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An investigation of heavy metals concentration in rainwater and their effects on human health in Kurdistan Region, Iraq

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Abstract

One possible source of fresh water is rainfall. Nonetheless, the natural composition of rainwater may change due to air pollution in any areas. The Kwashe and Gara in the Duhok Governorate, in the Kurdistan region of Iraq, was selected as the study areas. Heavy metals concentration of rainwater was investigated. Seven samples were taken during rainy January and February 2023 for this investigation, and a statistical analysis was carried out to identify the factors influencing the quality of the rainwater. The concentrations of heavy metals (Zn, Pb, Ni, Cr, Cd, Mn, Cu, Fe, and Co) were measured with an atomic absorption spectrophotometer (AAS) and compared to WHO standards. The purpose of the study was to compare the heavy metal content of study area rainwater to WHO standards in order to determine the effects of these metals on community members' individual health as well as the environment. The heavy metal concentrations dropped in the following order: (Zn, Pb, Ni, Cr, Cd, Mn, Cu, Fe, and Co in Kwashe and Zn > Ni > Cu > Pb > Cr > Fe > Mn > Cd > Co in Gara). The following heavy metals are within the WHO's permissible limit: Fe, Cu, Zn, Mn, and Co; the others exceeded it. The results indicate that the rainwater sources in the study areas are unsafe and unfit for human consumption. Because of this, rainwater from research areas needs to be treated before drinking in order to prevent Pb, Cd, Ni, and Cr-related health problems.

Keywords: Heavy metals; Rainwater; Duhok areas; Health risks; WHO

1. Introduction

Rainwater is a free, renewable source of almost clean water [1]. Rainwater is still regarded as a good and safe source of drinkable water in many places. Rainfall is a valuable supply of fresh water, particularly for those who reside in rural regions or in places with low surface and subsurface water quality, where water use is constrained by scarcity [2]. One of the primary sources of water for residential and industrial use is rainfall, which can also be used in place of drinking water supplies [1]. Rainwater has long been thought to be pure water that does not affects the environment [3]. Although rainfall is the cleanest type of naturally occurring water, untreated rainwater is no longer acceptable for human consumption due to pollutants in the atmosphere [4].

Human activity has an impact on the atmosphere's inherent chemical composition [5]. According to Obaidy and Joshi [6], the chemical makeup of rainwater indicates the amount and calibre of air pollutants that are released into the atmosphere by both natural and man-made sources. The quantities of heavy metals in atmospheric deposition have significantly grown due to anthropogenic sources. Many heavy metals can be harmful to human health if consumed through drinking water or aquatic life if the concentrations are too high [7]. Numerous pollutants are released into the ambient air by anthropogenic sources as gas flaring, industrial plants, electric utility facilities, metal mining, automobile exhaust, and pesticides [8]. Even though they are located distant from the point source, these sources have also increased the amount of metals in the air, on land, and in aquatic habitats [9, 10]. The presence of many gases such as CO2, H2S, CO and ozone has already been proven in the Kwashi area and this is obviously affected by the quality of

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rainfall [11]. Additional sources of heavy metals include ground-surface mineral particles, parts of vehicle emissions, emissions from industries, and products of fuel combustion released into the atmosphere [12]. Because heavy metals have detrimental impacts on the environment and human health, research on them in rainwater has intensified in recent decades [13, 14]. Some researchers have included the study of heavy metals [15-20].

Water is an essential component of the environment, and heavy metal pollution of it is regarded as a global environmental issue [21, 22]. The United States Environmental Protection Agency regulates heavy metals in drinking water because of their extreme toxicity, which makes them a constant source of concern [23].

Metal ions like Cr, Zn, and Pb that are present in rainwater have an adverse effect on the physical and chemical properties of soil and can be harmful to human health when consumed [24]. Previous research has shown that the first flush of rainwater, particularly following an extended dry season, contains the highest levels of contaminants [1, 25]. After respiratory disorders, diseases brought on by the consumption of tainted water and inadequate hygiene practices account for the majority of child deaths globally [26]. Depending on the kind and quantity of the metal involved, heavy metals can readily bind to essential cellular components when they enter the human body and accumulate in organisms, leading to a variety of diseases and disorders, such as cancers, osteomalacia, kidney malfunction, etc. [27, 28]. Numerous heavy metals, including cobalt, mercury, lead, arsenic, nickel, cadmium, beryllium, chromium, and others, are thought to be carcinogenic. As an illustration, numerous studies have demonstrated that drinking water with high levels of arsenic increases the risk of bladder, kidney, lung, colon, liver, and skin cancer [29]. Moreover, aluminum can cause bladder and lung cancer, and cadmium is known to cause kidney, prostate, and lung cancer. With the impact of pollution on the health aspects, also having an unpleasant odour and this caused inconvenience to the people of the region [30].

Given that Kwashe's atmosphere is among the most polluted in the Kurdistan Region, it was thought to be crucial to examine the major heavy metals of Pb, Cu, Zn, As, Ni, Hg, and Fe. The goal of the current study is to ascertain whether rainwater is safe and appropriate for human consumption by analyzing the concentrations of heavy metals in it and evaluating its quality for the purpose of monitoring environmental pollution caused by anthropogenic activities in the study area. This will assist in identifying environmental pollution at an early stage that contributes to the prevalence of water-borne illnesses in the research area.

2. Material and methods

2.1. Study area

The study area is in the Kurdistan Region of Iraq, specifically in Semel district (Kwashe) and Amedi district (Gara natural area) in the province of Duhok. Figure 1 shows that Kwashe is located between latitude 36.9906°N and longitude 42.7894°E, and Gara is located between latitude 37.0357°N and longitude 43.3678°E [31]. Kwashe is an industrial area located 20 km west of the city of Duhok [32] and Gara is a natural area with a large expanse of green space, which situated 53km east of Duhok city [1], it is a control point. One of the most rapidly growing and polluted industrial areas in the Kurdistan region is Kwashe. It includes numerous factories, such as those that process oil, produce electricity, tanneries, dye, steel, cement, and municipal solid waste. There are other land uses, such as residential, commercial, and urban agriculture. Kwashe has a warm, temperate climate. In Kwashe, there is significantly more rainfall in the winter than there is in the summer. Dohuk has an average temperature of 18.5 °C, and Kwashe experiences precipitation from September to April, with an average annual rainfall of 437–534 mm over the course of 48 years [33, 34]. The majority of rainfall falls during five to six month-long, clearly defined rainy seasons (November to April). The driest months of the year are typically June through September.

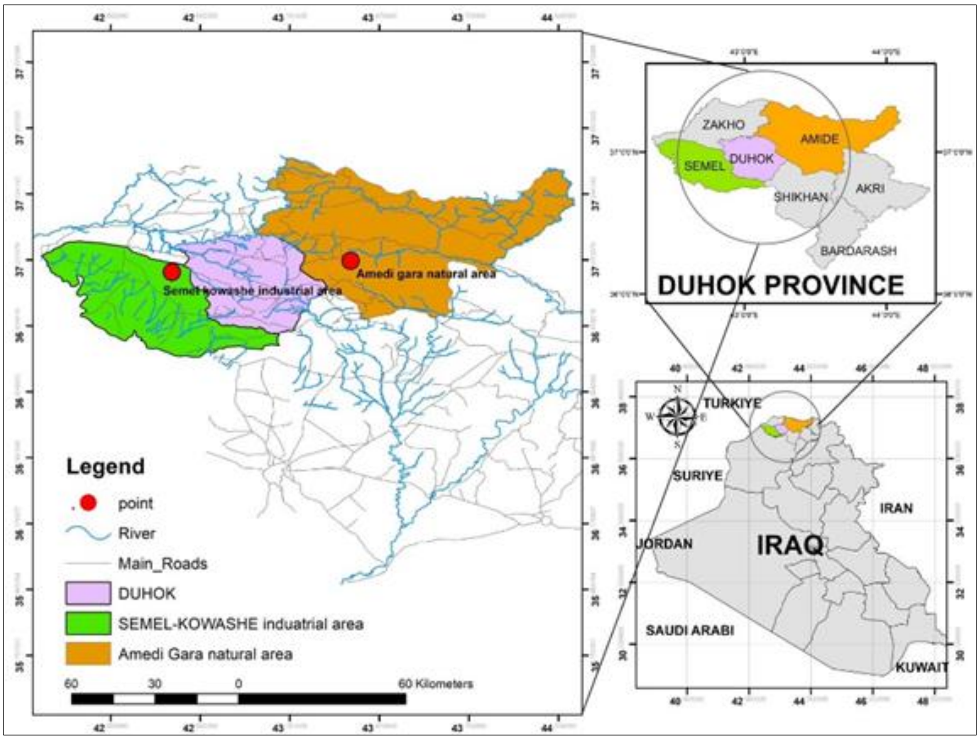

Figure 1 Locations of the study areas

2.2. Sample collection and analysis

When it rained, samples of rainwater were taken on January 28, 29, 30, and 31, 2023, and on February 1, 2, and 4, 2023, respectively. Every day, water samples were randomly taken from five open locations in the Kwashe and Gara areas, and in the end mixed together. Test samples of atmospheric precipitation were gathered using a series of flat, sterilized plastic jars with a surface area of one square meter. Samples for metal analysis were collected using two-liter plastic bottles. The plastic bottles were treated with 5% nitric acid after being cleaned with detergent solution prior to collection. Ultimately, these bottles were cleaned and allowed to air dry using deionized water. During sampling, the sample bottles were securely screwed. After being collected, the rainwater samples were promptly labelled and brought to the Environment laboratory at the University of Zakho's Faculty of Sciences for analysis. The rain water was filtered using a Whatman filter paper to remove sediment and other particulate matter. The water samples were kept in ice-pack coolers and chilled to 4 °C in the lab before being analyzed. The content of heavy metals in the samples was analyzed by using atomic absorption spectrophotometer (AAS). The analyzed heavy metals includes: lead (Pb), cadmium (Cd), manganese (Mn), chromium (Cr) and arsenic (As). In this study, all the data were statistically analyzed using the GraphPad Prism5.

3. Result and discussion

Tables 1 and 2 display the findings of the investigation into the concentration of heavy metals in rainwater. 51 mm of rain fell in total during the sampling period in Kwashe and 109 mm in Gara (Fig. 2). The concentration of Co is not found in any area, whereas the mean concentrations of Pb, Cd, Fe, Cu, Zn, Ni, Mn, and Cr in Kwashe are (1.446, 0.331, 0.099, 0.261, 1.687, 0.744, 0.269, and 0.477, respectively) and in Gara are (0.083, 0.0077, 0.059, 0.092, 0.891, 0.1, 0.046 and 0.066, respectively). In general, the concentrations of some of the heavy metals parameters that were analyzed did not fall within safe drinking limits established by the WHO (Tables 1 and 2). The sources of the various air pollutants' scavenging processes may be the cause of the high concentration of heavy metals [11]. A detailed discussion follows regarding the heavy metal analysis results of the rainwater samples collected, with all values compared to the World Health Organization (WHO) standards, as shown in Table 1 and 2.

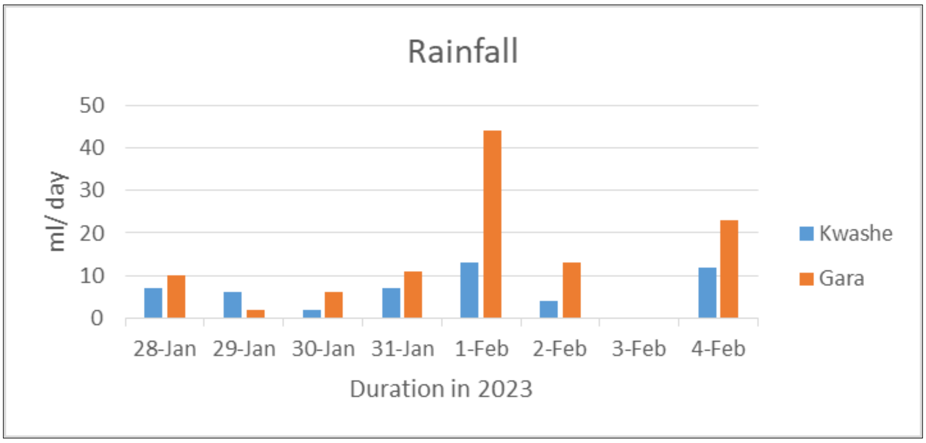

Figure 2 The quantity of rainfall in the designated areas throughout the study

Table 1 Statistical analysis of heavy metals concentrations in rainwater samples from study areas

Parameters		Pb	Cd	Fe	Cu	Zn
Min - Max	Kwashe	1.23-1.95	0.12-1.06	0.087-0.142	0.15-0.76	1.49-2.23
	Gara	0.02-0.15	0.002-0.015	0.053-0.07	0.021-0.092	0.69-1.07
Mean	Kwashe	1.446	0.331	0.099	0.261	1.687
	Gara	0.083	0.0077	0.059	0.092	0.891
SD	Kwashe	0.246	0.342	0.019	0.221	0.273
	Gara	0.045	0.0042	0.006	0.025	0.119
Std. error	Kwashe	0.093	0.129	0.007	0.084	0.103
	Gara	0.017	0.0016	0.002	0.009	0.045
Variance	Kwashe	0.06	0.117	0.0003	0.049	0.075
	Gara	0.002	1.724	3.890	0.0006	0.014
Skewness	Kwashe	1.726	2.105	2.357	2.568	1.668
	Gara	0.067	0.616	1.09	1.902	-0.325
Kurtosis	Kwashe	3.392	0.240	5.786	6.670	2.29
	Gara	-0.542	0.846	0.313	3.572	0.99
Coeff. var	Kwashe	16.985	103.285	19.236	84.714	16.184
	Gara	53.85	53.82	10.623	62.617	13.327
Threshold= X+2s	Kwashe	1.94	1.02	0.14	0.7	2.23
	Gara	0.173	0.0161	0.07	0.14	1.13
WHO limit [35]		0.01	0.003	0.5	2.0	3.0

3.1. Lead (pb)

The mean lead concentration in the rainwater samples was (Kwashe= 1.446 and Gara= 0,083 mg/L), which is higher than the maximum value that is advised. and significantly higher still than the well water value that local researchers looked at [19]. The upper limit is 0.01 mg/L, per WHO (2011) [35]. Compared to the WHO, the lead value is higher in two regions (8 times in Gara and 144 times in Kwashe). This range is higher than what Ebong et al. [4] and Williams and

Tighiri [36] reported in rainwater from Nigeria. The minimum lead concentration (1.23 mg/l) found in the examined rainwater samples is significantly greater than the recommended maximum value. This may be a sign of the detrimental effects on the atmosphere of intensive gas flaring and exhaust emissions in the studied area. Moreover, Pb is primarily obtained from municipal solid waste incinerators [37]. This fuel can lead to cancer, disrupt the absorption of vitamin D, harm the nervous system, and cause brain disorders [19, 38]. The mean is also higher than the WHO's allowable limit of 0.01 mg/l [35], indicating potential health risks associated with consuming untreated rainwater collected from these areas.

Even at very low concentrations, lead is a very toxic and cumulative element. Children under the age of six are most at risk from small levels of lead exposure, which can result in a number of health problems [19]. Humans who are exposed to low levels of lead may experience issues with their heart, kidney, liver, and respiratory systems [39]. Lead can have a wide range of detrimental effects on health, from mild blood pressure increases at 100 µg/L to severe retardation and even death at 1,000 µg/L [2]. Both adult and newborn brain damage are among the harmful effects of excessive lead (Pb) levels in humans [40]. Lead is consumed by breathing or gulping, and its most harmful effects are felt in the sensory system [19]. Premature labour in expectant mothers and shortness in the fingers, wrists, or lower limbs are additional consequences of lead exposure [41].

3.2. Cadmium (Cd)

The average cadmium content in the rainwater samples in Kwashe is 0.331 mg/l, which is significantly less than the well water value that local researchers looked at [19]. In addition to being higher than the WHO's recommended threshold of 0.003 mg/l [35] for the heavy metal in potable water, the tested rainwater value for Cd was deemed unsafe in both location of the study area. Compared to the WHO, the Cd value is higher in two regions (1 time in Gara and 110 times in Kwashe). The combustion of fossil fuels and agricultural practices in these areas may be to blame for the high cadmium levels found in the rainwater under study [42, 43]. Additional sources of this metal in rainwater include pesticides, vehicle exhaust, engine leaks, ashes and dust that contain Cd that are carried by the wind to residential roofs [44].

The levels of cadmium (Cd) found in the rainwater under investigation are in line with those of studies conducted in Varanasi, India by Pandey and Singh [45], in Akwa Ibom State, Nigeria by Ubuoh et al. [46], in Camaguey, Cuba by Alvarez et al. [47], and in Palestine by Malassa et al. [44]. Because cadmium is toxic and carcinogenic by nature, even small amounts of the element can have negative health effects on humans [38, 48]. Drinking and household water contaminated with high levels of cadmium can cause severe lung damage, vomiting, diarrhea, and severe stomach pain [19]. Therefore, there may be health risks associated with cadmium toxicity if rainwater from these areas is not treated before consumption.

3.3. Iron (Fe)

The average iron concentration found in the investigated rainwater (0.099 mg/l in Kwashe and 0.059 mg/l in Gara) are less than the 0.5 mg/l that the WHO recommends for drinkable water [35]. Therefore, in the areas under study, iron could be considered non-polluting. Anthropogenic sources of iron addition may primarily stem from the burning of fossil fuels [49, 50]. In comparison to previous study, Huston et al. found that 88 samples taken from rainwater tanks in Brisbane, Australia, had a Fe concentration of 0.068 mg/L [51]. Mendez et al. found that the Fe concentration in galvanized aluminum roofing material was 0.590 mg/L, whereas Lee et al. found that the Fe concentration in galvanized steel roofing material was 0.302 mg/L [51, 52].

Iron is a necessary cofactor for numerous enzymes and is important for all living things, especially plants, to have healthy metabolism. Iron deficiency in human blood can lead to two major health problems: anemia and neurodegenerative disorders [32]. Excessive levels of iron in the body can cause damage to the liver, pancreas, and heart when they persist there [53]. Iron is a necessary element because it is a part of many enzymes, myoglobin, and hemoglobin in the majority of living cells [54]. High concentrations, however, have the potential to cause iron toxicity and its side effects.

3.4. Copper (Cu)

At the sites, the average concentration of copper was (0.261 mg/L in Kwashe and 0.092 mg/l in Gara). The WHO's maximum permissible limits (2.0 mg/L) for drinking water were found to be below these readings [35]. The measured rainwater had copper (Cu) concentrations ranging from 0.15 to 0.76 mg/l; this is less than what Pandey and Singh [45] from Varanasi, India and Ebong et al. [4] from Nigeria, which reported for rainwater. Copper may find its way into rainwater from sources such as heavy traffic, pesticides, vehicles exhaust, and industrial emissions and activities [55, 56].

While excess copper accumulation can lead to health issues, copper is necessary for the human body to function normally [57, 58]. High levels of copper in drinking water have been found to damage some people's kidneys and livers [19]. Because it is difficult for infants under a year old's body to eliminate copper, it can be toxic to them. Long-term copper exposure results in headaches, nausea, dizziness, and loose stools in addition to irritation of the mouth, nose, and eyes [41].

3.5. Zinc (Zn)

The samples of rainwater had a mean zinc concentration of (1.687 mg/l in Kwashe and 0.891in Gara), which was less than the WHO limit (Table 1). The tested samples had metal Zn concentrations ranging from (1.49 to 2.23 mg/l in Kwashe and 0.69-1.07 in Gara), while well water in the Kwashe region had zero concentrations when studied by researchers [19]. The amounts of zinc (Zn) found in the investigated rainwaters are greater than those found in rainwater from Uyo, Nigeria [4], Camaguey, Cuba [47], and research reviewed by Sánchez et al. [59]. High concentrations of zinc discovered in collected rainwater samples are typically the result of burning coal, burning fossil fuels, and smelting non-ferrous metals [60]. The primary sources of zinc in the atmosphere are pesticides, deodorants, disinfectants, and vehicle emissions [61]. The vast majority of zinc sources are found in coal-burning power plants, metal fabrication processes, home wastewater discharge, and climate-related effects [41].

Table 2 Statistical analysis of heavy metals concentrations in rainwater samples from study areas

Parameters		Ni	Mn	Cr	Co
Min - Max	Kwashe	0.33-1.65	0.07-0.91	0.22-1.31	ND
	Gara	0.05-0.17	0.02-0.12	0.04-0.11	-
Mean	Kwashe	0.744	0.269	0.477	-
	Gara	0.1	0.046	0.066	-
SD	Kwashe	0.483	0.31	0.416	-
	Gara	0.037	0.034	0.026	-
Std. error	Kwashe	0.183	0.117	0.157	-
	Gara	0.0139	0.013	0.01	-
Variance	Kwashe	0.233	0.096	0.173	-
	Gara	0.0013	0.001	0.0007	-
Skewness	Kwashe	1.228	1.932	1.759	-
	Gara	0.8317	2.246	0.804	-
Kurtosis	Kwashe	0.981	3.424	2.440	-
	Gara	2.1402	5.341	-0.446	-
Coeff. var	Kwashe	64.918	115.334	87.169	-
	Gara	36.193	74.565	40.124	-
Threshold= X+2s	Kwashe	1.71	0.89	1.31	-
	Gara	0.174	0.11	0.118	-
WHO limit [35]		0.07	0.4	0.05	0.01

ND = Not detected

Zinc is a vital minor component for higher plants, animals, and humans alike. The effects of zinc deficiency, such as slow wound healing, acute diarrhea in children, and stunted growth, are treated and prevented with zinc. Zinc not only strengthens the immune system but also helps with recurrent colds and ear infections and prevents lower respiratory infections. On the other hand, taking excessive amounts of zinc in the form of food, beverages, or dietary supplements may be harmful to your health [19]. Zinc is necessary for the majority of biochemical processes that keep life alive, according to studies, but its toxicity has grave health risks [62]. Paleness, pancreatitis, and lowered HDL cholesterol levels have all been related to long-term ingestion of indubitably high zinc doses [41]. Increased zinc levels could be the dangerous element causing fevers, diarrhea, stomachaches, and colic [63].

3.6. Nickel (Ni)

The rainwater under investigation had nickel (Ni) concentrations ranging from (0.33 to 1.65 mg/l in Kwashe and 0.05-0.17 in Gara). The samples of rainwater had a mean nickel concentration of (0.744 in Kwashe and 0.1 mg/l in Gara). This is higher than that reported by Kim et al. [64] in rainwater from Vietnam, but it is not consistent with the range of Ni reported in rainwater collected in India by Pandey and Singh [45]. Compared to the WHO, the Ni value is higher in two regions (1 time in Gara and 10 times in Kwashe). This suggests that there are anthropogenic sources of nickel in the studied areas, which could include motor vehicles, fossil fuel combustion, and refining operations. The obtained mean also exceeds the WHO (2011) recommended limit of 0.07 mg/l for Ni in potable water. Because untreated rainwater from studied areas may cause nickel toxicity and related health issues, it is not safe for domestic use or drinkable [65].

3.7. Manganese (Mn)

Rainwater had Mn concentrations ranging from (0.07 to 0.91 mg/L in Kwashe and 0.02-0.12 in Gara), with an average of (0.269 mg/L and 0.046, respectively). The concentrations of Mn are within the WHO-recommended drinking water standard's permissible limit of 0.4 mg/l [35]. It is evident from our results that the Mn concentration in the study area's rainwater falls within the recommended range, making it suitable for human consumption. The outcome is higher than that of another study conducted in Ontario, Canada (with a range of 0.005 mg/L) [66], but it is comparable to a prior study that examined the concentration of Mn in South Korea (between 0.07 and 0.170 mg/L) [51].

According to published research, dust that is carried by wind to residential roofs could be a potential source of manganese [44]. Manganese, which exists in the earth's crust as hydroxides and oxides, is one of the most prevalent metals. The majority of the suspended particles that cause soil erosion, volcanic eruptions, burning human activity, and industrial emissions are the cause of manganese contamination in some parts of the world's water [31]. In addition to staining clothes, metal pads, and food, high manganese levels can cause neurological disorders and promote the growth of algae in reservoirs [38]. Excessive consumption of Mn can cause serious respiratory disorders, damage to the central nervous system, and Parkinson's disease [32].

3.8. Chromium (Cr)

The range of chromium concentrations in the study area's rainwater are (0.22–1.31 mg/l in Kwashe and 0.04-0.11 mg/l in Gara), which shown in table 2. Evidently, our findings demonstrated that the rainwater over the both area is contaminated with the heavy metal Cr, making it unfit for human consumption and not safe for the presence of the metal. The WHO recommends a maximum allowable limit of 0.05 mg/l for chromium in drinking water [35], and the mean concentration of our results is higher at (0.477 mg/l in Kwashe and 0.066 mg/l in Gara). Compared to the WHO, the Cr value is higher in two regions (1 time in Gara and 9 times in Kwashe). According to [67], rainwater that has been let through a roof and contains fly ashes in the atmosphere frequently has high levels of chromium contamination [68]. Road dust, asbestos brakes, and human activity around the house are potential sources of Cr [52]. Moreover, the steel industry, the burning of fossil fuels, and solid waste all release Cr [55].

3.9. Cobalt (Co)

There was no discernible cobalt concentration in the research areas. It is clear from our findings that the rainwater over the study areas is free of copper contamination, making it safe for human consumption and low in the heavy metal's presence. The World Health Organization recommends a maximum allowable limit of 0.01 mg/l of cobalt in drinking water [35].

4. Conclusion

The results of this study only address heavy metals; nevertheless, drinking water safety requires taking into account a number of other significant contaminants. According to the research findings, half of the water samples were deemed unsafe due to heavy metal contamination. The samples for Fe, Cu, Zn, Mn, and Co were below WHO limits, while all of the samples for Pb, Cd, Ni, and Cr were exceeded WHO limits. The heavy metal concentration sequence for chemical analysis of the rainwater was (Zn > Pb > Ni > Cr > Cd > Mn > Cu > Fe > Co in Kwashe and Zn > Ni > Cu > Pb > Cr > Fe >

Mn > Cd > Co in Gara). Every sample that was larger than the WHO guidelines had its health risk evaluated. However, the samples were some deemed unsafe due to the metal concentrations exceeding the limits in significant amounts. This indicates that rainwater in the study areas poses health risks to users, both adults and children, and that it is unsafe to use for heavy metal-containing domestic, industrial, or agricultural purposes without treatment. The level of these characteristics in the rainwater from the studied areas may have increased as a result of anthropogenic activities that released a significant amount of contaminants into the surrounding air. Finally, in the current study area, rainwater cannot serve as a substitute water source. The water quality from the current study needs to be treated as much as possible using filtration and disinfection techniques.

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