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Appraisal of Heavy Metal Content in The Groundwater at W-W El Minya District of Egypt

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Abstract

In W-W El Minya district, 33 groundwater samples were collected, analyzed, and rated using various indices to assess water quality. The samples exhibited weakly acidic to faintly alkaline pH levels, excessive mineralization, weak to moderate salinity, and high hardness. The prevailing ions in the samples were Cl, Na, HCO_3, and SO_4 due to silicate weathering and hydrolysis of evaporite minerals. However, the World Health Organization's (WHO) recommended limits for Ca, Na, and Cl contents were exceeded in some samples. Piper's graph showed that all samples were of the SO_4. Na-Cl type. Among heavy metals, Cd was the most prevalent, with 36% of samples exceeding the WHO safe level and 18% exceeding Food and Agriculture Organization (FAO) permissible values. The Heavy Metal Pollution Index (HPI) indicated that 48% of samples were suitable for drinking, while the Heavy Metal Evaluation Index (HEI) showed negligible levels of heavy metal pollution. The health risk assessment revealed non-carcinogenic and carcinogenic effects of Cd in the contaminated water. The Corrosion Ratio (CR) index suggested that metallic pipes could contaminate water with heavy metals over time. The Chloride Mass Balance (CMB) approach estimated that groundwater supply in the area was only 20.6% of total precipitation. To prevent adverse effects on residents' health, it is recommended that contaminated water be treated for cadmium pollutants.
Keywords: Multivariate statistics; Oral non-carcinogenic effects; Oral carcinogenic effects; Corrosivity ratio; Chloride mass balance.

1. Introduction

Water quality is strongly intertwined with public health, food supply, economic reform, ecological habitats, sustainable growth, and development in our communities [1]. Increased urbanization, building, farming, industrial activity, and natural cycles have harmed the quality of water, as well as their implications on human health globally [2]. A typical water quality analysis focuses on the purity of water bodies and their potential usage in industries, home use, drinking water, and irrigation [3, 4]. As a result, the water quality index (WQI) is regarded as a mathematical method that considerably reduces the complexity of raw data related to water quality and provides a single classification value that reflects the status of the quality of aquatic bodies or the level of contaminants [5].

Water that is healthy to drink is essential for maintaining human health, so drinking water contamination poses a serious threat to people's health [6]. Freshwater forms 3% of the planet's water supply. Only a modest percentage (0.01%) of it is usable for humans [7]. Because of rapid overpopulation, urbanism, climate variability, the use of natural resources, and the desire for food, this meager amount of freshwater is still in severe demand [7]. With development comes an increase in the requirement for freshwater for industrial and agrarian uses, which could lead to a serious water crisis over the decades ahead [7]. The metabolism of the human body only requires some heavy metals in low doses, such as Cu, Se, and Zn [8]. There is a detrimental effect on human health when these elements exceed their safe limits [8, 9]. The various diseases, such as cancer, that are caused by elevated levels of heavy metals have an increasing negative effect on health every day [8]. Human activities that emit heavy metals into the water include unregulated manufacturing operations,

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municipal trash, and extensive uses for superfluous chemicals in agriculture [10]. Exposure to cadmium can damage the liver, blood, and bones, besides causing kidney disease [11]. According to health reports, there is ample proof that cadmium causes cancer [11].

Compared to drinking water guidelines as defined by WHO standards, the application of health risk indices has clear advantages because it considers body weight, metal content, and daily intake [8]. Therefore, estimating the human risk of Cd for children and adults (both cancer-causing and non-cancerous dangers) is vital. By evaluating the health impacts of toxic metal exposure to a reference dose (RfD) and cancer slope factors (CSF), the hazard quotient (HQ) is applied to define the carcinogenic and non-carcinogenic health impacts of toxic metals [12, 13]. Many scientists used the WQI and health hazard identification to gauge the purity of the water [5, 10, 14-23].

The primary purpose of this research is to evaluate the heavy metal content that can affect groundwater by comparing their concentrations to safe limits prescribed by the WHO and FAO [6, 24], and the safe limits of health risk for its usage in drinking and irrigation applications. In the framework of sustainable development through the 1.5 Feddan Project, the Egyptian Governorate is interested in the research area.

2. Materials and Methods

2.1. Location

The research area spanned between longitudes 29º 50´- 30º 15´ E and latitudes 28º 10´- 28º 30´ N, W-W El Minya district, Egypt, which is within the 1.5 million Feddan project (Fig. 1). It represents the western lime-stone plateau; the ambient zone contains a stratigraphic succession built up of rock units from base to top: Minia, Samalut, Makattam, Moghra Formations, Pleistocene-Oligocene gravels, and Quaternary sediments (Fig. 2); [25, 26]. It derives its groundwater from the fractured Middle Eocene limestone aquifer, one of the most significant limestone aquifers in the Arab Republic of Egypt. Where the water-bearing layer is about 400m thick and the depth to the water table is 70–110 m (Fig. 2); [27].

2.2. Sampling and Methodology

Thirty-three groundwater samples were picked up from the study area in April 2022 after being filtered and acidified with nitric acid (pH< 2); [28], and kept in close, pre-rinsed polypropylene containers (Fig. 1). The pH, total dissolved solids (TDS), and electric conductivity (EC) values were measured on-site using a HANNA pH-meter model HI 991300. In the laboratories of the National Water Research Center (NWRC), the principal elements and trace contents of the water samples under investigation were analyzed. The total hardness (TH) was titrated using the Eriochrome black T indicator and Na_2-EDTA standard solution (0.01 M), [29]. While calcium, magnesium, sulfate, phosphorus, and heavy metals were measured using a HANNA spectrophotometer (HI 83215). Sodium and potassium levels were measured using a flame photometer (model Genway FPF-7). Carbonate and bicarbonate were identified using a sulfuric acid standard solution (0.01 N), phenolphthalein (1%) as an indicator for carbonate, and methyl orange (0.01%) as an indicator for bicarbonate [29]. Chloride was measured using a potassium chromate indicator solution and a silver nitrate standard solution [29]. The ionic balance error (e%) for the measured ions was less than 5%.

The water quality index (WQI), developed by the Canadian Council, is applied to check whether water is fit for human, animal, and irrigation consumption [30]. Where its values were divided as less than 45 is poor,
45–65 is marginal, 65–80 is fair, 80–95 is good, and 95–100 is excellent [31].

The heavy-metal pollution index (HPI) rates the water's purity and suitability for drinking consumption regarding the metals [32]. It is computed from the following arithmetic equation (Eq. 1); [33]:

$$\text{HPI} = \sum_{i=1}^{n} QiWi / \sum_{i=1}^{n} Wi \quad (1)$$

Wi is the weight unit; Wi = 1/Si; Si is the permissible limit for metal; Qi=Ci/Si*100; and Ci is the metal content in water samples. HPI values were categorized as < 25 being excellent, 26–50 being Good, 51–75 being poor, 76–100 being very poor, and >100 being unsuitable for drinking [34].

The heavy-metal evaluation index (HEI) analyzes the cumulative influence of various metals on water purity [35]. It was estimated from this formula (Eq. 2):

$$\text{HEI} = \sum_{i=1}^{n} Hc/Hmac \quad (2)$$

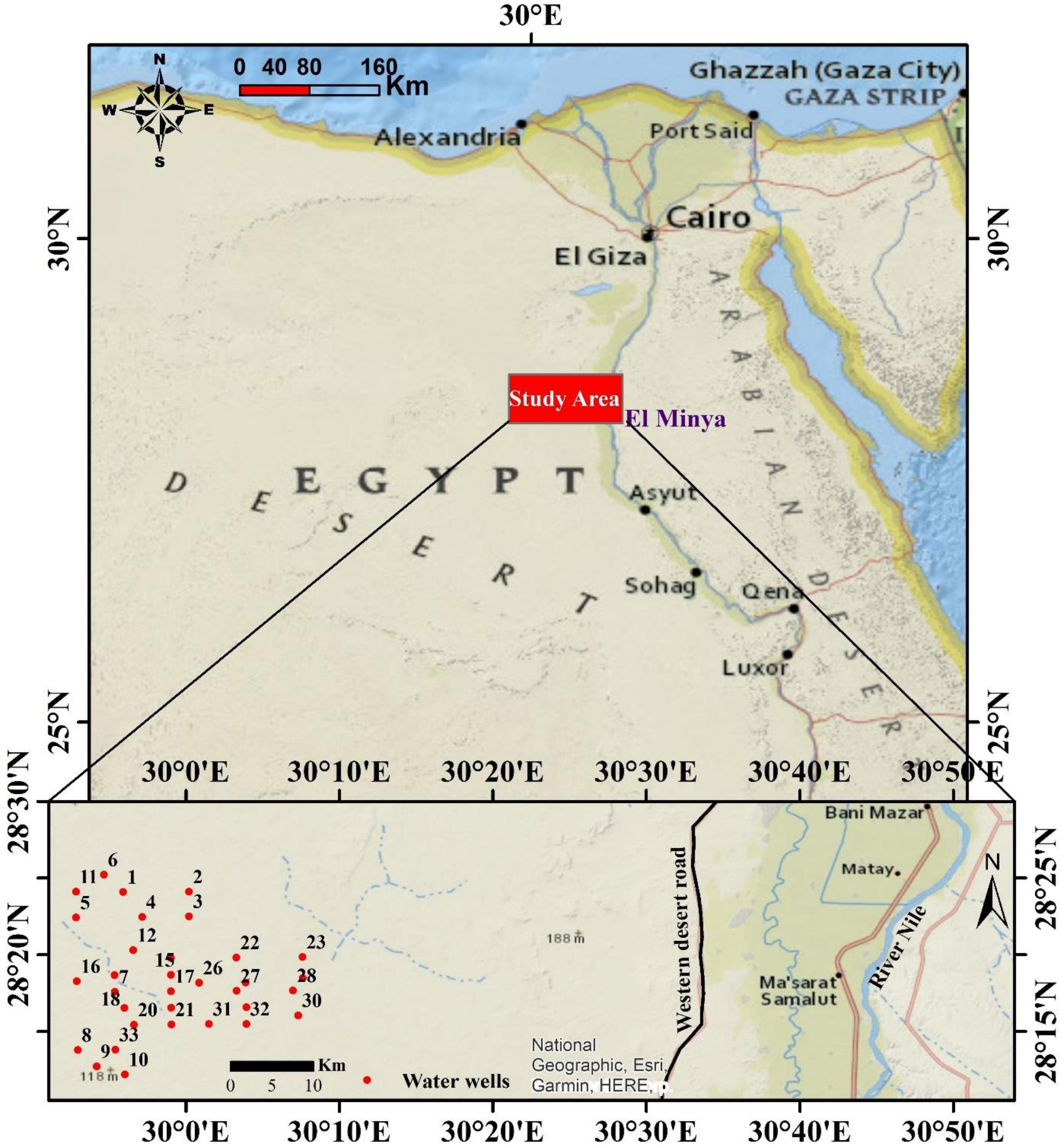

Fig.1. Location map of the study area.

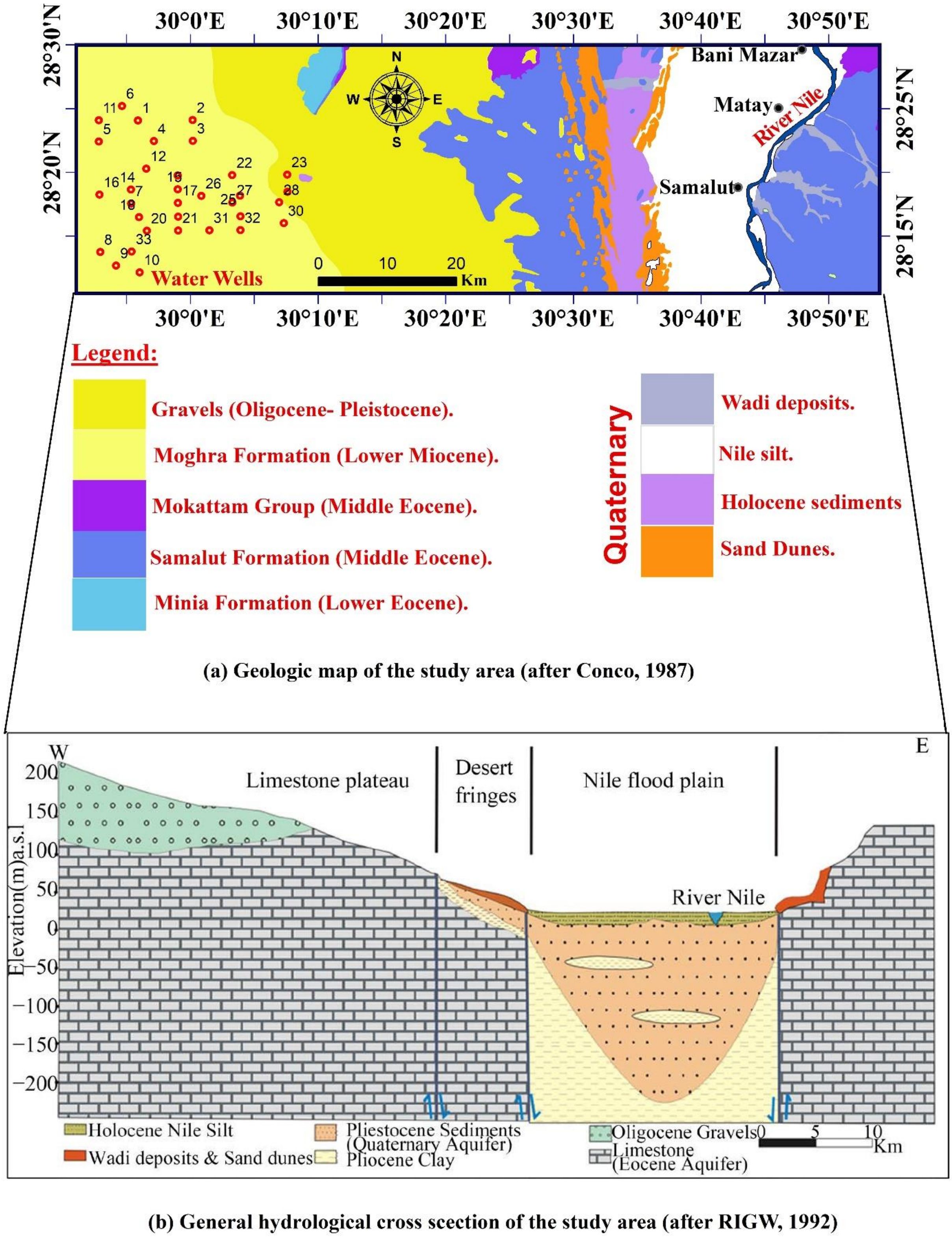

Fig. 2. Geologic map and geological cross section for the research area [57, 58].

Hc is the metal content in water samples, and Hmac is the allowable limit for metal. HEI numbers were specified as < 10 being low, 10–20 being medium, and >20 being highly polluted [36].

Several methods are used to estimate the potential health risks associated with the oral ingestion of water contaminants. These concepts are exemplified by the hazard quotients for the non-carcinogenic effects (HQ_{N-C}) and the carcinogenic effects (HQ_C) for each chemical, the hazard index (HI) for the non-carcinogenic impacts in multiple pathways, and the target cancer risk (TCR) for pathways. All the terms listed above were calculated using the following equations: eqs. 3, 4, and 5; [37-39].

$$CDI_{Oral} = C \times IR / BW \quad (3)$$
$$HQ_{N-C} = CDI_{Oral} / RfD \quad (4)$$
$$HQ_C = CDI_{Oral} \times CSF \quad (5)$$

C is the element content in water (ppm); IR is the daily intake rate for adults, which is 2 L/day, and for children, it is 1 L/day [9, 13]. BW is the body weight, which is estimated to be 73 kg for adults and 32.7 kg for children [9, 13]. Oral reference dose is R*f*D for Cd is 0.0005 mg/kg/day, respectively [8, 13]. Cd also has a cancer slope factor (CSF) of 6.3 [8, 13].

The corrosivity ratio (CR) reflects how reactive groundwater is to corrosion [40, 41]. The values of ions are indicated in ppm in the equation applied to estimate CR (Eq. 6); [40, 41].

$$CR=(Cl+SO_4)/2(HCO_3+CO_3) \quad (6)$$

Chloride Mass Balance (CMB) is applied to quantify the recharge rate for groundwater wells in a dry environment, depending on the Cl content of both precipitation and groundwater [42]. Because Cl in the watershed is more stable, is constant over time, and only derives from direct rainfall on wells [42]. CMB was applied by numerous scholars [43-46]. CMB is estimated from the following equation (Eq. 7); [47].

$$R=P*Cl_p/Cl_{gw} \quad (7)$$

R is the recharge rate (mm/yr.); P is the annual mean of precipitation (mm/yr.); Cl_p is the mean chloride content in rainfall (ppm); and Cl_{gw} is the average chloride concentration in the groundwater. The Cl content average in rainwater was computed using the formula (Eq. 8); [43].

$$Cl=1.25+3/P \quad (8)$$

3. Result and Discussion

3.1. Major Ions Chemistry

Water samples' pH spanned from 6.2 to 7.94, fluctuating between a weakly acidic and a somewhat alkaline state (Table 1). According to Table 1, EC readings for water samples varied from 2930 to 4570 µs/cm, which revealed that the water was excessively mineralized and that the concentrations were above the maximum allowable limit (MAC) set by FAO and WHO [6, 23, 48]. TDS concentrations fluctuated in the investigated water samples between 1784 and 3199 ppm to vary from weakly to moderately saline [49] and surged on the MAC (Table 1). TH values in water samples varied from 373 to 805 ppm, which is regarded as a very hard water type (Table 1); [50]. Alkalinity contents in the analyzed samples fluctuated between 128 and 402 ppm (Table 1).

According to the mean of the pivotal ions, which are 897, 652, 244, 143, 50, and 21 ppm, respectively, they can be sorted in descending order as Cl > Na > HCO_3 > SO_4 > Ca > Mg > K (Table 1). All water samples had Ca, Na, and Cl contents that were greater than the WHO MAC; vice versa, most samples' K, HCO_3, and SO_4 concentrations were less than the WHO MAC (Table 1). Therefore, Cl, Na, HCO_3, and SO_4 predominate due to evaporite mineral dissolution, silicate weathering, and cation exchange [51-53]. Additionally, K and Cl contents rose above FAO MAC in most water samples (Table 1). Na dominance relates to the fact that rainfall recharge proceeds more frequently than upward seepage from deeper wells [53-56]. The WQI findings showed that 69% of the samples were of fair purity quality for human drinking, fit for irrigation, and fit for livestock drinking (Fig. 3); [6, 16, 30].

Table 1: Physicochemical variables and indices in. the investigated water samples

Variables	Min.	Max.	Mean	Median	Q1	Q3	WHO ,2022	FAO, 1994	Samples exceeded the safe limits	
									WHO	FAO
T°C	32	40	35	34.7	34	36				
pH	6.2	7.94	7.40	7.39	7.27	7.66	6.5-8.5	6-8.5		
EC (µS/cm)	2930	4570	3636	3630	3530	3760	1500	3000	All	Except 8 & 9
TDS (ppm)	1764	3199	2402	2451	2270	2541	1000	2000	All	Except 8 & 9
TH (ppm)	373	805	562	565	495	617	500		Except 10, 11, 19, 21, 23, 24 & 27	
Alk (ppm)	128	402	233	229	160	281				
Ca (ppm)	88	274	143	143	124	154	75	406	All	
Mg (ppm)	18	88	50	48	32	64	100	61		1-9 & 26
Na (ppm)	366	810	652	559	510	600	250	920	All	
K (ppm)	11	28	21	22	20	24	12	78	Except 10 & 33	
CO_3 (ppm)	0	0	0	0	0	0	-			
HCO_3 (ppm)	156	402	244	229	195	281	250	610	18, 20-22, 30 & 32	
Cl (ppm)	729	1109	897	896	825	922	250	1063	All	2, 3, 6 & 18
SO_4 (ppm)	157	403	230	198	186	249	250	960	20, 21 & 31-33	
Al (ppm)	0	1.1	0.07	0.01	0.002	0.04	0.9	5	18	
Ba (ppm)	0.0002	0.21	0.07	0.05	0.04	0.07	1.3			
Cd (ppm)	0.001	0.04	0.01	0.002	0.001	0.01	0.003	0.01	1, 3, 5, 7-9, 18, 19, 24, 27, 29 & 33	1, 3, 8, 18, 19 & 33
Cr (ppm)	0.0005	0.03	0.004	0.001	0.001	0004	0.05	0.1		
CO (ppm)	0	0.02	0.01	0.003	0.003	0.003	0.01	0.05	1, 3, 7, 10 & 33	
Cu (ppm)	0.001	0.46	0.05	0.02	0.003	0.05	2	0.2		18, 26 & 29
Fe (ppm)	0.001	3.8	0.25	0.014	0.008	0.3	0.3	5	10, 14, 18, 20, 22, 29, 30 & 32	
Pb (ppm)	0.001	0.05	0.008	0.003	0.003	0.007	0.01	5	1, 8, 10, 19 & 33	
Mn (ppm)	0.005	0.202	0.036	0.022	0.005	0.05	0.4	0.2		26
Ni (ppm)	0.0004	0.05	0.012	0.006	0.001	0.017	0.07	0.2		
Zn (ppm)	0.0002	0.12	0.02	0.01	0.001	0.03	3	2		
P (ppm)	0	0.24	0.135	0.2	0.000	0.2	0.24			

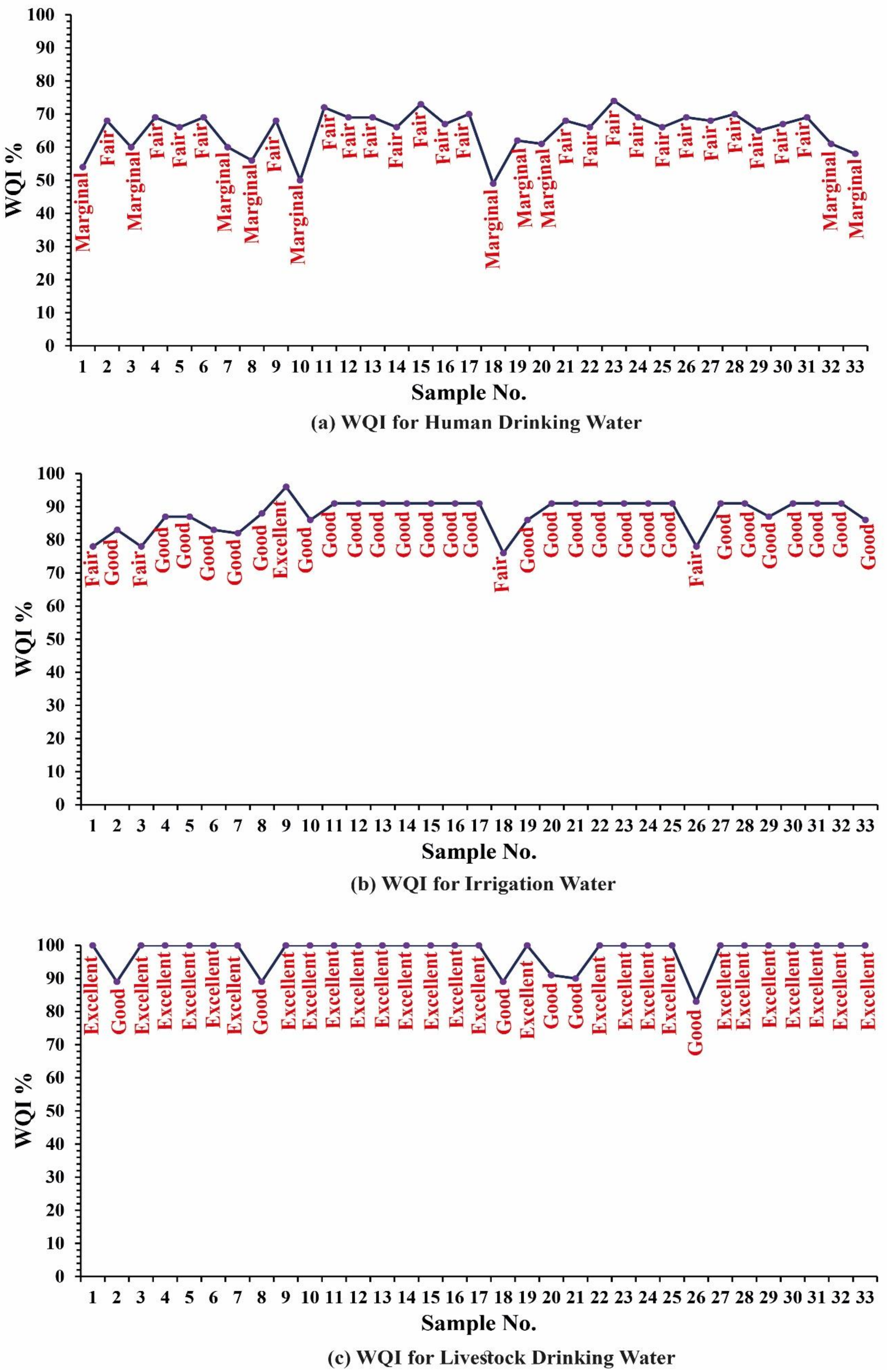

Fig. 4. Classification of WQI values for water samples.

3.2. Heavy metals (HM) Evaluation

Excessive HM content on the MAC generally has serious adverse health consequences for humans [10]. Table 1 lists the twelve metals that were investigated in water samples. Al contents are lower than the WHO MAC in water samples except for 1 sample (Table 1). Cd levels were significantly higher than the WHO MAC in 36% of samples, and according to the FAO MAC, they rose in almost 18% of samples; consequently, it has more influence on sample purity than the other metals (Table 1). All samples had Co and Pb contents within WHO MAC except for 15% (Table 1). Fe concentration increased on the WHO MAC in 24% of samples (Table 1). In 9% of water samples, the quantity of Cu was higher than the FAO MAC, whereas the amount of Mn was higher in one water sample (Table). Because the levels of Ba, Cr, Ni, Zn, and P were below the MACs, they hadn't influenced the water (Table 1).

To quantify the level of heavy metals in drinking water, HPI and HEI are used [20]. HPI values for the water samples rose from 9.74 to 856.5, which were categorized as 33% unsuitable, 6% very poor, 6% poor, 48% good, and 3% exceptional (Table 2 and Fig. 4); [34]. HEI values vacillated between 0.58 and 28, which were identified in the analysed samples as 85% low pollution, 9% medium pollution, and 6% high pollution (Table 2 and Fig. 4); [10, 36].

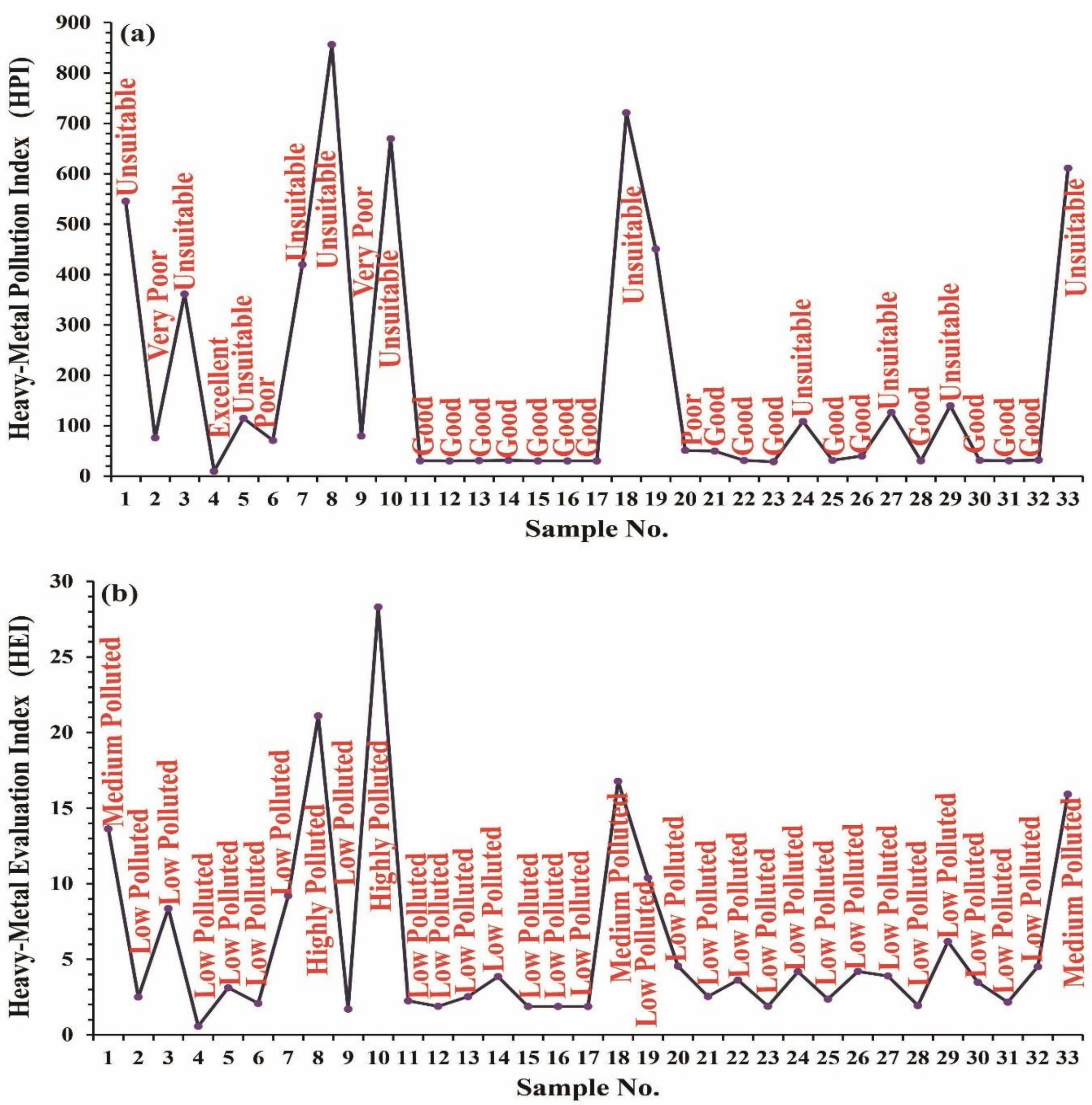

Fig. 4. HPI & HEI values classification for water samples.

Now that groundwater is the only substantial water supply in the desert territories, which are featured in the research area, the water supply is more crucial [10]. Considering that 36% of water samples were contaminated with cadmium, a metal that causes cancer, The health risk indices were applied to the oral exposure pathway for those waters contaminated with Cd to evaluate how much it would damage adults and children. According to $HQ_{N\text{-}C}$ findings, 50% of the influenced samples are above the acceptable level (1) for the non-carcinogenic impact of Cd on adults and children (Table 2 and Fig. 5); [8, 9, 13]. All contaminated samples were over the guideline value (10^{-6}) for carcinogenic effects of Cd on adults and children, according to HQ_C results (Table 2 and Fig. 5); [8, 9, 13].

Table 2: Statistical indices values for water samples

Indices	Minimum	Maximum	Average
HPI	9.739875	856.5340	179.7148
HEI	0.578631	28.30165	5.921310
CR	1.294759	3.886931	2.454223
CDI_{Adults}	0.00011	0.001096	0.0005029
$CDI_{Children}$	0.219178	2.191781	1.0058708
$HQ_{N\text{-}C\ for\ Adults}$	0.000122	0.001223	0.0005614
$HQ_{N\text{-}C\ for\ Children}$	0.244648	2.446483	1.1227610
$HQ_{C\ for\ Adults}$	0.000690	0.006904	0.0031685
$HQ_{C\ for\ Children}$	0.000771	0.007706	0.0035367

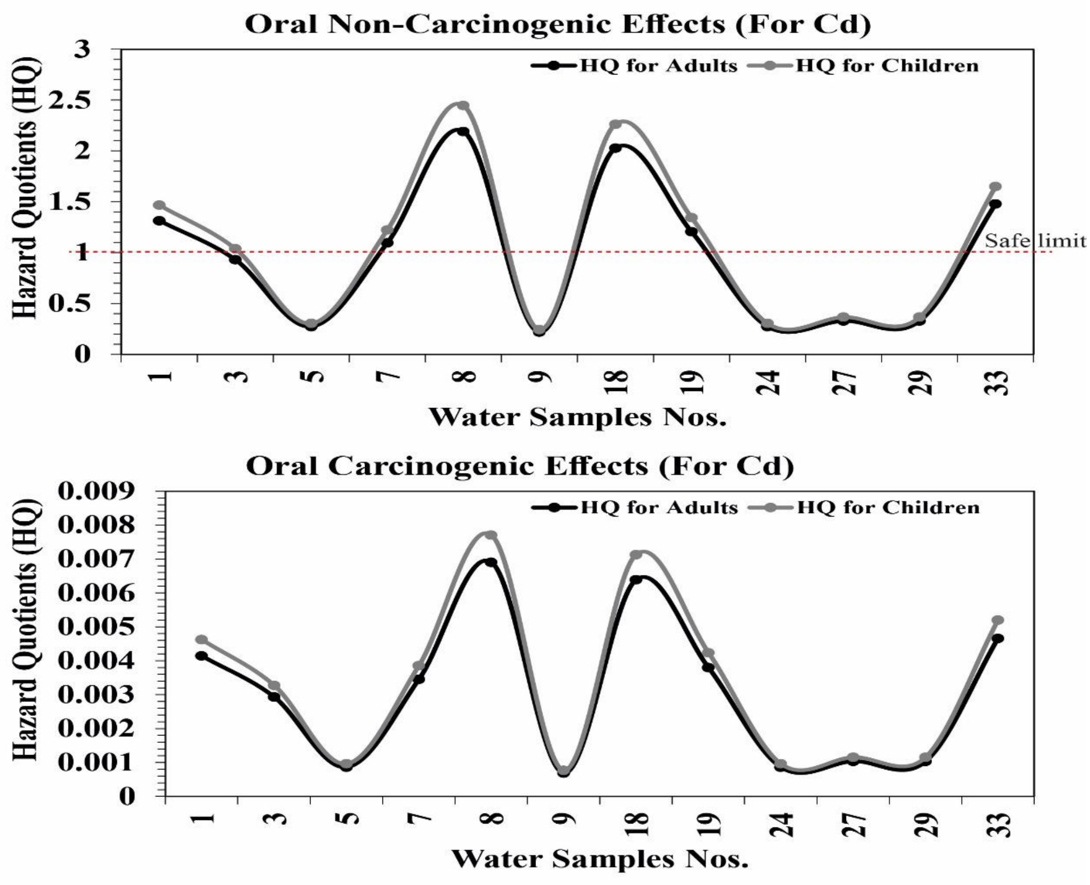

Fig. 6. HQ values of oral exposure pathway for water samples polluted with Cd.

3.3. Corrosivity Ratio (CR)

CR assesses the rate at which water reacts with the metallic pipes that transport it, which produce a layer of rust that causes water pollution with HM [40, 41]. CR varied from 1.3 to 3.9 in water samples that exceeded the acceptable limit (1), as listed in Table 2. studied water considered more exposure to pollution with HM due to transport in metallic pipes over time for far distances (Table 2); [40, 41].

3.4. Chloride Mass Balanced (CMB)

Based on the annual mean of precipitation and the average amount of Cl in rainwater and groundwater, CMB estimates the rate of groundwater recharge [46, 47]. Groundwater recharge (R) in the research region was 4.04 mm/year and represented 20.6% of the annual Consequently, the rest of the rainwater precipitated in various forms but didn't recharge the groundwater [46].

4. Conclusion:

The pH of the water varied from slightly acidic to weakly alkaline; EC showed severely mineralized water that was above the MACs in all samples. The TDS in the water sample was classified as weakly and moderately saline and exceeded the MAC. The TH in the water samples was identified as a very hard water type. The contents of Ca, Na, and Cl are higher than the WHO MAC, and vice versa. In most samples, K, HCO_3, and SO_4 values were below the WHO MAC. Cl, Na, HCO_3, and SO_4 dominance in water samples indicated that evaporite dissolution, silicate weathering, cation exchange, and rainy recharging were the potential reasons. WQI established that water samples were appropriate for irrigation and livestock consumption, but their purity for human consumption was inferior. Cd content is more toxic than the other metals observed in water samples, which were polluted with 36% according to WHO MAC and 18% according to FAO limits. 48% of the samples, according to HPI, were suitable for potability. According to HEI, 85% of the water samples were low in HM contamination, and the remaining percentages varied from medium (9%) to high (6%). As Cd content polluted more than a third of samples, its content in those samples was evaluated and found to have non-carcinogenic impacts on adults and children in 50% of contaminated samples. Also, it had carcinogenic influences on adults and children in all the polluted samples, according to health risk results. The studied water is very harmful when transported over long distances in metallic tubes because it reacts with the pipes, forming a rust coating and polluting the water with HM according to CR values. Because the recharge rate represented 20.6% of the annual precipitation in the studied area, groundwater recharge is very limited, depending on the CMB approach. It is recommended to treat 36% of the water to remove Cd to reduce the threat to the health of the study area's occupants. Due to the studied groundwater's constrained supply resources, it is advised that it be used carefully.

Conflict of interest/Competing interests

The authors declare that there are no competing interests.

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