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A Comparative Investigation of Rain Water Quality Parameters Between Natural and Industrial Areas in Duhok Governorate, Kurdistan Region-Iraq

Najmaldin Ezaldin Hassan
Faculty of Science, Environmental Department, University of Zakho, Kurdistan region, Iraq
Correspondence should be addressed to NEH (email: najmaldin.hassan@uoz.edu.krd)

Abstract
Even though rainfall is thought of as a source that is free from contamination, human activities, especially those in the industrial and agricultural sectors, contaminate this clean kind of water. This study was conducted in two regions (Kwashe industrial area and Gara natural area) for the evaluation of rain water quality and indirectly the comparison between the evaluation of air pollution load created in both areas in Duhok governorate, the Kurdistan Region of Iraq. For this investigation, seven samples of each area were collected in the months of January and February 2023 during rainfall and they were compared. After data collection, a statistical analysis was carried out to determine the variables that affected rainwater quality. According to the current study, the first rain's water quality was significantly worse than the second rain's due to pollution. It was determined that there was a substantial difference between the first and second rain, favoring increased air pollution in the industrial region. The variation in pollutant concentrations of rainfall provides a general idea of the area's air pollution load. The outcomes of the quality evaluation program largely agreed with those found by a number of other researchers. The findings of the rainwater quality test show that pH values were lower in the Kwashe area and that some values throughout the research period exceeded the WHO-recommended limits for transportable. The results of the quality analyses indicate that it is not recommended to drink rainwater that has not been treated when it falls directly on an industrial area since it poses a health risk. The most samples of rainwater that were taken at the study site were inside of acceptable ranges for drinking use, except pH in industrial area. pH, EC, TDS, DO, alkalinity, acidity, hardness, Ca2+, Mg2+, COD, BOD, Cl-, and etc. were among the water quality metrics measured. The pollutants in the rainwater can be removed and before being used as drinking water, it should often go through some form of filtration treatment to reduce the sediment load.

Keywords: Rain Water; Environmental Pollution; Acid Rain; Water quality assessment

Introduction
One of the main sources of water for domestic and industrial use, rainwater is a renewable resource. It serves as a substitute for a drinking water supply (Lee et al., 2017). The earth's atmosphere, seasonal cycles, and the survival of all plants and animal life all benefit greatly from rainfall. Rain has numerous positive effects on the environment, such as reviving wild plants, hydrating the air, forming streams and rivers, replenishing the water table, and producing highly beneficial negative ions. Rearranging clean, fresh water throughout the water cycle is the principal benefit of rainfall (Sakai et al., 2004; Levine and Yang, 2014). There are many households uses for rainwater, including washing clothes, cleaning the house, watering plants and lawns, and washing cars. Rainwater is also regarded as drinking water in locations where there is a high probability of a water shortage (Evans et al., 2007).

In many respects, rain is really good for people, but too much of it is bad for the ecosystem. Because rainwater contains less additional contaminants than artificial irrigation systems do, including chlorine, it is typically preferred over synthetic agriculture equipment. There is one potential issue, though: the advantages of rainfall are diminished when a polluted atmosphere creates acid rain, which is exceedingly dangerous for both the environment and human health (Mehta, 2010). The majority of pollutants in rainwater come from the atmosphere being washed away, but the worst contamination happens when rainwater runs off of topography, roofs, gutters, or pipeline networks. However, the introduction of microbial pathogens, such as bacteria, viruses, and protozoa, is what leads to the most contamination (Helmreich and Horn, 2009).

The pure quality of rainfall is under jeopardy due to anthropogenic activity in recent years. These operations include burning gas flares, producing chemicals, building things, fixing cars, and disposing of rubbish, among others. They discharge pollutants such as CO_2, SO_2, NO_2, and methane, which dissolve in precipitation and cause acid rain and global warming (Mohamed et al., 2019). The quality of the water will vary when the air in the vicinity is contaminated because rain captures or traps pollutants as it falls before they reach the ground (Amin and Alazba, 2011). Rainfall can be a source of pollution for soil, water, and terrestrial vegetation as well as a technique to lessen the number of pollutants in the atmosphere (Cerqueira et al., 2014). The chemistry of rainfall is greatly influenced by dust particles, both created by humans and naturally occurring. Cations totally neutralize the acidity of rainfall before it hits the ground (Ali et al., 2004).

Metal particles and various nutritional ions are present in the atmosphere. Aerosols in the atmosphere that include nutrient ions like NO_3 and SO_4 are frequently linked to the acidity or alkalinity of rainwater. Agriculture and terrestrial ecosystems are both impacted by these nutrient ions (Kuo et al., 2013). Meanwhile, metal ions, including Cr, Zn, and Pb that are present in rainfall have an adverse effect on soil physico-chemical characteristics as well as human health (Khanh, 2000). Many evaluation studies of the characteristics of rainwater quality have been conducted by several researchers in different parts of the world, including Canada (Despins et al., 2009), Spain (Farreny et al., 2011), Ghana (Cobbina et al., 2013), Brazil (Cerqueira et al., 2014), Nigeria (Achadu et al., 2013), Pakistan (Chughtai et al., 2014) and India (Prasad and Mukesh, 2010). Sources of pollution in rainwater in the majority of industrialized urban areas, the air is frequently so contaminated that drinking rainwater is discouraged. Due to fertilizer and pesticide residues in the air and/or crops, precipitation in agricultural areas may include a higher quantity of pollutants. Because there are more particulates in the air in industrial regions, rainfall samples may have slightly higher suspended solids concentration and turbidity values (Thomas and Greene, 1993).
The aim of this study was to evaluate the rainwater's quality in comparison to drinking water quality standards established by the World Health Organization (WHO). As part of this study, numerous properties of the samples of collected rainwater were tested in order to determine the potential uses of rainwater in agriculture and municipal applications. The findings that have been made public could mark the start of a bigger investigation into the quality of rainwater, aid in the creation of new technologies for its purification, and identify potential uses for it.

Material and Methods

Study area

The study was conducted at Kwashe industrial area (lies between latitude 36.9906°N longitudes 42.7894°E) (Hassan and Umer, 2022) and Gara natural area (lies between latitude 37.0357°N longitudes 43.3678°E) in Duhok governorate, Kurdistan Region of Iraq (Fig. 1). Kwashe is an industrial area which is far 20 km west of Duhok's city (HASSAN and UMER, 2023) and Gara is a natural area and has a large area of green space which far 53km east of Duhok city. Kwashe industrial area as one of the most fast developing and polluted industrial area in Kurdistan region, which includes many factories as municipal solid waste (Hassan and Umer, 2022), oil refineries, electric power station, tanneries, dying, steel, cement etc (Hassana and Umerb, 2022). The range of its average rainfall is about 400-500 mm/year in Kwashe (Hassan and Mohammed, 2023), but in Gara is about 500-600 mm/year. Most rainfall occurs in well-defined rainy seasons of five to six months (November to April).

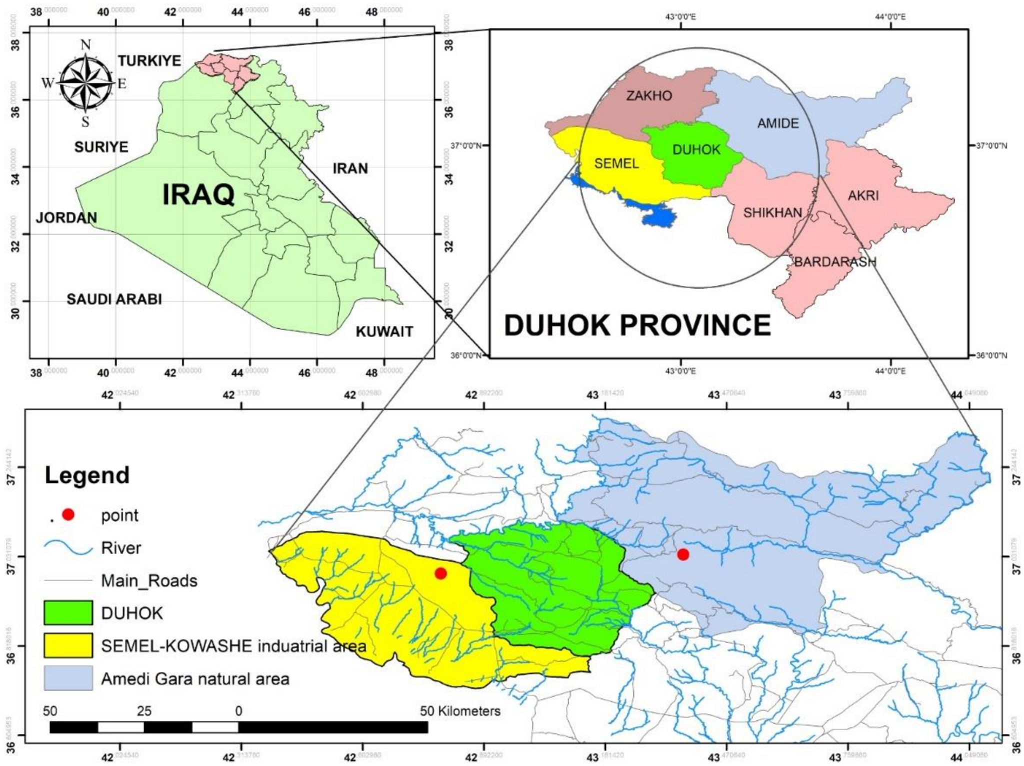

Fig. 1. Location of the study area in Duhok Province of Iraq

Water sampling and analysis

The rainwater samples were collected in the (28, 29, 30, 31 January and 1st, 2nd and 4th February 2023 respectively) when rainfall happened. Randomly water samples for each day were collected from 5 different locations within the Kwashe and Gara area and in the end mixed together. A series of flat, sterilized plastic jars having a surface area of 1 m^2 were used to collect test samples of atmospheric precipitation. Two liters of plastic bottles were used for collecting samples for physicochemical analysis. Prior to collection, the plastic bottles were cleaned with detergent solution and followed by it was treated with 5% nitric acid. Finally, deionized water was used to wash and air dry these bottles. The sample bottles were tightly screwed during sampling. The rainwater samples were labeled accordingly and transported immediately after collection to the Environment laboratory in Faculty of Sciences/ University of Zakho for examination (Yousif, 2016). The water samples were analyzed for rain water quality assessment.

Water Sample Analysis

In this study, water samples analysis covers the water quality parameters. The in-situ and ex-situ parameters are examples of measured parameters. The in-situ parameters are conducted for pH. The ex-situ parameters that were analyzed including the electrical conductivity (EC), total dissolved solids (TDS), turbidity, Ca^{2+} hardness, Mg^{2+} hardness, total hardness (TH), total alkalinity (TA), dissolved oxygen (DO), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), sodium (Na^+), chloride (Cl^-), chemical oxygen demand (COD) and biological oxygen demand (BOD) using standard methods and quality assurance procedures. The water analyses were conducted at Environmental laboratories in the Faculty of Science, University of Zakho. Standard analytical techniques were used to measure the concentrations of selected chemical species and physico-chemical variables (Rice et al., 2012). The observed values are compared with the acceptable values of the drinking water quality parameters.

The mean, standard deviation (SD), and coefficient of variation of the physico-chemical characteristics of rainfall were determined through additional statistical analysis GraphPad Prism5 was used to statistically analyze all the data in this study.

Result and Discussion

The rainwater samples collected for seven days (Fig. 2) were analysed for physicochemical parameters, and the results are given in Table 1 and 2. Generally, most of the water quality parameters analyzed were within WHO recommended limit for portability (Table 1 and 2). The total amount of rain during the study in Kwashe and Gara are (51, 109mm), respectively (Fig. 2). The rainwater of some samples contained undesirable amount of sediment load and other chemicals, some of them are not within safe limits for drinking and irrigation use. The results of physico-chemical analysis of the collected water samples are discussed in detail. All the measured values are then compared to the World Health Organization (WHO), as shown in Table 1 and 2.

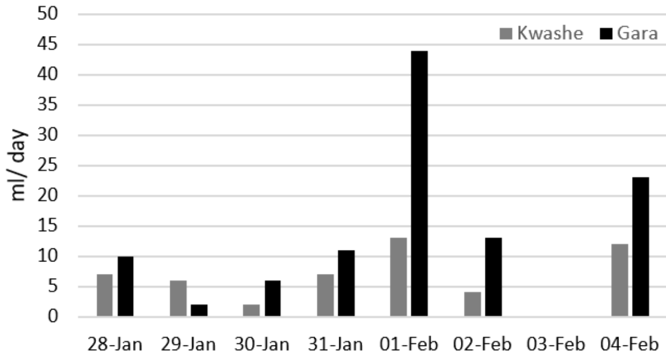

Fig. 2: The amount of rainfall in the specified areas during the study

pH

The results as presented in (Table 1) show that all the water samples were slight acidity in Kwashe area (pH 5.9-6.8) and below WHO standard limit, but majority of them were neutral in Gara area (pH 6.7-7.5) and within the permissible limit (pH 6.5-8.5) of drinking water standards of WHO (WHO, 2008). This is to be noted here that many industries are situated in Kwashe area and thus the emission of some gases might be responsible for the lower values of pH in that area (Hassana and Umerb, 2022).

The low pH found in some samples indicates high presence of CO_2 in the atmosphere as a result of excessive bushes burning within the environs (Hassana and Umerb, 2022). The growing use of fossil fuels, which releases significant amounts of SO_2, NO_2, and particulate matter into the atmosphere and reacts with rainwater to produce acid rain, can also be blamed for this. Acidosis and other health issues can result from pH levels that are lower than 5.5, which is regarded to be excessively acidic for human consumption (Asamoah and Amorin, 2011). In terms of extreme values (pH 5.0) and median values (pH 6.0), rainwater that was obtained directly from the air had the lowest pH readings (Zdeb et al., 2020).

Rainwater pH measurements showed lower and occasionally higher values of the WHO's drinking water standards (5.02-9) (Cobbina et al., 2013). In comparison to research of a comparable nature conducted in Obuasi, which found a mean pH of 4.67 ± 0.47 (Akoto et al., 2011), the mean pH was marginally higher. Most aquatic species cannot thrive in conditions with pH levels of more than 9.5 or less than 4.5 (Sardana et al., 2022)

EC and TDS

A good air environmental quality is indicated by low rainwater conductivity. The EC of rainwater was found to be (131-151 µS/cm) in Kwashe area and (110-133 µS/cm) in Gara area, were in both areas are within the desirable limit for drinking water (WHO, 2008) and within the safe limit of 2.25 dS/m for use as irrigation water (Sharma et al., 2008). The germination of almost all crops would be impacted by an EC value of 3 dS/m, which could lead to a significantly lower yield. The higher values of EC obtained for rainwater of Kwashe and Gara regions were in good agreement with the EC values reported by other researchers on the basis of their study (Palanisamy et al., 2007; Karunakaran et al., 2009).

The TDS value of Kwashe area was (81-94 ppm), while that in Gara area it was (67-83 ppm). The analysed data showed that all of the rainwater samples have less TDS than the maximum permissible limit of drinking water and irrigation use (WHO, 2008; Sharma et al., 2008). The values of TDS obtained for rainwater of Kwashe and Gara regions were in less with the TDS values reported by other researcher on the basis of his study (Bharti et al., 2017). High solids concentrations in water might have constipation-inducing effects, and high TDS levels can make water unattractive for bathing and cleaning (Jameel et al., 2006).

Turbidity

The presence of particulate matter in the local ambient air may be the cause of the high levels of turbidity of precipitation observed. Local activities like bushes burning and the presence of particle matters or dust have an impact on the quality of the rainfall in the research region (Hassana and Umerb, 2022). The samples' turbidity levels, which compared to the WHO limit of 5 NTU, were in the ranges of (1.2-3.4 NTU) in the Kwashe area and (0.3-1.2 NTU) in the Gara area, indicating that the rainwater is optically clear enough (Table 1). In turn, rainwater gathered for his study was found to have the maximum turbidity (11–19 NTU) (Bharti et al., 2017).

Turbidity levels above 5 NTU have a propensity to interfere with treatment processes and serve as a breeding ground for microorganisms. Excessive levels of turbidity can shield microorganisms from the effects of disinfection, promote bacterial development, and increase the need for substantial amounts of chlorine (John et al., 2021). Iron and other metals, whether as natural impurities or as corrosion products, have a significant impact on color (WHO, 2008).

Calcium, magnesium and total hardness

The samples of rainwater revealed a lower hardness than what is ideal for drinking water. Mean concentration of calcium and magnesium hardness were (4.857 and 4.5) respectively. The results less than to other study which did in Kurdistan (Abduljabar et al., 2020). Total hardness, however, stayed within irrigation water's acceptable range. Total hardness concentration of the rainwater ranged from (8.2-10.7 mg/L and 10.7-12.3mg/L) with a mean of (9.357 and 11.114 mg/L) in Kwashe and Gara respectively. The amount of total hardness in the rainwater sample was very high (120 mg/L) (Bharti et al., 2017). In another research of drinking water, the total hardness ranged from 346 to 574 mg/L, with a mean rate of 394 (Hassan and Ali, 2016). Kidney stones, cardiovascular disease, and digestive problems can all be brought on by drinking water that is too hard (Dušek, 2002).

Total alkalinity

The amount of ions in water that can neutralize hydrogen ions is known as alkalinity. The toxicity of numerous compounds in the water is influenced by alkalinity, pH, and hardness (Pandiarajan et al., 2023). For both the Kwashe and Gara locations, the total alkalinity of the rainwaters were below the safe threshold. In comparison to the WHO limit of 1000 mg/l for drinking water (Table 1), the total alkalinity concentration of the rainfall in the Kwashe and Gara areas during the study ranged from (7.2 to 8 mg/L) and (7.9-8.7 mg/L) and had a mean of (7.7 and 8.3 mg/L) respectively. In comparison to other studies for drinking water, the average total alkalinity was lower (Abduljabar et al., 2020; Hassan and Ali, 2016), with mean values of (142 and 64,75), respectively.

Dissolved oxygen (DO)

Throughout the study period, the dissolved oxygen level was found to be (5 and 5.4 mg/L) in both locations (Table 2), which was within the recommended range of dissolved oxygen in drinking water. In turn, rainwater gathered for his investigation contained the lowest DO (3 mg/L) (Jamal et al., 2020). Our findings are close to other studies of DO for drinking water (Hassan and Ali, 2016). Dissolved oxygen (DO) is important to evaluating the quality of the water because it affects the guar and palate. The pressure, temperature, and exposure of a surface are the key determinants of the DO. Water's dissolved oxygen can be depleted by the breakdown of organic materials (Hassan and Ali, 2016).

Table 1: Major quality parameters of rainwater in selected areas.

Parameters		pH	EC	TDS	Turbidity	Ca hardness	Mg hardness	Total hardness	Total alkalinity
Min - Max	Kwashe	5.9-6.8	131-151	81-94	1.2-3.4	4.2-5.5	4-5.2	8.2-10.7	7.2-8
	Gara	6.7-7.5	110-133	67-83	0.3-1.2	5.6-6.5	4.6-5.8	10.7-12.3	7.9-8.7
Mean	Kwashe	6.51	138.1	85.857	1.871	4.857	4.5	9.357	7.7
	Gara	7.2	117.3	72.429	0.571	6.01	5.043	11.114	8.329
SD	Kwashe	0.323	7.426	4.562	0.739	0.479	0.458	0.902	0.3
	Gara	0.279	7.994	5.593	0.298	0.313	0.454	0.615	0.298
Std. error	Kwashe	0.122	2.806	1.724	0.279	0.181	0.173	0.341	0.113
	Gara	0.105	3.021	2.114	0.113	0.118	0.172	0.232	0.113
Variance	Kwashe	0.105	55.143	20.81	0.546	0.23	0.21	0.813	0.09
	Gara	0.078	63.904	31.286	0.089	0.098	0.206	0.378	0.089
Skewness	Kwashe	-1.293	0.857	0.926	1.776	-0.062	0.611	0.166	-0.83
	Gara	-0.974	1.437	1.25	1.913	0.363	0.896	1.541	-0.228
Kurtosis	Kwashe	1.364	-0.187	0.356	3.655	-.1.438	-1.178	-1.163	-0.388
	Gara	1.006	2.18	1.297	4.21	-0742	-0.583	1.555	-1.601
Coeff. var	Kwashe	4.969	5.375	5.313	39.474	9.864	10.184	9.635	3.896
	Gara	3.873	6.816	7.723	52.221	5.208	9.004	5.532	3.583
Threshold= X+2s	Kwashe	7.156	152.95	94.98	3.35	5.82	5.42	11.16	8.3
	Gara	7.758	133.29	83.62	1.17	6.64	5.95	12.34	8.93
WHO (2008)		6.5-8.5	1500	1000	5	75	50	500	1000

Sodium, potassium, calcium and magnesium

The concentration of sodium, potassium, calcium and magnesium of the rainwater compared to WHO recommended limits for drinking water (table 2). Concentration of Na^{+}, K, Ca^{2+} and Mg^{2+} in all the sources of water were within safe limits for drinking and irrigation. The concentration of sodium ranged from (7.7-8.9 and 5.6-6.8 mg/L) with a mean of (8.229 and 6.243 mg/L) in Kwashe and Gara respectively, compared to WHO limit of 200 mg/l for drinking water (table 2). However, it is reported that for individuals suffering from health problems such as heart disease or high blood pressure the maximum recommended sodium concentration in drinking water is 20 mg/l (Younos et al., 1998). While that of Ca^{2+}, K and Mg^{2+} were (17.6-19.8 mg/L), (18.3-21.2 mg/L) and (8.9-10.2 mg/L) respectively.

The mixing of salts in overland flow may be the cause of the high concentration of Na^{+}, Ca^{2+}, and Mg^{2+}. The Ca^{2+} and Mg^{2+} levels corresponded to those given by researcher (Jothivenkatachalam et al., 2010). The observed K^{+} concentration values and the matching range of values reported by researcher (Usharani et al., 2010) were in good agreement. The measured average mean is significantly lower than the value given by a comparable study conducted in Egypt (Thomas and Greene, 1993). Compared to hard water and water with a high magnesium content, water lacking in calcium and magnesium is linked to higher rates of morbidity and mortality from cardiovascular illnesses (Donato et al., 2003). Intake of soft water may be linked to a significant risk of fracture in youngsters, according to recent studies (AC and JM, 1992).

Chloride

The most prevalent anion in water is often chloride, which can cause corrosion and pitting in iron plates or pipes. The mean of Cl concentration was found less in both Kwashe and Gara (4.385 and 1.914 mg/L) water samples compared to WHO limit of 250 mg/L for portable water. However, rainwater samples had relatively lower values of Cl than in contrast to the other study sites. In Egypt, the average chloride content is a tiny bit lower than that of rainfall (Thomas and Greene, 1993). The district of Coimbatore recorded a similarly high value of 891 mg/L for chloride (Jothivenkatachalam et al., 2010). Human activity and the burning of waste materials like PVC, which produces HCl in the gas phase, are the sources of chloride ions (Younos et al., 1998).

BOD and COD

Some important parameters related to human health were also analyzed in which BOD (6-11 mg/L and 2-5 mg/L) and COD (21-45 mg/L and 13-23 mg/L) were found in Kwashe and Gara rainwaters, respectively. The results near to other study which are done in India (Bharti et al., 2017) and lower to study which did in Kurdistan (Abduljabar et al., 2020; Hassan and Al-Barware, 2016). If BOD is 2 mg/L or below, the water bodies are not polluted (Chigor et al., 2012).

Table 2: Major quality parameters of rainwater in selected areas.

Parameters		DO	Ca	K	Mg	Na	Cl	COD	BOD
Min - Max	Kwashe	4.5-5.3	17.6-19.8	18.3-21.2	8.9-10.2	7.7-8.9	3.9-5.3	21-45	6-11
	Gara	5.1-5.7	14.3-16.6	10.8-12.6	6.7-8.3	5.6-6.8	1.7-2.3	13-23	2-5
Mean	Kwashe	5	18.586	19.543	9.614	8.229	4.385	28.286	7.857
	Gara	5.442	15.3	11.614	7.514	6.243	1.914	16	3.571
SD	Kwashe	0.258	0.786	0.993	0.46	0.431	0.456	8.118	1.773
	Gara	0.199	0.866	0.641	0.59	0.404	0.195	3.464	0.976
Std. error	Kwashe	0.098	0.297	0.375	0.174	0.163	0.172	3.068	0.67
	Gara	0.075	0.327	0.242	0.223	0.153	0.074	1.309	0.369
Variance	Kwashe	0.067	0.618	0.986	0.211	0.186	0.208	65.904	3.143
	Gara	0.04	0.75	0.411	0.348	0.163	0.038	12	0.952
Skewness	Kwashe	-1.22	0.37	0.641	-0.373	0.409	1.545	1.747	0.80
	Gara	-0.655	0.35	0.517	-0.101	-0.31	1.418	1.583	-0.277
Kurtosis	Kwashe	2.202	-0.933	-0.189	-0.844	-.1.009	2.839	3.477	0.44
	Gara	0.348	-1.273	-0.771	-1.224	-0.17	2.523	2.961	0.042
Coeff. var	Kwashe	5.164	4.23	5.081	4.783	5.237	10.401	28.701	22.563
	Gara	3.653	5.66	5.523	7.852	6.464	10.196	21.651	27.325
Threshold= X+2s	Kwashe	5.52	20.16	21.53	10.53	9.09	5.3	44.52	11.4
	Gara	5.84	17.03	12.9	8.69	7.05	2.3	22.93	5.52
WHO (2008)		5-8.6	200	30	150	20	250	250	50

Conclusion

The results of the quality analyses indicate that it is not recommended to drink rainwater that has not been treated when it falls directly on an industrial area since it poses a health risk. The findings of the rainwater quality test show that pH values were lower in the Kwashe area and that some values throughout the research period exceeded the WHO-recommended limits for transportable. The mean pH value was 6.5, with pH values ranging from 5.9 to 6.8. This indicates a high concentration of CO_2 in the air due to burning of oil and wastes in the area. This is also due to increased fossil fuel consumption, which releases significant amounts of SO_2, NO_2, and particulate matter into the atmosphere. The physical and chemical quality of the rainfall in the Gara area is suitable for drinking, according to WHO drinking water guidelines. Rainwater in Gara area is better than in Kwashe area due to the differences in the air masses reaching the sampling location from different sources like illegal factories, electric power production station, traffic conditions, Landfill sites and local atmospheric circulation. Before being used as drinking water, rainwater should often go through some form of filtration treatment to to reduce the sediment load. The pollutants in the rainwater can be removed by treating it with the appropriate technologies. Finally, this evaluation technique may also be utilized as a novel assessment method for monitoring pollutant loads and air quality.

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