath the cloud, impact the acidity, alkalinity, and ionic concentrations of RW (Herrera *et al*., 2009). It has been observed that RW on a global scale is contaminated due to the release of numerous chemicals into the atmosphere, which subsequently dissolve during the washout process, altering the chemistry of the rainwater (Cao *et al*., 2009). The chemistry of RW remains a significant environmental concern in various regions worldwide (such as North America, Europe, and Southeast Asia) due to the environmental consequences of acid deposition (acid rain), deposition of trace metals, aquatic eutrophication, disruptions in biogeochemical cycling, and global climate change (Anon., 2003; Huang *et al*., 2010; Huang *et al*., 2008).

The chemical composition of rainwater (RW) provides valuable information about the atmospheric quality of a particular location, which is influenced by emission sources, atmospheric chemistry, and weather patterns (Zunckel *et.al*., 2003). As a result, extensive research over the past three decades has been carried out with a special focus on the study of RW chemistry in the global atmosphere (Chandra *et al*., 2005; Vet *et al*., 2014). Atmospheric chemical species can travel long distances through wind before being deposited as rain, impacting not only local temperature, soil, and plants but also contributing to the chemical composition of RW (Niu *et al*., 2014). In RW, certain constituents are frequently found in higher concentrations, including sea salt ions (Na^+ and Cl^-), soil dust elements (Ca^{2+}, Mg^{2+} and K^+), and acidic components $(SO_4)^{2-}$ and $(NO_3)^-$. These components reflect both natural sources such as sea salt and soil dust as

well as anthropogenic sources such as gases emitted from industrial areas and vehicles (Sakihama *et al.,* 2008; Huang *et al*., 2009). Additionally, regional environmental factors like weather conditions, terrain, and geography also influence the chemistry of RW (Zhang *et al*., 2012). Studies on RW chemistry during the Southwest summer monsoon season have been conducted in various urban, rural, and high-altitude locations in India over the past three decades. However, research on the chemistry of RW during the dry (non-monsoon) season has been relatively limited, except for a few isolated incidents (Ali *et al*., 2004; Kumar *et al*., 2014). It is worth noting that while there has been no significant evidence of acid rain in these regions, the presence of alkaline dust often acts to neutralize the acidity (multiple sources).

As in Balochistan's rural and industrial districts, an epidemiological study established a connection between health problems such as irritation and respiratory illnesses among the people living close to areas having industrial activity. These findings have compelled our research to evaluate the perceived health risks and levels of air pollution annoyance in an industrialized region compared to a rural location, to identify and analyze in rain water aerosols particulates matter; The anionic and cationic accumulation like sulfate and nitrates, chlorides and metals ions etc. related to health effects and additionally, epidemiological research and perception studies are necessary to assess the health risks associated with aerosols particles in these areas.

Material and Methods

Sample collection: Rainwater samples were collected during rainfall in the regions of Hub (the city of Balochistan where many industries are established and this city is very near to industrial city Karachi) and Quetta (Quetta is the capital of Balochistan province and has extremely a smaller number of industries as compared to Hub) reference to monsoon season rains during the months of August-September, 2022.

Particle digestion: Total 12 samples (07 samples from Hub and 05 samples from Quetta) were collected of rain waters from different places of Hub and Quetta in clean buckets. Sample storage waters samples were transferred to polypropylene bottles that were pre rinsed with deionized water A15-mL Teflon flask was filled with 3 mg of tiny particles, approximately one-sixteenth of the backup filter containing the quasi-ultrafine particles. The samples were mineralized by acid digestion at 120°C for 4 hrs. The remaining droplets were dissolved in 2 to 3 mL of ultrapure water and then heated to 90°C for an hour to solubilize all the concentrated components after the acid had virtually completely evaporated at 170°C over a period of around 4 Hrs. Before analysis, the cooled solution was filtered over a PTFE membrane (0.45 µm, 25 mm) and then diluted with MilliQ® water and 0.2% nitric acid up to 15 mL. The filtrate was collected in a polyethylene container and kept at -20°C until the day of the analysis, as it contained the components to be examined. To account for possible contamination from the filter fiber and the acid combination used during the preparation and analysis stages, the same technique was applied to a blank filter (Ledoux *et al*., 2006).

Ion chromatography technique: Ion chromatography technique was used to identify and measure the principal water-soluble ions. A number of factors were examined for an appropriate description of the particles gathered in industrial and rurally impacted regions. According to Baccarelli & Bollati, (2009) and Ledoux *et al.*, (2006), the bulk of these components are harmful to humans. Ion Chromatography was utilized to analyze their resulting solutions. Many regulatory and standards organizations such as ASTM, AOAC, ISO, AWWA, and US EPA, have validated Ion Chromatographic methods for the analysis of inorganic anions in drinking water (Baccarelli & Bollati, 2009). Metrohm 761 Compact IC with suppressed Module equipped with an anion separator column (Dual 2) for the analysis. In the experiment, the eluent was 2.0 mmol/L, Na_2CO_3 and1.3 mmol/L, $NaHCO_3$,2.0 mmol/L Na_2CO_3 and 1.3 mmol/L, $NaHCO_3$ were prepared from analytical reagent grade anhydrous sodium carbonate and sodium hydrogen carbonate respectively. The mobile phase and eluent were degassed and filtered using 0.45µm filters before use. 20Mm sulfuric was used as regeneration solution. Calibration standards of appropriate concentration were prepared on daily basis by diluting IC Multi element standard (Merck) containing 100 ppm F^- 250 ppm Cl^- 500ppm NO_3^+ and SO_4^{-2}and1000 ppm PO_4^{-3} etc. All solutions were prepared in HPLC grade deionized water. All the working standards and water samples were also, filtered before analysis.

Analysis of rainwater aerosol particulates: For rainwater samples, regular measurements of variables including temperature, turbidity, electrical conductivity (EC), and pH were made. Samples from bulk deposition (BD) were examined in a similar manner. Separate tank water samples were obtained for each analysis, and the BD samples were separated into sections of the required sizes. Before sub-sampling BD, the sample was physically stirred to remix any accumulated particles. Other analytical procedures were carried out through advanced instruments like HPLC, ion chromatograph and statistical methods.

Results and Discussion

Rainfall is often associated with an unstable environment, which makes it easier for air contaminants to spread. Additionally, it causes the release of certain soil contaminants and could potentially hasten the release of others. When it rains, there are fewer contaminants in the air, including dust and soluble substances like SO_2. Acid rain, which derives from sulfuric acid from SO_2 and nitric acid from NO_X, may sometimes develop from primary pollutants being processed too quickly due to humidity (Solomon *et al*., 2010). Fly ash and/or the re-suspension of dust are encouraged by the lack of precipitation.

Rainwater pH and conductivity over Quetta and Hub: During the monsoon season, rainwater in Quetta had a slightly higher pH value than the value for pure water (i.e., 7) and lower specific conductivity compared to rainwater in Hub. In the non-monsoon season, the trend was reversed, with Quetta rainwater showing lower pH value and higher conductivity values compared to Hub rainwater. Conductivity serves as an indicator of dissolved particles

in precipitation, and lower conductivity in Quetta rainwater suggests better air quality and possibly better pollution dilution due to higher rainfall. Similar kinds of results have been supported by Gioda *et al*., 2013 and Xu *et al*., 2015.

The seasonal variations in conductivity and pH values of rainwater could be attributed to the movement of air masses. Quetta receives fresher air from the Arabian Sea during the dry season, while Hub is influenced by air masses from the polluted North-western IGP region. Previous studies have reported high concentrations of particulate matter in the IGP region from both anthropogenic and natural sources (Xu *et al*., 2015; Kaskaoutis *et al*., 2014; Raju *et al*., 2016; Tiwari *et al*., 2016a; Tiwari *et al*., 2016b; Tiwari *et al*., 2015).

Rainwater with a pH below 5.6 is considered acidic, and the study found that rainwater samples from Hub were more acidic as compared to Quetta rainwater samples. This indicates a higher proportion of acid rain in Hub, especially during the monsoon season. In contrast, Quetta had relatively less acidic rain. The alkaline species present in rainwater contribute to higher pH values (Bisht *et al*., 2015; Moreda-Piñeiro *et al*., 2014).

Principal inorganic components of rainwater in Hub and Quetta: The inorganic chemical components of Quetta rainwater for the years 2012-2014 and Hub rainwater for the years 2011-2013 are presented in (Fig. 2). During these periods, the observed ionic concentrations displayed considerable standard deviations and modifications in the ionic concentration distributions. High air pollution levels were associated with volume-weighted mean (VWM) concentrations of total ionic species, specifically 304.7 µeq/L and 536.4 µeq/L in Quetta and Hub, respectively. The two most abundant ions in rainwater samples were Ca^{2+} and SO_4^{2-}, constituting 43% of the total ions for Quetta and 54% for Hub. These patterns are in close agreement with earlier studies conducted with reference to both Quetta and Hub, Pakistan (Oliviera *et al*., 2012; Budhavant *et al*., 2011; Safai *et al*., 2004).

Moreover, Quetta exhibited the highest anion concentrations (57%) of SO_4^{2-} and Cl^- and is attributed to the extensive coal burning in the area. Owing to the region's heavy dependency on coal, Hub demonstrated the highest anions concentrations (66%) of SO_4^{2-} and NO_3^-. The highest quantities of Ca^{2+} and Na^+ ions were found in Quetta, whereas in Hub, Ca^{2+} and Mg^{2+} composed 62% and 77%, respectively, of the total recorded cations. These ionic representations suggest the combined influences of calcareous soils, wind-transported dust, human construction activities, and sea salt in both locations.

Ca^{2+} and Mg^{2+} are involved in precipitation process in atmospheric samples, in wet type like snow and rain and dry types like fog, dew, cloud droplets and aerosols (Tiwari *et al*., 2012). There has been report on the affirmative impact of rainfall through Ca^{2+} and Mg^{2+} on soil water and connected with substantial changeability of both concentrations along with amount of Ca^{2+} in precipitation process. It is true that Ca^{2+} fixes more intensely to soil as compared to Mg^{2+} giving rise a constructive effect of Ca^+ regarding soil solution. Moreover, the valuable effect of Ca^{2+} on soil solutions from rainwater relies on the acidic reaction of soil and is also concerned with pH (Van-Loon & Duffy, 2007).

The process of particulate matter removal from the atmosphere is influenced by a number of variables, including particle size and climatic conditions, including wind, temperature, and humidity. There are a number of dry and wet strategies that may be used to lower air particulate matter concentrations. The particulate matter is transported to surfaces, such as soil, plants, and structures, by dry deposition without the help of precipitation. Sedimentation, impaction, and Brownian diffusion are the main factors in particle deposition. According to Raju *et al*., 2016, the physical qualities of the particles, such as size, shape, and density, as well as the features of the atmosphere and surface (including the latter's chemical and biological reactivity), all have an impact on these processes.

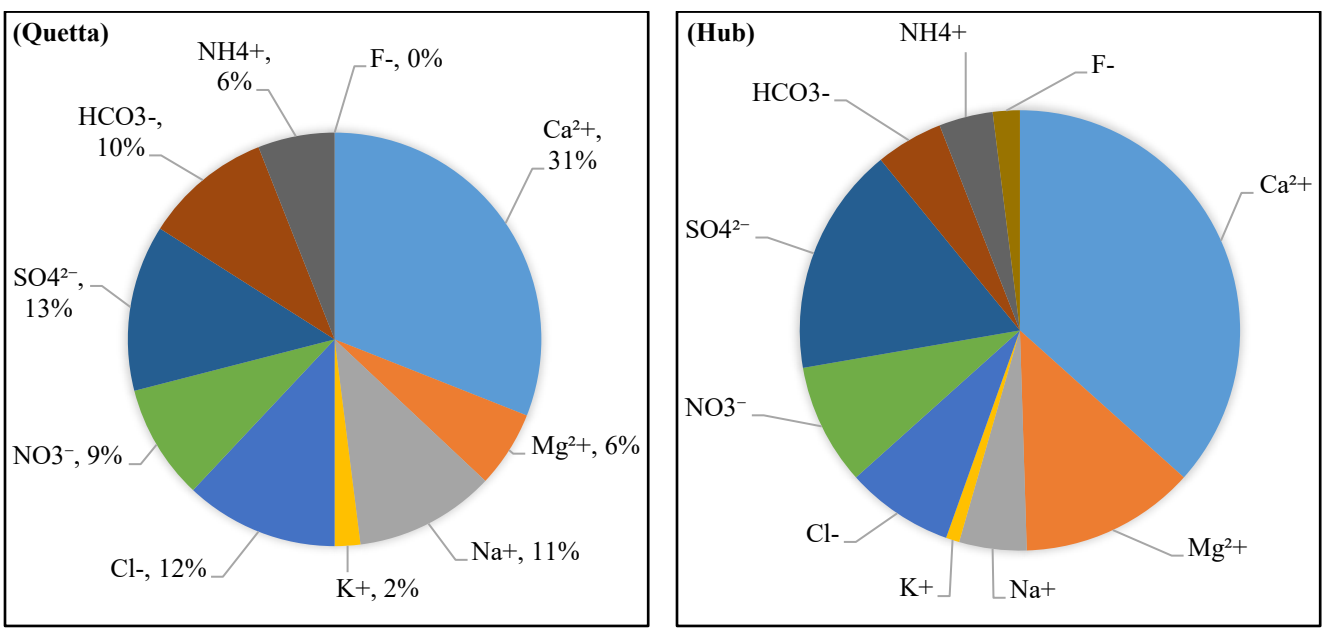

Fig. 2. Yearly proportion breakdown of inorganic chemical constituents in rain falls.

The coarse particles may remain suspended in the atmosphere for a period of a few minutes to a few days, and the main method of their removal is through sedimentation process, which is aided by gravity. Large particles between 2.5 μm and 20 μm are deposited by impaction, which is often accelerated by wind. Particles sized between 0.1 μm and 2.5 μm might remain suspended in the atmosphere for several days before being eliminated by moist deposition. The ultrafine particles have a short lifespan in the atmosphere because they have a tendency to undergo quick transformation into bigger particles.

Wet deposition refers to two procedures known as "washout" and "rainout" that include the precipitation of particles in the form of rain, fog, or snow. “Washout” refers to the capture of air particles by raindrops, while “rainout” occurs when water vapor condenses on particles to create water droplets that are then ejected during precipitation (Solomon *et al*., 2010).

The monsoon (MN) and non-monsoon (NMN) seasons were designated as the two categories for the study of rainwater samples. In Quetta, the monsoon season is from June to September, while it is from July to September in Hub. The NMN (dry) season is defined as the remaining months. The rainfall features at Quetta and Hub throughout the MN and NMN eras are shown in (Fig. 2) with significant changes seen at both sites during both times.

For Quetta and Hub, the total ion concentrations measured during the MN and NMN periods were 278.4 and 412.1 μeq/L and 406 and 1037.7 μeq/L, respectively. Ion concentrations were greater during the NMN period than they were during the MN period in Quetta and Hub, respectively. Overall, Hub's chemical component loading in air was 76% higher than Quetta's, demonstrating that both megacities had significant particulate matter concentrations throughout the dry season.

The concentrations of anions and cations at both locations throughout the NMN and MN periods exhibit significant fluctuation, as shown in Fig. 2. In contrast to the rainy period, higher quantities were observed during the dry period, highlighting the important role played by climatic factors. The concentrations of the acidic species SO_4^{2-} and NO_3^- were 1.6 and 2.5 for Quetta and 1.3 and 3.5 for Hub respectively times higher during the NMN period than they were during the MN period. At Quetta and Hub, respectively, Ca^{2+} and Mg^{2+} concentrations were 0.4 and 1.8 times higher throughout the NMN period.

The contribution of sea salt (Na^+ and Cl^-), which was 47% lower in Hub during the NMN season than during the MN season, was a noteworthy observation. However, sea salt ions were 2.4 times more abundant in Quetta during the NMN season than during the MN season. The average concentrations of major constituents of rainwater in the present study are compared with selected sites worldwide and given in (Table 1).

The calculated total wet deposition (WD) fluxes of the total ions in Quetta were 48.6 kg/ha/season during the monsoon (MN) season and 14.1 kg/ha/season during the non-monsoon (NMN) season, for a combined total of 62.7 kg/ha/y. In Hub, on the other hand, the WD fluxes were 55.5 and 11.7 kg/ha/season for MN and NMN seasons, respectively, for a combined yearly total of 67.2 kg/ha/y. It is noteworthy that the WD fluxes in Quetta and Hub were, respectively, 3.5 and 4.5 times larger during the MN season than they were during the NMN season, demonstrating the considerable impact of total rainfall. Similar WD fluxes were reported by Tiwari *et al*., 2016a, in a number of northern Pakistani locales.

During the monsoon (MN) season, calcium exhibited the highest wet deposition (WD) flux in Quetta, amounting to 8.69 kg/ha/season, while nitrate held the maximum flux during the non-monsoon (NMN) season at 3.91 kg/ha/season. In Hub, calcium demonstrated the largest WD flux for both the MN (15.1 kg/ha/season) and NMN (3.2 kg/ha/season) seasons. Kulshrestha *et al*., 2003, noted the highest Ca^{2+} WD flux (14 meq/m^2/a) at an urban site in south-central India. Recently, Akpo *et al*., 2015, estimated a lower overall WD flux in West Africa at 51.3 kg/ha/year.

Acid neutralization: The acid-neutralizing ability (AN) of the precipitation was evaluated, taking into consideration the main acid-forming elements present in rainfall, namely SO_4^{2-} and NO_3^- (both sourced anthropogenically). This was gauged using the fractional acidity (FA) method as outlined by Balasubramanian & Qian, 2003.

Additionally, the formula [$(NO_3^-)/(SO_4^{2-} + NO_3^-)$] was used to determine the proportional contributions of acidification at both sites. For Quetta and Hub, the yearly mean values were 0.40 and 0.36, respectively. These numbers show that in Quetta, the acidity of RW is 40% due to nitrate and 60% due to sulphate, while these numbers are 36% and 64%, respectively, for the acidity of Hub RW. To evaluate the neutralization of rainwater, the primary alkaline chemical constituents (Ca^{2+}, Mg^{2+}, NH_4^+, and K^+) in the rainwater at both sites were used, employing the neutralization factor (NF) methodology as suggested by Tiwari *et al*., 2016a. The NF for Ca^{2+}, Mg^{2+}, NH_4^+, and K^+ in Quetta were 1.40, 0.29, 0.29, and 0.10, respectively, while in Hub, these were 1.40, 0.49, 0.17, and 0.04, respectively. These results clearly indicate that Ca^{2+} and Mg^{2+} (both elements of the earth's crust), along with NH_4^+ ions, were the primary substances counteracting acidity in the rainwater, with K^+ having a minimal contribution.

Through the examination of air parcel back trajectories, the origins of the detected ionic species were discovered. The origins of the observed air pollution concentrations may be determined from back trajectories (Huang *et al*., 2010). In combination with back trajectory analysis, the composition of samples of rainfall (RW) collected throughout the rainy season was examined.

The HYSPLIT model is employed at a height of 2000 m, which is reflective of average cloud heights during rainy seasons, to compute the back trajectories (Budhavant *et al*., 2016). For the duration of the research work, this analysis was done in Hub and Quetta. The daily 120-hour back trajectories were then subjected to cluster analysis, which grouped air masses coming from several source locations with unique climatic and meteorological features.

For the RW samples collected in Quetta and Hub, a total of seven significant trajectory clusters were found. Table 2 provides a summary of the mean concentrations of the observed ionic species in the associated clusters, while the coefficient correlations for the rain waters of Hub and Quetta are given in (Tables 3 and 4) respectively.

Table 1. The mean concentrations of the main chemical components in the rainwater.

Location	pH	SO_4^{2-}	NO_3^-	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	References
Quetta, Pakistan	6.33	39.7	26.8	5.3	93.4	19.1	19.5	Present study
Hub, Pakistan	6.35	91.6	50.5	5.3	198.6	69.2	23.7	Present study
Beijing, China	4.85	357	42.6	9.17	273	53.3	346	Xu *et al*., 2015
Italy	5.18	90	29	17.0	70.0	77.0	25.0	Ledoux *et al*., 2006
Thessaloniki, Greece	6.57	134	41.2	16.4	256	30.5	116	Anatolaki & Thessaloniki, 2009
Southeast, Brazil	6.57	0.6	24.1	14.2	27.2	12.2		Mimura *et al*., 2016
Jodan	6.91	112.4	67.3	85.2	165.3	92.1	75.4	Al-Khashman 2009
Coruna, Spin	5.55	72.5	31.5	15.1	121,7	53.7	32.5	Gioda *et al*., 2013
Djougou, West Africa	5.19	6.2	8.2	2.0	13.3	2.1	14.3	Akpo *et al*., 2015
Mexico, USA		76.7	42.9	2.04	34.6	63.7	95.0	Baez *et al*., 2007 USA
Belgium	5.19	47.3	31.3	2.0	28.9	9.3	65.7	Staelens *et al*., 2005

Table 2. Chemical components in RW (µeq/l), cluster number (C.N.), and trajectory proportion (P.T.: %) in Hub (A) and Quetta (B) throughout the robust period.

C.N.	P.T.	F^-	CI^-	SO_4^{2-}-	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	HCO_3^-
1 A	4	1.4	20.7	37.6	21.1	22.7	10.4	76.6	22.6	21.1	51.9
2 A	16	2	19.1	62.9	48.3	14.3	7.9	100.6	14.5	24.7	15.5
3 A	14	0.9	46.7	32.2	12.6	49.5	4.4	93.7	23.8	3	40.2
4 A	9	1.6	50.1	34.1	19	46.9	3.9	112	20.8	9.2	31.9
5 A	17	1.1	44.2	28.8	13.5	42.1	3.3	94.4	19.2	8.8	32.9
6 A	18	2.5	28	67.3	54.7	25.8	6.8	113.4	24.7	49.4	18.2
7 A	22	1.5	16.8	52	38.2	13.9	6.6	82.8	14.9	41	17.6
1 B	30	9.6	51.2	133.9	72.9	32.8	4.5	352.7	145.1	24.7	28.9
2 B	6	8.7	49.4	89.6	41.1	28.3	3	231.8	111.1	16	40.8
3 B	17	10.7	58.9	125.8	82.4	27.9	4.6	271	142.3	36.3	27
4 B	9	7.9	32.2	67.7	25.4	14	3.1	142.5	37.9	5.1	15.6
5 B	13	6.9	24.8	57.8	24	22.8	7.9	207	47.9	34.1	26.2

Table 3. Coefficients of correlation between the ionic components in RW at Hub over the MN and NMN periods.

	Monsoon								Non-monsoon							
	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH^+_4	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH^+_4
F^-	0	0.35**	0.26**	0.12	0.15	0.21	0.28**	0.27**	0.71**	0.79**	0.71**	0.66**	0.53**	0.58**	0.61**	0.39
Cl^-		0.74**	0.33**	0.97**	0.54**	0.81**	0.88**	-0.07		0.84**	0.85**	0.94**	0.55**	0.80**	0.85**	0.23
SO_4^{2-}			0.64**	0.75**	0.62**	0.82**	0.81**	0.35**			0.91**	0.72**	0.68**	0.81**	0.76**	0.35
NO_3^-				0.27**	0.27**	0.51**	0.31**	0.39**				0.78**	0.80**	0.86**	0.89**	0.28
Na^+					0.56**	0.79**	0.91**	-0.08					0.58**	0.77**	0.91**	0.28
K^+						0.55**	0.68**	0.12						0.68**	0.76**	0.42
Ca^{2+}							0.84**	0.01							0.85**	0.17
Mg^{2+}								-0.06								0.43

** Correlation is significant at the 0,01 level (2 etailed)

Table 4. Correlation coefficients in RW at Quetta over the MN and NMN periods.

	Monsoon								Non-monsoon							
	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH^+_4	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH^+_4
F^-	0.55**	0.46**	0.42**	0.70**	0.08	0.69**	0.32	-0.08	0.62**	0.81**	0.61**	0.79**	0.91**	0.59**	0.95**	-0.4
Cl^-		0.39**	0.60**	0.70**	0.38**	0.72**	0.59**	-0.24		0.75**	0.82**	0.99**	0.94**	0.93**	0.81**	-0.3
SO_4^{2-}			0.43**	0.83**	0.10	0.86**	0.65**	0.03			0.91**	0.09	0.36	-0.15	0.61**	0.39**
NO_3^-				0.40	-0.09	0.54**	0.47	0.18				-0.09	0.19	-0.27	0.43**	0.38**
Na^+					0.32	0.74**	0.58**	-0.16					0.94**	0.96**	0.89**	-0.2
K^+						0.06	-0.10	-0.14						0.81**	0.96**	-0.4
Ca^{2+}							0.80**	-0.12							0.62**	-0.3
Mg^{2+}								-0.24								0.09

** Correlation is significant at the 0,01 level (2 etailed)

Interrelationships among the measured ions: A Pearson correlation analysis was performed on data for Quetta and Hub throughout the monsoon and non-monsoon seasons in order to comprehend the relationship between the observed ions in rainfall (RW) and determined their probable origins, as shown in Tables 3 and 4. At both sites and in both seasons, significant correlations (>0.60) between SO_4^{2-} and NO_3^- were observed; however, the non-monsoon period's significant level was higher than the monsoon period's. This implies that their progenitors, like SO_2 and NOx, co-emitted one another and had comparable chemical activity. There has been a report related to change in concentration of SO_4^{2-} and NO_3^- in rainwater for one year from July 1991 to June 1992 along with average pH value of 4.4 (Kai *et al*., 2023). According to their findings, high pH was sometimes noticed at initial stage of rainfall despite higher concentration of SO_4^{2-} and NO_3^- which was supposed to be due to neutralization through various cations present in PM

with average of N/S as 0.58 for one-year study. However, in early stage this value was 1.0. This increased NO_3^- concentration in the initial stage of rainfall by PM was considered to be due to difference in scavenging manners of NO_3^- and SO_4^{2-}. Strong relationships between the chemical species (Ca^{2+}, Mg^{2+}, and K^+) originating from soil were also discovered, showing that these species originated from crustal (soil) sources. Na^+ and Cl^-, which make up sea salt, revealed substantial relationships in both seasons, pointing to marine origins during the monsoon and soil sources during the non-monsoon. The increased Cl/Na^+ equivalency ratio in RW at Quetta and Hub suggested the presence of non-sea salt sources from both natural and human-made sources in addition to sea salt. Cl^- and the components of soil dust (Ca^{2+}, Mg^{2+}, and K^+) showed significant correlations which has established that soil dust contributed to the measured ions at both locations. Composition of such ions have also been studied by other workers (Martellini *et al*., 2012). According to their study the concentration trend was Ca_2^+> NH_4^+> Na^+> HCO_3^-> Mg_2^+> SO_4^{2-}> NO_3^-> Cl^-> K^+. However, in our case this trend is not observed because of different changes in atmosphere, weather, climate and other conditions. The significant relationship between the ions that come from the soil and the acidic species ($SO_4^{2-}$and NO_3^-) emphasizes the role of atmospheric chemical interactions between the alkaline and acidic species in RW. Furthermore, industrial, automotive, and other human sources, including biomass burning and agricultural activities may be to blame for the link between NH_4^+ and acidic species (SO_4^{2-} and NO_3^-).

Source contributions estimation of ionic species: As a source apportionment technique, positive matrix factorization (PMF) was utilized to look into the potential origins of the ionic components in the RW samples. PMF version 5.0 developed by the US EPA, was used to implement PMF, a commonly used approach for air pollutants. Without needing previous knowledge of source characteristics, the approach relies on measurements and related uncertainty estimates of ambient samples. The model was run individually for variables ranging from 2 to 6 on the data from these two locations. Three parameters were chosen for Quetta and four parameters were chosen for Hub based on distributions of scaled residuals and physically interpretable source contribution profiles, as they offered excellent fits to the data. PMF study has also been applied for source recognition to PM_{10} in Sofia, Bulgaria for one complete year by some workers (Hristova *et al*., 2020) regarding chemical elements and soluble ions. These values were observed to decrease in summer and increase in winter. According to their findings, the main pollution contributors to PM_{10} included, re-suspension factor>biomass burning (BB) (23%) > mixed SO_4^{2-} (19%) > Sec (16%) >Traffic (9%) >Industry (IND) (4%), NO_3^- rich (4%) > Fuel oil burning (FUEL) (0.4%) in Sofia.

Epidemiological and toxicological studies: Increased death rates, hospitalizations for respiratory and cardiovascular conditions, changes in lung function, and asthma episodes have all been related to ambient air pollution's negative impacts on health. Childhood cancer risk has been observed to rise with exposure to nitrogen dioxide, a pollutant generated by automobile exhaust (Martins *et al*., 2019). The effects of air pollution on public health are especially severe in Lebanon, where cancer is the most significant issue and instances are said to be rising over time (Kulmala *et al*., 2004). Healthcare professionals have reported a marked increase in cases of asthma, rhino sinusitis, and interstitial lung disease over the past ten years, despite the lack of a direct connection between air pollution and health effects in Hub and Quetta, Balochistan. The studies have indicated that bringing air pollution to recommended levels might result in a 70% drop in asthma cases and a reduction in bronchitis cases.

Hospitals in Hub and Quetta are not obligated to send comprehensive discharge summaries to the Ministry of Public Health, and access to illness and treatment records is restricted and not available to the general public. The frequency of allergies, respiratory illnesses, and other problems linked to air pollution, however, was shown to be greater in several urban schools after a medical examination (Fig. 3). These findings showed that the prevalence of airborne infections has been rising over time and clearly indicates towards an increase in air pollution in metropolitan areas of Quetta. This research also emphasized how susceptible certain demographics are to the negative impacts of air pollution especially kids and those who already have health issues. Both the concentration and the duration of exposure have an impact on how serious are the health impacts, with prolonged exposure having cumulative effects that last over time (Martins *et al*., 2019). Another study (Nakhlé *et al*., 2015) is based on collection health information data on 11,567 people over the course of a year and has reported variances in hospital admissions by age and gender groups.

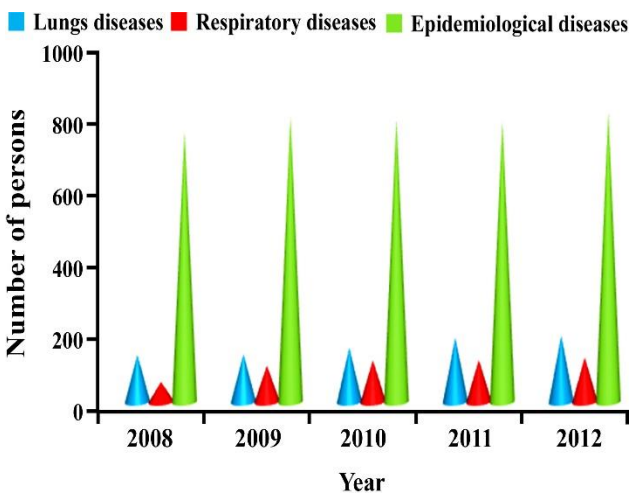

Fig. 3. Changes in the prevalence of airborne diseases from 2008 to 2012.

A case study on the effect of atmospheric aerosols on children's health was carried out in Chekka, Selaala, Koura, Batroun, and Jbeil, Koura. The research discovered a link between pollution exposure and the chance of developing lung conditions such as chronic bronchitis and asthma. Residents in Koura and Batroun's highly exposed areas (within 0-4 km) exhibited a statistically significant heightened risk. Although there was an observed increase in chest infections and bronchitis, the results didn't achieve statistical significance (Dizdaroglu & Jaruga, 2012).

Effects of particulate matter on plants: Distribution of large masses concentration of airborne particulate matter may lead to huge different phytotoxic reactions which depend on the adsorption of particulate matter and direct effects on plants/vegetation unavoidably which include (1) sulfate and nitrate and their derivatives in the form of acidity/acid and the adsorption of acid (acidifying) while on other hand (2) heavy metals and trace elements along with lead. However, the aerosols particulate matter from minerals are less dissolvable giving very little reaction as compared to the anthropogenic forming acid from nitrate and sulfate particles (Grantz *et al.*, 2003). The adsorption of aerosols particulate matter having value ≥ 9 of pH can cause directly the injury to leaf tissues (Abbasi *et al*., 2004) and sometimes indirectly by the changing of the pH of the surfaces of the soil (Bachelder *et al*., 2019). The aerosols particulate matter having toxic soluble salts may cause serious adverse effects on vegetation and plants (Prajapati & Tripathi, 2008a-d) because the exchange between atmosphere and vegetation is based on the conversion and absorption of the emission of long-wavelength radiation and short wavelength radiation (Bragazza *et al*., 2012). The adsorption of aerosols particulates on the surfaces of the leaves changes their optical character specifically the resistance of surface in infrared radiation (i.e., long wavelength region of electromagnetic spectrum) and visible range of radiation i.e., white light (Bonachela *et al*., 2012) reference to the available light for the requirement of photosynthesis. When the aerosols particulate matter changes the optical characteristics of the surfaces then it may lead to an increase in the temperatures of the surfaces of vegetation from 4 to 11.5ºC above the ambient environments (Bragazza *et al*., 2012), which bring alteration in composition and structure in the community of plants and vegetation (Bachelder *et al.*, 2019; Bragazza *et al*., 2012). Similarly, in the environment of desert and road, the aerosols particulate matter loads of 40 gm^{-2}In increase the temperature of leaves by 2-3ºC (Zhou *et al*., 2015). The accumulating of aerosols particles on the surfaces of leaves can interfere the diffusion of gas between air and leaf while the coarse particles of sedimentation affect more on the upper surfaces of leaves (Kim *et al*., 2000) but the fine particles affect lesson the lower surfaces (Beckett *et al*., 2000). In the environment of aerosols particulate matter the plants species covering of wax on stomata and stomata in grooves can be less effected as compared to the species in which the stomata at the outside of the surface of the leaf.

Summarily and precisely in the result of the present research, it was found that the incidence of chest symptoms (like breathlessness), respiratory illnesses, chest surgeries, heart complications, hypertension cases, chronic lung ailments, and deaths due to lung cancer were observed to be higher in the residents of industrial area as compared to the rural one. Male individuals exhibited a higher likelihood of these conditions than females, whereas females were more likely to experience lung issues before reaching 16 years of age, attacks of bronchitis, and allergies. Thus, there are diverse significant and indirect effects of aerosol particulates on ecosystem with reference to the indirect responses of plants in the greatest interest of chiefly soil-mediated and depend primarily on the chemical composition of the anions and cations of elements present in the aerosol particulate matters.

Conclusion

In conclusion, this study highlights the detrimental effects of air pollution, particularly in the industrial areas of Quetta and Hub, on respiratory health and overall well-being of their residents. These findings emphasize the need for government awareness and action to minimize the risks associated with the release of pollutants into the atmosphere by industries. The study underscores the importance of reducing air pollution to alleviate the burden of respiratory diseases and improve public health. Research and comprehensive evaluation are necessary to develop effective pollution reduction strategies and establish policies at the national and international levels. Strict regulations and constant monitoring of industrial emissions are crucial for mitigating the health risks posed by air pollution. To manage lead (Pb) contamination risk in water, adopt these measures: test water after heavy rain, replace Pb materials on roofs, paint Pb flashing, raise tank outlet height, adjust tank water pH, use filtration systems, consider first flush devices, maintain lawns, or use much to curb dust, especially in urban areas. Implementing these steps effectively reduces Pb concentrations in tank water, mitigating health hazards. The size of aerosols particulate matter affects more as compared to chemical composition of aerosols particulate matters on the ecosystem of plants is mediated by effects on vigor, reproductive fitness and competitive viability of the individual plants. So, plants species having large leaves can provide effective barriers near to coarse aerosols particulate matter and less effective as compared fine aerosols particulate matter travel through larger distances. Aerosol particulate matter affects the plants in terms of decrease in light available for photosynthesis, increase in leaf temperature and the interference of food diffusion of gases into and out of leaves. Therefore, it is very clear that the size of aerosol particulate matter is very important for the energy exchange in vegetation and plants. Aerosol particulate matter having alkalinity can exert direct effect on the surfaces of leaves which is a widespread threat to ecosystem function due to un-speculated aerosol particulate matter.

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