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Rain water quality assessment as air quality indicator in Pakistan

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Abstract

Rain is an effective way for removing pollutants from the atmosphere. The present study was initiated to determine rain water quality for its safe use as potable water, as well as a tool for indirect evaluation of air quality of different study areas. A total of 20 rain water samples were collected from areas including Kasur, Sheikhupura, Gujranwala and Lahore. The pH (5.49 $\pm$ 0.323), turbidity (12.267 $\pm$ 5.933NTU), Cl^- (4785 $\pm$ 1458.32ppm) and F^- (16.44 $\pm$ 4.52ppm) contents of samples are not in compliance with drinking water quality limits (Pakistan, WHO). Average sulphate (1.396 $\pm$ 0.384 ppm) and NO_3^- concentrations (52.35 $\pm$ 12.11ppm) varied between 1.005-2.05ppm and 36.79-81.3ppm, respectively. Heavy metals analysis showed presence of Cu, Co, Mn and Zn concentrations below WHO limits while Cd and Pb concentrations exceeded WHO limits with values ranging between 0.005ppm-0.017ppm and 19ppm-254ppm, respectively . Findings indicate that rain water can provide an insight into the air quality of an area and its potential use as an alternative to drinking water, especially in areas of short domestic water supply.

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Introduction

Rain is an important constituent of hydrological cycle. The increasing water scarcity problem, growing environmental concern, enactment of strict water quality regulations and requirements for sustainable water management approaches have necessitated the use of rain water, as an alternative water resource, for meeting water needs (Llopart-Mascaro *et al.* 2010). Today in many areas of the world, rain water is the only household water source or a supplementary supply in view of difficult collection of water from other sources.

Way back since 11,500 BCE in North America and 4500 BCE in Asia, rain water harvesting has been utilized for drinking water and agricultural irrigation water system (Ghimire *et al.* 2017). Rain water harvesting (RWH) offers an ancient technique to capture rain runoff from rooftops and different surfaces and its storage for later use. In developing countries, especially in arid and semi-arid areas facing water shortage, water harvesting is a common practice for domestic purposes (Notaro *et al.* 2016). Currently, RWH is a widely utilized technique for provision and supply of water for both drinking and non-potable uses especially in developing world where the mains water is inadequate to fulfill the growing demands of the society. In view of increased demand, rainwater can serve as a potential and attractive resource for safe drinking water if collected and stored through a well and suitably installed and maintained water catchment system (Olaoye and Olaniyan, 2012).

However, on account of increased atmospheric pollution, rainwater quality has also gradually deteriorated; rain fall being a dominant mean for removal of dissolved and suspended pollutants from the atmosphere (Migliavacca *et al.* 2005). Pure rainfall is generally not significantly polluted; nonetheless it depends on the season, dry period, wind, location, vehicular intensity and industrial density. Pollutants like pesticides, solids and heavy metals can be easily taken up by rain (Meera and Mansoor, 2006).

In rapidly developing urban areas of the world, air pollution has become an alarming issue which threatens human health. Substantial rise in industrial and vehicular emissions, solid waste combustion,

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rapid population growth and urbanization together within adequate strategies for air quality management and emission control are the major causes of worsened air quality (Ali *et al.* 2015). In Pakistan, environmental issues are closely linked with escalating economic growth and social development. Migration of rural population to urban areas and cities is a causal factor forill-organized and unplanned expansion of all major cities of Pakistan which has an effect on the deterioration of natural resources and worsening of the already stressed resources (Waseem *et al.* 2014).

Formation of rain comprises initially nucleation on aerosol particles; it is the result of natural distillation. The condensed water interacts with substances present in air and dissolves many of these substances. When rain falls, it collects many other impurities. In effects, the amount of pollutants in first rainwater can be much more but as rainfall continues rainwater becomes cleaner. After rain fall, air also becomes clean and aerosols i.e. sulfate, ammonium and nitrate can be reduced by 30 to 73% while the gases i.e. sulfur dioxide (SO_2), ammonia (NH_3), chlorine (Cl_2) and nitrogen dioxide (NO_2) can go down by 24 to 63% (Del Rosario and Palmes, 2011).

Since, rainwater has ability to dissolve pollutants due to dissolution of gaseous and particulate material present in the atmosphere, study of rainwater chemistry allows us to know about biogeochemical cycles of pollutants, understand the relative contribution of different sources and fluxes of pollutants present in atmosphere and provides us information on the prevailing state of the atmospheric environment of an area (Moreda-Pineiro *et al.* 2014; Egwuogu *et al.* 2016).

Moreover, the potential health hazards linked with intake of contaminated rain water limit the large scale use of harvested rain water. On account of the importance of rain and rainwater chemistry, the present study was carried out to measure concentration of different pollutants. Atmospheric wet deposition (rain water samples) was used as a tool for determining the water quality for use as potable water source as well as indirectly assessing air quality in study area.

Materials and methods

Study area, sample collection and analysis

A total 20 rain water samples, two samples from each selected area were collected. Different areas of Lahore city (Wapda Town, Nishter Road, Model Town, Walton Cantonment, Baghbanpura, Daroghawala and Wagha Border) and its surroundings (Kasur, Sheikhupura and Gujranwala) were selected for collection of rain water samples. Figure 1shows the location map of all selected areas. Sampling was done in the month of January 2017 after a four months long dry period .

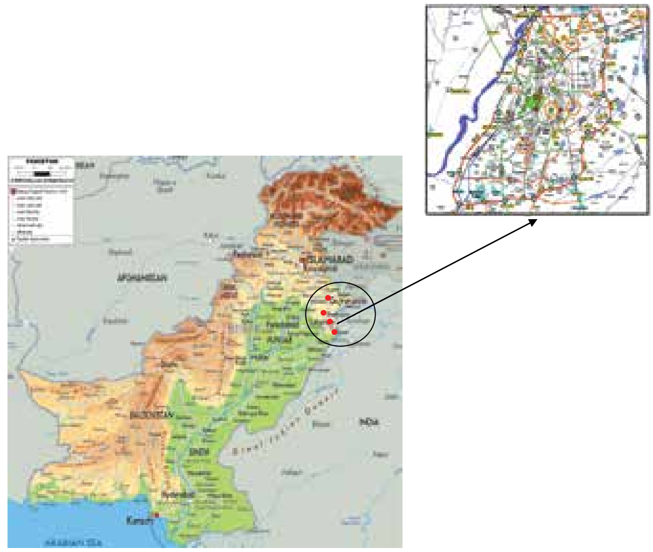

Fig. 1. Map of selected areas for sampling

All samples were analyzed for physical parameters including pH (pH meter; EUTECH Instruments PC 510/USEPA method: 150.1), electrical conductivity (Conductivity meter; EUTECH Instrument PC 510/USEPA method: 9050A), total suspended solids (USEPA method: 160.2) and Turbidity (Turbidity meter; HI 93703/USEPA method: 1801). Cations studied included Na^+ (Flame Emission Spectrophotometer; Sherwood 410, Scientific (Corning) UK/), K^+ (Atomic Absorption Spectrophotometer; 210 VGP, Buck Scientific USA), Ca^{2+} and Mg^{2+} (USEPA method: 130.2) and air pollutants anions were Cl^- (USEPA method: 9253), F^-(UK/USEPA method: 9214,NO_3^-(UK/USEPA method: 9210A) by using Ion selective electrode(930, Spectrum, Scientific) and SO_4^{2-} (USEPA method: 375.4). Heavy metals such as Cd, Cu, Co, Pb, Mn and Zn were determined by Atomic Absorption Spectrophotometer; 210 VGP, Buck Scientific USA.

Results and discussion

The ability of rainwater to uptake air pollutants makes it an appropriate medium for studying the extent of pollution in an area. The results of analysis of rain water samples are described in this section.

Chemical composition and the pH of rain water are affected by the presence of pollutants. Acid rain indicates the presence of acidic gases (mainly NO_2 and SO_2) emitted by anthropogenic sources such as industries, fuel burning and vehicles. On interaction with water in atmosphere, these are converted into acids such as nitric acid (HNO_3) and sulphuric acid (H_2SO_4). These acids bind with air moisture and become responsible for acid rain (Khan and Sarwar, 2014; Mishra *et al.* 2012).

In the present study, pH values of rain water samples ranged from 5.02-6.00 (Average 5.5±0.32) with lowest pH (5.02) in water sample of Kasur while Daroghawala sample had highest pH value (average 6.04). Kasur city, an industrial area which, coupled with vehicular emissions, may provide the reason for lower pH values.The pH value below 5.60 is generally considered as acid rain (Mishra *et al.* 2012). In the present case, majority samples qualify as acid rain and are not in compliance with Pakistan and WHO drinking water quality standards Dil *et al.,* 2008. Presence of high CO_2 levels in the atmosphere may possibly account for low pH of rain water samples since presence of NO_2 and SO_2 would have made it more acidic (Egwuogu *et al.* 2016). Earlier, rain samples from Lahore city reported pH value of 6.40 (Khattak *et al.* 2012) while a similar study carried out to assess air quality indirectly at Karachi showed pH values in the range 5.55-7.55 (Khan and Sarwar, 2014).

Electrical Conductivity of samples ranged from 62.95-485µS/cm with the highest value from Sheikhupura sample (average 485µS/cm), while sample from Gujranwala had lowest average conductivity value (62.95µS/cm). Turbidity of collected rain water samples ranged from 7.57 NTU-23.685 NTU. It was noted that Model Town had highest average turbidity (23.685 NTU) value while Wagha Border had lowest (7.57 NTU). All turbidity values exceeded Pakistan and WHO standard values. Turbidity in rain water may be attributed to the presence of suspended particles of clay or silt and colloidal organic materials as described by Khan and Sarwar, 2014.

TSS ranged from 500-4500 ppm; highest TSS (4500 ppm) was reported in Wagha Border samples and Model Town and lowest TSS (500 ppm) was found in Wapda Town and Baghbanpura's rain water samples. Average values of parameters forall collected rain water samples are given in Table I.

Sodium ions in samples ranged from 93.5-1054 ppm whereas K^+ concentration varied from 0.018-0.166 ppm. Rain water

Table I. Average values of physical parameters (pH, Conductivity, Turbidity, TDS and TSS)

Sampling Areas	Physical Parameters			
	pH	Electrical Conductivity (µS/cm)	Turbidity (NTU)	TSS (ppm)
Gujranwala	5.17	62.95	22.76	1500
Sheikhupura	5.58	485	9.53	1100
Kasur	5.02	124.6	11.07	2000
Wapda Town	5.66	101.45	8.62	500
Nishter Road	5.4	81.25	11.845	4000
Model Town	5.87	107.65	23.685	4500
Walton Cantonment	5.54	84.7	10.67	1500
Baghbanpura	5.15	134.3	8.905	500
Daroghawala	6.04	114.35	8.02	4000
Wagha Border	5.44	135.1	7.57	4500
Mean ± SD Value	(5.4870 ± 0.323)	(143.135 ± 122.409)	(12.267 ± 5.933)	(2410 ± 1654.25)
Standard values for Pakistan/ WHO	6.5 – 8.5	----	< 5 NTU	----

sample collected from Sheikhupura showed extremely high average Na^+ (1054 ppm) and K^+ concentration (0.166 ppm) while lowest average Na^+ concentration was found in Gujranwala rain water sample (93.5 ppm) while lowest mean K^+ concentration (0.018 ppm) was present in Walton Cantonment and Wagha Border's rain water samples. In a study (Khemani *et al.* 1994) the observed concentration of K^+ in rain water samples collected in India ranged from 0.13-1.40 ppm which was higher than detected values of K^+ in the present study.

Measurement for Ca^{2+} and Mg^{2+} ions was alsocarried out. Ca^{2+} ranged between 32 -1600ppm with highest Ca^{2+} (1600ppm) detected in samples collected from Kasur and Nishter Road while Gujranwala's rain water sample had lowest Ca^{2+} (32ppm). Highest average Mg^{2+} (960ppm) were present in Nishter Road sample with minimum in Walton Cantonment rain water (24ppm). Whereas samples collected from Sheikhupura, Kasur, Wapda Town, Nishter Road, Model Town, Baghbanpura, Daroghawala and Wagha Border had high Mg^{2+} ions when compared with WHO standard (WHO, 2016). Ca^{2+} in rain water mainly originates from daytime convection and vehicle/wind-driven roadside dust (Zhao *et al.* 2013). In Nigeria also, rain water samples showed high Ca concentrations (69.5mg/L-122.3mg/L) for on set of rain and between 40.1mg/L- 115.7mg/L for peak of rain (Ezemonye *et al.* 2016).Other ions, like Na^+, K^+, Cl^- and Mg^{2+} arise from natural sources. Chughtai *et al.* (2014) also reported sources of Ca^{2+}, Mg^{2+} and K^+ ions in rain water as dust from land surfaces and oceanic salts in the atmosphere. Neutralization reactions take place between acidic ions and alkaline ions and net effect results in acidity of rain water.

Table II summarizes the average concentration of $Cl^–$, F^-, $NO_3^–$ and SO_4^{2-} for all rain water samples. As can be observed, none of the samples complied with standard values for Pakistan and WHO for either $Cl^–$or F^-. Chloride in rain water samples ranged from 3550-7100 ppm, highest $Cl^–$ (7100 ppm) was found in Kasur and Wagha Border samples, while samples of Gujranwala, Sheikhupura, Nishter Road, Walton

Table II. Results of analysis of cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions ($Cl^–$, F^-, $NO_3^–$ and SO_4^{2-}) in rain water samples

Sampling Areas	Cations				Anions			
	Na^+ (ppm)	K^+ (ppm)	Ca^{+2} (ppm)	Mg^{+2} (ppm)	Cl^- (ppm)	F^- (ppm)	$NO3^–$ (ppm)	$SO4^{2-}$ (ppm)
Gujranwala	93.5	0.065	32	28.2	3550	18.05	55.5	1.194
Sheikhupura	1054	0.166	80	48	3550	21.8	49.39	1.09
Kasur	148	0.046	1600	48	7100	12.19	81.3	1.139
Wapda Town	130	0.082	240	48	5300	10.29	41.7	1.95
Nishter Road	245	0.103	1600	960	3550	11.16	36.79	1.31
Model Town	176	0.042	304	76.8	5300	14.31	54.45	1.005
Walton Cantonment	137	0.018	64	24	3550	17.4	48.95	1.52
Baghbanpura	109	0.134	40	48	5300	21.12	59.66	1.02
Daroghawala	185	0.028	160	42	3550	15.30	47.67	1.68
Wagha Border	301	0.018	80	48	7100	22.79	48.165	2.05
Mean ± SD Value	257.85 ± 286.75	0.0702 ± 0.0506	420 ± 628.14	143.10 ± 289.48	4785 ± 1458.32	16.44 ± 4.52	52.35 ± 12.11	1.396 ± 0.384
Standard values for Pakistan	----	----	----	----	<250	< 1.5	≤ 50	----
WHO Standard	----	----	----	----	250	1.5	50	----

Cantonment and Darogawala showed low concentrations. Emissions from industries, vehicles and also marine aerosols are considered mainly responsible for Cl^- ions in rain water (Khan and Sarwar, 2014). Wagha Border also showed highest F^- (22.79ppm) in rain water sample, while lowest was measured for Wapda Town (10.29 ppm). Average F^- ranged from 10.29-22.79 ppm, which far exceeds the safe limit for human consumption, as intake of excessive amounts leads to fluorosis (dental and skeletal). Apart from other ailments to human, extensively reported in literature, high fluoride levels also affect animals as well as impact adversely on plant growth (Maheshwari, 2006). Studies report that fluorosis is widespread in more than 25 nations with approximately 200 million people effected (Ayub and Gupta, 2006).

Sulphur and nitrogen oxides are precursors to acid rain. NO_3^- concentration ranged from 36.79-81.3 ppm with highest average concentration (81.3 ppm) in Kasur, while Nishter Road rain water sample had lowest average concentration (36.79 ppm). Comparison with standard values discerns that water samples of Model Town, Baghbanpura, Kasur and Gujranwala had high NO_3^- concentration. SO_4^{2-} concentration in rain water samples fluctuated between 1.005-2.05 ppm with Wagha Border having highest average SO_4^{2-} concentration (2.05 ppm) while rain water sample of Model Town had lowest average SO_4^{2-} concentration (1.005 ppm). Intake of high nitrate is reportedly linked with adverse impacts on environment and human health.

Air quality studies in different cities of Pakistan carried out by Pak-EPA/JICA, 2006 reports nitrogen oxides as 2nd emerging air pollutant in Pakistan with highest concentration detected in Karachi followed by Lahore city. Ashraf *et al.* 2013 assessed the ambient air quality of Lahore city and

Table III. Average concentrations of metals in rain water samples of selected areas

Sampling	Heavy Metals					
Areas	Cu (ppm)	Mn (ppm)	Co (ppm)	Cd (ppm)	Pb (ppm)	Zn (ppm)
Gujranwala	0.010	0.004	0.003	0.012	254	0.022
Sheikhupura	0.006	0.006	0.002	0.011	199	0.004
Kasur	0.003	0.002	ND	0.013	240	0.002
Wapda Town	0.005	ND	0.001	0.017	236	0.005
Nishter Road	0.006	0.002	ND	0.011	184	0.004
Model Town	0.006	0.001	0.001	0.008	229	0.012
Walton Cantonment	0.004	0.002	ND	0.013	19	0.008
Baghbanpura	0.005	0.001	ND	0.012	138	0.005
Darogawala	0.007	ND	0.001	0.005	88.1	0.006
Wagha Boder	0.006	0.003	ND	0.007	155	0.009
Standard values Pakistan	2	< 0.5	----	0.01	<0.05	5.0
WHO Standard	2	0.5	----	0.003	0.01	3

results of analysis revealed that concentration of NO_2 in 72% areas of Lahore city was higher than the standards value set by Pakistan and United States EPA.

These results are indicative of the worsened air quality in urban areas. Source apportionment study of ambient air of Lahore has also recognized sulfate (6$\pm$2%), nitrate (3$\pm$1%), chloride (3$\pm$1%), and ammonium (2$\pm$ 1%) as most significant inorganic ions constituents in particulate matter ($PM_{2.5}$) while Na^+ and K^+ contributed to <1% to fine PM (Stone *et al.* 2010).

In atmosphere, vehicles with diesel fuel are major source of SO_4^{2-} emissions since diesel fuel contains high sulfur content (Khattak *et al.* 2012). Similar to nitrogen oxides, air quality assessment has shown highest SO_2 levels i.e. 127 µg/m^3 (0.0450 ppm) in Lahore city as compared to those reported by Hashmi *et al.* 2005, in Karachi and Ghauri *et al*. 2007, who reported SO_2 level in Lahore, Karachi, Peshawar and Islamabad close to 57.4µg/m^3 (0.0186 ppm) to 57.6 µg/m^3 (0.020 ppm). While in Quetta and Rawalpindi reported concentrations were 68.1 µg/m^3 (0.0238 ppm) and 41.9 µ g/m^3 (0.014 ppm) respectively. Abrar *et al.,* 2014 reported higher levels of NO_2 220µg/m^3 (0.109ppm) and SO_2, 118µg/m^3 (0.0418 ppm) during four months monitoring in Lahore city. Neighbouring countries like India and Bangladesh are also facing air pollution problems in their cities. Monitoring for ambient air quality in Chittagong city Bangladesh showed highest levels of $PM_{2.5}$ while other gaseous pollutants such as SO_2, NO_2, O_2 and CO were within NAAQS permissible limit (Hossen and Hoque, 2018). Dadhich *et al.,* 2018 also reported SPM and PM_{10} as major contributor to air pollution while NO_X and SO_2 levels were lower than standards in Jaipur city, India.

Rain water elsewhere has also shown presence of Cl^-, SO_4^{2-} and NO_3^- varying from 1.31 ppm-5.94 ppm,0.09 ppm-0.38 ppm and0.00-0.25 ppm respectively, but within WHO prescribed limits (Egwuogu *et al.* 2016).

Heavy metals (Cu, Mn, Co, Cd, Pb, and Zn) were also analyzed in rain water samples and compared with Pakistan and WHO water quality standards. Results of analysis are presented in Table III. It is observed that Cu, Co, Mn and Zn concentrations were below the WHO prescribed limits. While Cd concentration in rain water samples (0.005 ppm-0.017 ppm) was higher than the prescribed limit given by WHO. Concentration of Pb ranged from 19 ppm-254 ppm, which was extremely elevated. This may have its presence due to higher level in ambient air as is proposed by Awan *et al.* (2011), who determined heavy metals Cd, Pb and Zn in ambient air of four cities (Gujranwala, Bahwalnagar, Faisalabad and Islamabad) of Pakistan and reported Cd in Gujranwala and Faisalabad to be 320ng/m^3 (0.000064 ppm) which was 80 and 4.2 times higher than in Islamabad and Bahwalnagar respectively. The high Cd concentrations are linked with steel production units, traffic density and vehicular emissions, tyre abrasions, open burning of plastic containing pigments and Ni Cd batteries. Sources of heavy metals in rain water include urban traffic (Zn and Cr) and industrial emissions and processes (Llopart-Mascaro *et al.* 2010). Khan and Sarwar (2014) also tested rain water samples of Karachi for heavy metals concentrations and reported presence of Cr, Pb, Ni, Cu, Zn, Fe, Hg, Cd and Aswhich were also below the WHO standards. Concentration of trace metals in atmospheric deposition is enhanced by anthropogenic activities. Particulate matters are considered to be most important in attracting trace metals (Mohiuddin *et al.* 2010). These metals can deposit into air of area up to a distance of 100 km from emission source (Khan and Sarwar, 2014). Dissolution of heavy metals in rain enhances the availability of heavy metals causing adverse effects on human health if used as potable water. Through precipitation these heavy metals can also accumulate in soil and water resources which results in negative impacts on forest ecosystems and aquatic organisms (Baez *et al.* 2007).

Conclusion

Rain water samples collected from Kasur, Sheikhupura, Gujranwala and different areas of Lahore were analyzed to measure concentrations of air pollutants and heavy metals. These areas generally have elevated air pollution levels in excess of standards. Consequently, rain water samples from urban and industrialized areas deviate from drinking water quality criteria. Hence, it can be concluded that use of rain water for drinking may be considered with caution and after careful examination of the quality. It is recommended to carry out bacteriological analysis of rain water due to possible bacteriological contamination. Requisite level of treatment must be applied prior to consumption of harvested rainwater in order to protect human health.

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