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Valuation of Groundwater Contaminated with Nitrates and Human Health Risks (HHR) Between Villages of Sinjar and Tal Afar Districts, Iraq

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Abstract

Nitrates are one of the most common pollutants in groundwater. To assess the risk of exposure to nitrates in drinking water for age groups, we monitored the concentration of nitrates in the drinking water of the Al-Jazeera region. The climate of this region is characterized as dry and semi-arid, and its inhabitants depended on the water in the aquifers as a source of drinking for many years, without monitoring, treatment, or filtration system, as there is no public drinking water network. A model was also used to assess the risks of nitrate pollution in groundwater to human health. Samples were taken from 30 wells distributed equally over the three villages to collect water samples and measure the concentration of nitrate ions in groundwater. The concentration of nitrate ions in well water is less than 50 mgL^{-1} and ranged between (4.2 – 48.1) mgL^{-1}**.** The mathematical model results showed that the ages under 11 years and pregnant women have a higher hazard quotient of nitrate value (HQ) than one except for wells No. 2 and 9, which are higher than the permissible limits for drinking. As for age groups above 11, well water was suitable for drinking, and the HQ value was mainly less than one. The reason for this age group's lower chronic daily intake (CDI). In other words, the groundwater was suitable for adults and not for children under 11 years and pregnant women**.**

Keywords: HQ, CDI, Nitrate, Cancer, Drinking water.

Introduction

The issue of the environment and environmental pollution has received the attention of specialists and global public opinion, and there have been many studies that dealt with groundwater pollution after it was contaminated with chemical, and biological pollutants, which has contributed greatly to the increase in diseases and the deterioration of environmental components [1]. The use of well water regardless of the degree of pollution and the severity of their use, leads to diseases that may be fatal, and these diseases may not appear when using water until some time has passed; pollution of groundwater with nitrates is an important problem for the rural population of the world, as there are hundreds of wells and tens of thousands of hectares of agricultural land whose groundwater cannot be used for drinking purposes due to nitrate pollution, as in Morocco [2], Germany [3], and France [4, 5]. Therefore cannot use its water to exceed the nitrate concentrations permissible limit [6]. From the above, we note the magnitude of the problem, considering the negative effects of pollution on general human health and infants in particular. The health effects of nitrates in humans are most closely related to infants, as their consumption of water containing nitrates with milk leads to the transformation in the stomach that can combine with oxygen molecules in red blood cells leading to oxygen depletion and the possibility of suffocating the child. As for adults, drinking water containing higher concentrations of nitrates than infants may not pose a health risk [7, 8]. However, some studies indicate the possibility of bleeding in the spleen due to the ingestion of water containing large amounts of nitrates. World health organization (WHO) standards state that nitrate concentrations exceeding 50 mgL^{-1} can be dangerous for adults and children; also, a low nitrate content can become hazardous when the water containing it boils because nitrites and nitrates are not evaporable [9, 10]. The concentration of nitrates in groundwater and surface water is normally low. Still, it may reach High levels due to various nitrogen sources, whether (agricultural or animal) on the earth's surface, in the soil layer, or the shallow layers under the soil, which is transmitted by the filtration process, surface runoff, or others [11, 12]. When the added quantities of chemical fertilizers exceed certain proportions, this often happens through repeated, unexamined, and random additions in many countries, leading to many negative effects, directly or indirectly, on the biological system in particular and the environment in general. The direct repercussions of chemical fertilizers are Direct damage to the living components of the ecosystem, including human, animal, and plant health. As for the indirect effects, they negatively affect the vital parts of the ecosystem (water, air, and soil). They occur in a defect in the composition of these natural components and the natural balance between them. On the other hand, the leakage of nitrates into the groundwater is one of the most important risks of pollution with nitrogen fertilizers [13, 14].

In some countries where groundwater is the main source of drinking. Some reports indicate groundwater pollution increases the risk of cancer of the pancreas, brain, large intestine, bladder, and thyroid [15, 16]. Geospatial technology, such as satellite remote sensing, geographic information systems (GIS), and satellite navigation system, are widely used in groundwater research. The most common applications of geospatial technology in groundwater research include identifying and mapping groundwater exploration areas and producing spatial and sensitive groundwater quality for pollution maps using GIS [17].

Among the studies that were conducted was to measure the concentration of nitrates in groundwater, which are dangerous to human health: Noor and others studied the nitrate ion concentration in the groundwater of several wells in the city of Mosul, whose concentration ranged between (0.39-10.88 mgL^{-1}) attributed this to pollution with wastewater [18], and the study of Al-Saffawi and Awad of the village of Abuwajnah Village in the Zammar sub-district in Nineveh Governorate indicated that there is no risk of drinking water by rural consumers due to its low concentrations, as its HQ value ranged between (0.0228 - 0.1125) [19].

The study aims to find out the suitability of drinking water for different age groups by applying the nitrate model.

Material and Methods

Description of the Study Area

The study was conducted on groundwater in the northwestern part of Nineveh Governorate (Al-Jazirah region). It includes the Kakhirta village, the village of Ein Al-Hussan and the village of Shoueira, where various agricultural and animal activities are spread that depend on the groundwater sources in the area for drinking and various uses [1, 20].

Sample Collection

Samples were collected regularly for five months to cover part of the area, and GPS determined the coordinates of each well. From there, they were projected onto the map as identified 30 wells. Table 1 shows the number of wells and samples collected from the sites according to geographical division. The total number of samples taken was 150 during the study period, with a sample from each well for each month.

Table 1. **Coordinates (E, N) and altitude of the studied wells.**

	Well	E	N	Altitude (m)
Kakhirta village	1	42°34′88″	36°55′90″	406
	2	42°34′71″	36°55′87″	406
	3	42°34′93″	36°55′73″	407
	4	42°34′45″	36°55′68″	406
	5	42°34′59″	36°55′45″	407
	6	42°34′95″	36°55′60″	407
	7	42°35′01″	36°55′34″	407
	8	42°34′68″	36°55′31″	407
	9	42°34′70″	36°55′12″	407
	10	42°35′00″	36°55′06″	407
Ein Al-Hussan village	11	42°21′79″	36°31′16″	335
	21	42°21′53″	36°31′43″	335
	13	42°21′42″	36°31′64″	335
	14	42°21′47″	36°30′26″	332
	51	42°21′26″	36°31′26″	332
	61	42°21′11″	36°31′11″	342
	71	42°20′87″	36°32′02″	348
	81	42°21′13″	36°32′08″	348
	91	42°22′19″	36°30′54″	327
	20	42°22′18″	36°31′02″	335
Shoueira village	12	42°22'86"	36°28'61"	324
	22	42°24'04"	36°29'34"	313
	23	42°24'24"	36°28'75"	317
	24	42°24'26"	36°27'66"	318
	25	42°24'94"	36°26'57"	310
	26	42°25'01"	36°25'01"	308
	27	42°22'80"	36°26'08"	320
	28	42°25'59"	36°30'07"	325
	29	42°26'53"	36°29'59"	319
	30	42°26'32"	36°26'80"	304

Sample Preparation

At 220 nm, the nitrate ion absorbs UV light, but not at 275 nm. Because dissolved organic stuff absorbs light at 220 nm, this is achieved by measuring the absorbance of a water sample at 275 nanometers, a wavelength at which organic matter can absorb electromagnetic radiation but not by nitrates. Once known, an experimental correction factor at 220 nm can discriminate between nitrate and organic matter. There are two phases to sample preparation. The sample will first be filtered to prevent UV light from being scattered by suspended particles in the water sample. To avoid interferences caused by the absorption of OH^- or CO_3^{2-}, both of which may absorb at 220 nm, the samples were acidified with 1 N HCl. Up to 1000 $CaCO_3$ mgL^{-1}, acidification should preclude interference from these ions. Hydrochloric acid is employed because Cl^- does not absorb light in the spectrum's 250 – 290 nm region. Samples were collected for five replicates of each sample in pyrex glass containers of 250 ml capacity and routinely followed the standard method for taking samples from the source as they filled the sample. The air was expelled inside the package, sealed after washing the container twice or three from the same source, and transferred to the Industrial Chemistry Lab at the University of Mosul. The measurement was carried out according to the (Ultraviolet screening method) by taking a known volume of the well-filtered sample, then adding to it (1 mL) of HCl (1 N) acid and measured at wavelengths of 220 and 275 nm using a UV spectrophotometer [21].

Assessment of the Human Health Risk of Nitrates (HHR) by Drinking Water for the Studied Wells

Well water was evaluated for the studied area HHR, according to the United States Environmental Protection Agency

(USEPA), which is widely used to determine the risks of nitrates to human health. A special model was used to calculate the nitrate concentration in well water. This model calculates the CDI and the HQ or the following equations:

$$CDI = Sw \times IS \times ES \times DE / BZ \times ZT$$

$$HQ = CDI / DN$$

CDI stands for chronic daily intake (mg/kg day), and Sw stands for nitrate content in drinking water (mgL^{-1}). DE indicates the exposure period in years and IS represents the average daily intake of water (liters) for different ages of adults, children, and babies. The local population in the study region relies on groundwater for drinking. Therefore, the frequency of exposure (ES) is 365 days/year. BZ: Average body weight in kg, meantime values (ZT) in days, DN represents the reference dose of nitrates (1.6 mg/kg/d), and these data are obtained from Risk Information Systems. If the HQ values are more than one, then it is considered hazardous to human health, and water is not suitable for drinking, but when it is equal to or less than one, drinking water is not dangerous and can be used for drinking [22, 23].

Inverse Distance Weighting

Used the (IDW) method to predict the spatial distribution of nitrates in the groundwater of 30 wells, one of the geostatistical methods and one of the most advanced techniques. Fig 2, 3 and 4 show the distribution of nitrates in groundwater over the area of each village [24].

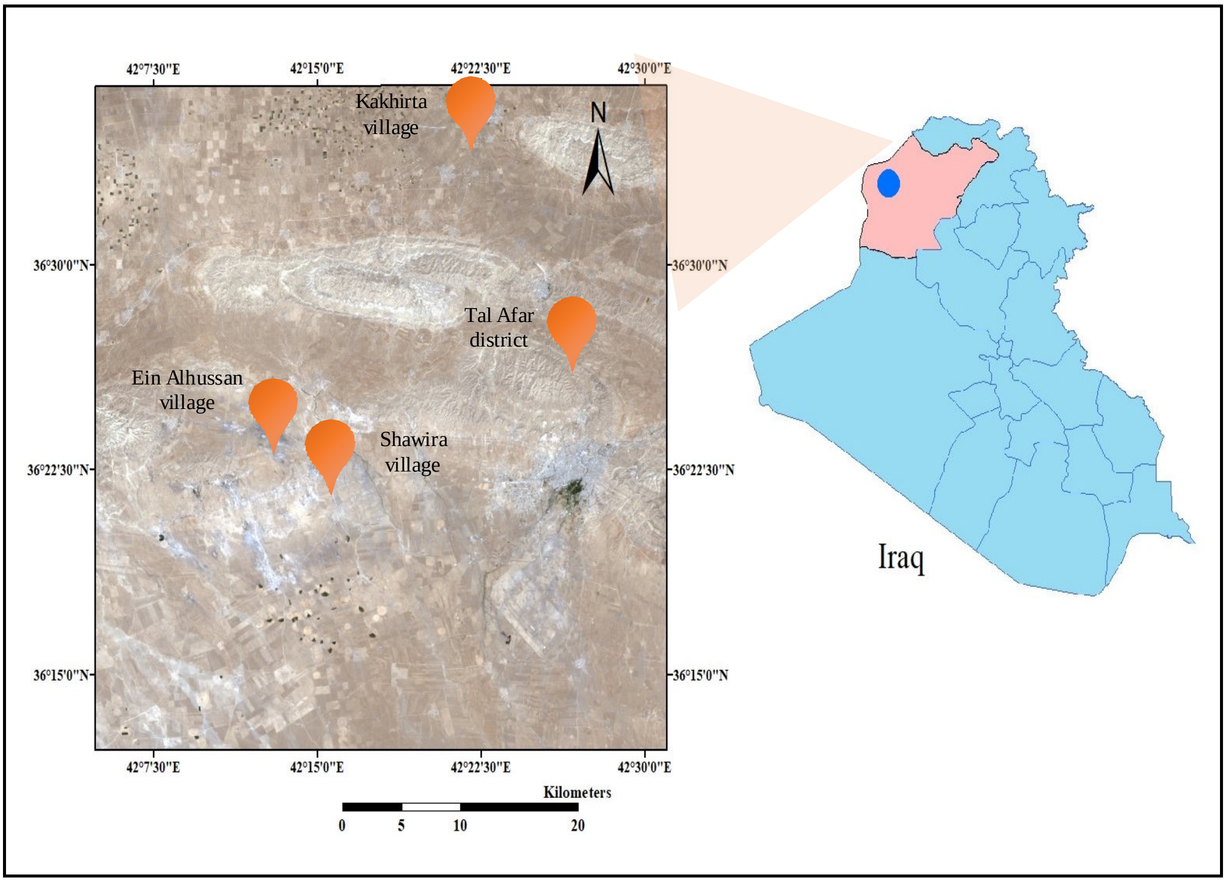

Figure 1. **Village sites in the study area in Nineveh Governorate [23, 24]**

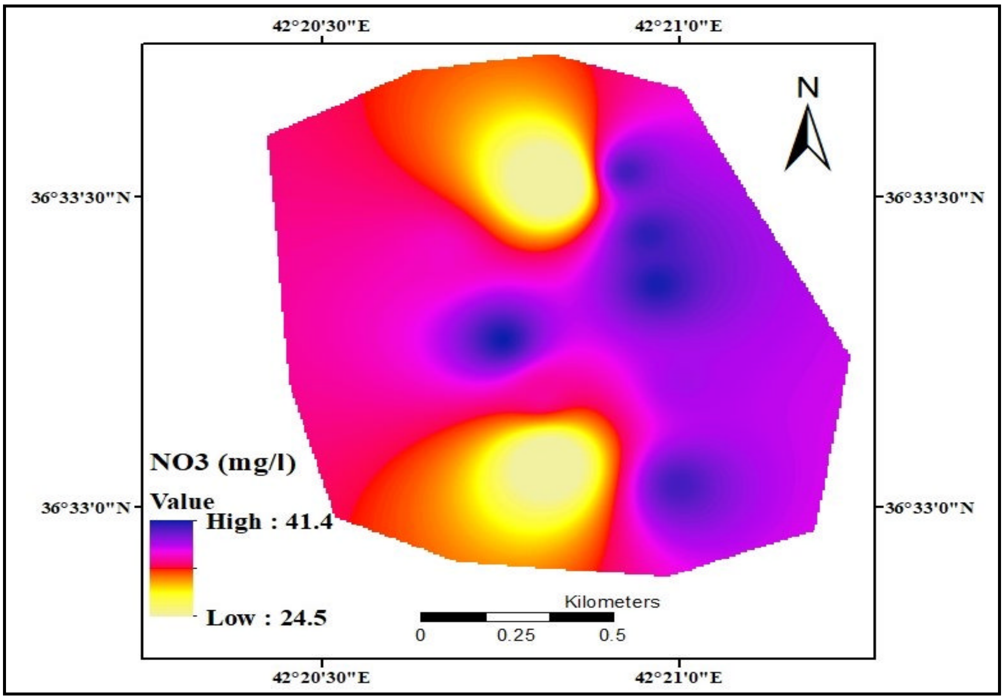

Figure 2. **Spatial distribution of nitrates in the Kakhirta village**

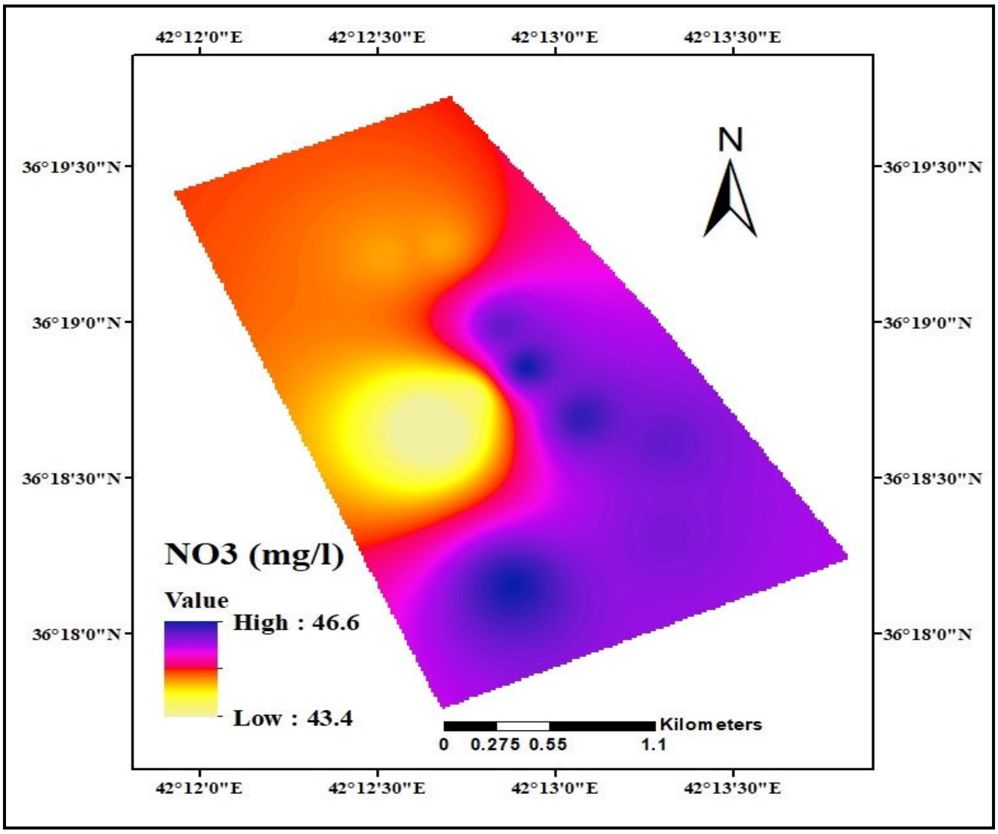

Figure 3. **Spatial distribution of nitrates in the Ein Al-Hussan village**

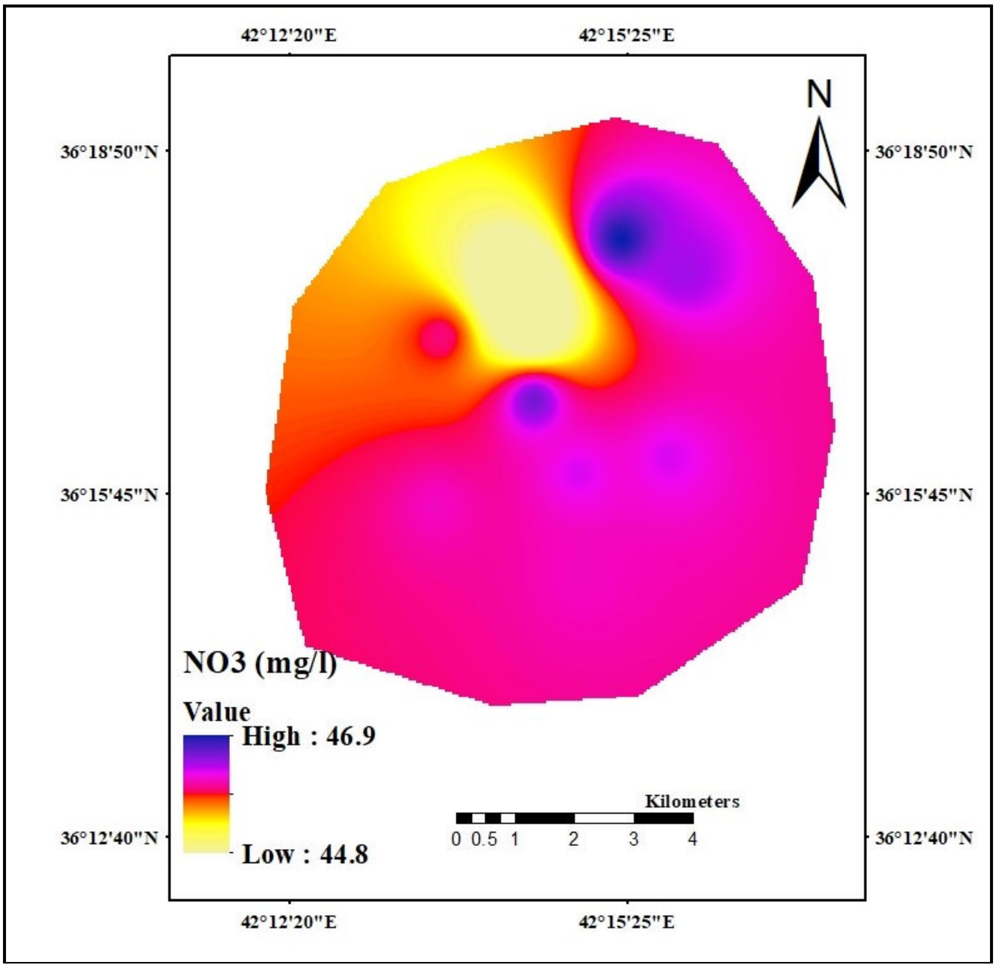

Figure 4. **Spatial distribution of nitrates in the Shoueira village**

Results and Discussion

Nitrogen fertilization is one of the most important agricultural applications that contribute to the pollution of groundwater, which causes health risks, including the carcinogenic effect. So, the amount of nitrates that a person takes in a day should not exceed 200 mg, since nitrates in the body are transformed into nitrites and are toxic through the formation of amines (nitrosamines) [25], which in turn cause liver cancer or esophageal cancer, Nitroso compounds are formed in the human body due to the intake of nitrates [26]. After drinking water containing nitrates, about 20% is converted to nitrite by bacteria in the digestive system. The nitrates in the acid conditions of the stomach turn into nitroso-acid (HNO_2), which reacts with the amines to form N-nitroso compounds (NOCs) that may cause cancer when present in high concentrations [27].

$$N_2O_3 \rightarrow NO^+ + NO_2^-$$
$$NO^+ + RRNH \rightarrow RRNNO + H^+$$

The results in this study showed values of nitrate concentration in well water, which ranged between (4.2 - 48.1) mgL^{-1}, and their means do not exceed 47 mgL^{-1}, meaning it is less than 50 mgL^{-1} Table 2, The rise is due to the intrusion of animal and agricultural waste into the groundwater. As a result of the biodegradation processes by microorganisms, the amino acids are transformed into ammonia and then into nitrates by the nitrification process, as in the following equation:

$$RNH_2 \rightarrow NH_4^+$$

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$

Table 2. **Nitrate ion values for the studied water wells (mgL^{-1}).**

	Wells	Min	Max	Mean ± SD
Kakhirta village	1	19.3	48.0	40.7±12.0
	2	4.2	31.0	24.5±11.4
	3	20.0	47.0	41.1±11.8
	4	18.9	45.2	37.4±10.5
	5	20.2	48.0	41.5±11.9
	6	20.0	48.0	41.4±11.9
	7	17.6	45.2	38.9±11.9
	8	20.0	45.8	36.9±12.1
	9	6.5	34.8	26.8±12.0
	10	19.9	46.5	40.7±11.6
Ein Al-Hussan Village	11	45.5	47.7	46.6±0.8
	12	45.5	47.6	46.7±0.8
	13	45.7	47.1	46.4±0.6
	14	46.1	47.4	46.7±0.6
	15	43.0	45.4	44.4±1
	16	39.6	45.8	43.4±2.9
	17	43.8	46.8	45.1±1.2
	18	44.2	46.2	45.1±0.9
	19	45.5	47.2	46.3±0.7
	20	45.8	47.0	46.4±0.6
Shoueira Village	21	43.2	46.3	44.8±1.3
	22	43.3	46.5	45.2±1.3
	23	46.1	47.6	46.8±0.6
	24	45.6	47.4	46.6±0.7
	25	45.7	47.6	46.5±0.8
	26	45.0	47.7	46.5±1
	27	46.1	48.1	47.0±0.8
	28	45.3	47.6	46.7±0.9
	29	45.3	47.7	46.6±0.9
	30	44.2	45.9	44.9±0.8

These values are considered permissible for drinking according to the standards of the World Health Organization (WHO). The harmful effect of the nitrate ion appears through the presence of methemoglobinemia in the blood of infants. Thus nitrates are reduced to nitrite by the reductase enzyme, both inside and outside the human body; the formed nitrite binds with hemoglobin to form methemoglobinemia (MetHb), which cannot transport oxygen to various body tissues as a result of the oxidation of iron (Fe^{+2} to Fe^{+3}), Fig. 5. This creates a health problem known as a blue baby syndrome. Children over three months old are more likely to have this disease, as they get large amounts of nitrates by consuming drinking water through artificial feeding; the effect of nitrates on this group of children appears more than on adults because of low concentrations of nitrates cause them disease. The study showed that all water samples from wells for ages under six years are not suitable for drinking due to exceeding the HQ value of one, which ranged between (1.0910 - 2.0939). The HQ value of more than one exceeded 80%. For ages between 6-11 years, it ranged between (0.6894 - 1.3242), which poses a threat to health safety, whereas, for ages above 11 years, the HQ value was less than one and varied between (0.5026 - 1.0145) and thus be suitable for drinking, shown in Table 3 [28-32].

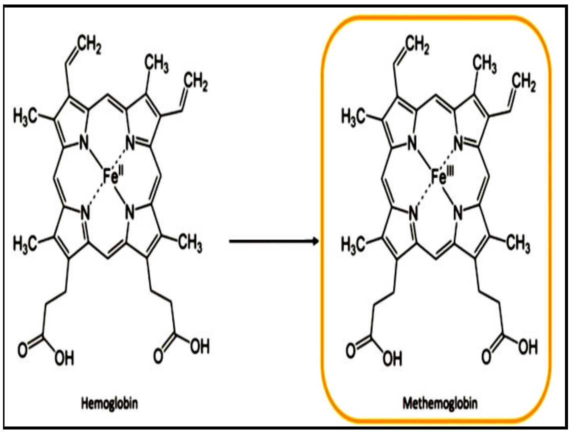

Figure 5. **Hemoglobin converts to Methemoglobinemia in the blood**

***Table 3*. CDI and HQ values for well water.**

	Wells		Age Groups						
			< 1.0	**6 - 11**	**11-16**	**16-18**	**18-21**	**21 -65**	**> 65**
Kakhirta Village	1	CDI	2.8976	1.8326	1.3359	1.0919	1.4039	1.3525	1.3882
		HQ	1.8110	1.1454	0.8349	0.6825	0.8775	0.8453	0.8676
	2	CDI	1.7442	1.1031	0.8041	0.6573	0.8451	0.8141	0.8356
		HQ	1.0901	0.6894	0.5026	0.4108	0.5282	0.5088	0.5223
	3	CDI	2.9271	1.8512	1.3495	1.1031	1.4182	1.3663	1.4023
		HQ	1.8294	1.1570	0.8434	0.6894	0.8864	0.8539	0.8765
	4	CDI	2.6650	1.6854	1.2286	1.0043	1.2912	1.2439	1.2767
		HQ	1.6656	1.0534	0.7679	0.6277	0.8070	0.7774	0.7980
	5	CDI	2.9541	1.8683	1.3619	1.1132	1.4313	1.3788	1.4153
		HQ	1.8463	1.1677	0.8512	0.6958	0.8945	0.8618	0.8845
	6	CDI	2.9492	1.8652	1.3597	1.1114	1.4289	1.3766	1.4129
		HQ	1.8432	1.1657	0.8498	0.6946	0.8931	0.8604	0.8831
	7	CDI	2.7708	1.7524	1.2774	1.0442	1.3425	1.2933	1.3275
		HQ	1.7318	1.0952	0.7984	0.6526	0.8391	0.8083	0.8297
	8	CDI	2.6252	1.6603	1.2103	0.9893	1.2719	1.2253	1.2577
		HQ	1.6407	1.0377	0.7564	0.6183	0.7949	0.7658	0.7860
	9	CDI	1.9057	1.2052	0.8786	0.7181	0.9233	0.8895	0.9130
		HQ	1.1911	0.7533	0.5491	0.4488	0.5771	0.5559	0.5706
	10	CDI	2.8999	1.8340	1.3370	1.0928	1.4050	1.3536	1.3893
		HQ	1.8125	1.1463	0.8356	0.6830	0.8782	0.8460	0.8683
Ein Al-Hussan Village	11	CDI	3.3210	2.1003	1.5311	1.2515	1.6091	1.5501	1.5910
		HQ	2.0756	1.3127	0.9569	0.7822	1.0057	0.9688	0.9944
	12	CDI	3.3289	2.1053	1.5347	1.2545	1.6129	1.5538	1.5948
		HQ	2.0805	1.3158	0.9592	0.7840	1.0080	0.9711	0.9968
	13	CDI	3.3056	2.0906	1.5240	1.2457	1.6016	1.5429	1.5837
		HQ	2.0660	1.3066	0.9525	0.7786	1.0010	0.9643	0.9898
	14	CDI	3.3243	2.1024	1.5326	1.2527	1.6107	1.5517	1.5926
		HQ	2.0777	1.3140	0.9579	0.7830	1.0067	0.9698	0.9954
	15	CDI	3.1653	2.0019	1.4593	1.1928	1.5336	1.4774	1.5165
		HQ	1.9783	1.2512	0.9121	0.7455	0.9585	0.9234	0.9478
	16	CDI	3.0881	1.9530	1.4237	1.1637	1.4962	1.4414	1.4794
		HQ	1.9300	1.2206	0.8898	0.7273	0.9351	0.9009	0.9247
	17	CDI	3.2099	2.0301	1.4799	1.2096	1.5552	1.4983	1.5378
		HQ	2.0062	1.2688	0.9249	0.7560	0.9720	0.9364	0.9611
	18	CDI	3.2156	2.0337	1.4825	1.2118	1.5580	1.5009	1.5405
		HQ	2.0097	1.2710	0.9266	0.7573	0.9737	0.9381	0.9628
	19	CDI	3.2992	2.0866	1.5210	1.2433	1.5985	1.5399	1.5806
		HQ	2.0620	1.3041	0.9507	0.7770	0.9991	0.9625	0.9879
	20	CDI	3.3030	2.0889	1.5228	1.2447	1.6003	1.5417	1.5824
		HQ	2.0643	1.3056	0.9517	0.7779	1.0002	0.9636	0.9890
Shoueira Village	21	CDI	3.1908	2.0180	1.4711	1.2024	1.5460	1.4894	1.5287
		HQ	1.9943	1.2613	0.9194	0.7515	0.9662	0.9309	0.9554
	22	CDI	3.2202	2.0366	1.4846	1.2135	1.5602	1.5030	1.5427
		HQ	2.0126	1.2729	0.9279	0.7584	0.9751	0.9394	0.9642
	23	CDI	3.3331	2.1080	1.5367	1.2560	1.6149	1.5557	1.5968
		HQ	2.0832	1.3175	0.9604	0.7850	1.0093	0.9723	0.9980
	24	CDI	3.3179	2.0984	1.5297	1.2503	1.6076	1.5487	1.5896
		HQ	2.0737	1.3115	0.9560	0.7815	1.0047	0.9679	0.9935
	25	CDI	3.3133	2.0955	1.5275	1.2486	1.6053	1.5465	1.5873
		HQ	2.0708	1.3097	0.9547	0.7804	1.0033	0.9666	0.9921
	26	CDI	3.3152	2.0967	1.5284	1.2493	1.6063	1.5465	1.5883
		HQ	2.0720	1.3104	0.9553	0.7808	1.0039	0.9666	0.9927
	27	CDI	3.3502	2.1188	1.5445	1.2625	1.6232	1.5637	1.6050
		HQ	2.0939	1.3242	0.9653	0.7891	1.0145	0.9773	1.0031
	28	CDI	3.3265	2.1038	1.5336	1.2536	1.6117	1.5527	1.5937
		HQ	2.0790	1.3149	0.9585	0.7835	1.0073	0.9704	0.9960
	29	CDI	3.3174	2.0981	1.5294	1.2501	1.6073	1.5484	1.5893
		HQ	2.0734	1.3113	0.9559	0.7813	1.0046	0.9678	0.9933
	30	CDI	3.1991	2.0233	1.4749	1.2056	1.5500	1.4932	1.5327
		HQ	1.9995	1.2646	0.9218	0.7535	0.9688	0.9333	0.9579

Finally, the use of chemical fertilizers is increasing, resulting from the increase in the proportion of nitrogen and the lack of vegetation during the winter to the disruption of the nitrogen cycle. This led to groundwater supplies with high concentrations of nitrates, which slowly seep nitrates into the soil at a rate of 1 meter annually until it reaches the underground water level. However, a large amount of nitrogen enters groundwater through surface runoff and seepage every year [33, 34].

Good agricultural practices should be encouraged to avoid excessive nitrogenous fertilizers. Large quantities of nitrogen fertilizers will increase nitrate concentrations in groundwater by losing a large proportion of the fertilizer used by leaching into the soil [35, 36].

Conclusion

Nitrate concentrations for all well water in the study area were within the permissible limits, less than 50 mgL^{-1} according to WHO standards. The study relied on the nitrate ion model, which requires age groups, body weight, exposure rate, and human consumption of drinking water containing nitrate concentrations. The study showed that the main HQ values were inappropriate for ages under 11 years and therefore posed a health risk to children, while older ages were good and safe to drink and did not pose a health risk in cancerous diseases. It also showed that the main reason for the high concentration of nitrates in groundwater is farmers' excessive use of nitrogen fertilizers, animal waste, and wastewater. We must try to keep the current nitrate levels from rising. By reducing agricultural fertilizers, future generations will pay the price for the current bad practices in agriculture. International water quality guidelines allow a maximum of 25 mgL^{-1} for infants and pregnant women and 50 mgL^{-1} for adults. Individuals with weaker immune systems, such as children and the elderly, are more vulnerable to the harmful consequences of nitrate pollution.

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Conflict of Interest

The author declares no conflict of interest.

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