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Possible human health risks of nitrates in drinking water: a case study of groundwater in Wana District, northern Iraq

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ABSTRACT: The purpose of this research is to determine how dangerous nitrates ($HHRNO_3$) in the drinking water of the Wana district northeast of Mosul are to human health. Where 100 water samples were taken from 10 wells across the region, between July 2022 and January 2023, to determine the average nitrate ion concentration, the average chronic nitrate ion intake, and the risk quotient (QHI) for people of varying ages. According to the study's findings, nitrate concentrations ranged from (3.0 to 15) ppm at a rate that did not exceed (12.3 ± 0.05) ppm, which is within limits recommended by the World Health Organization, which was reflected in the NPI values to range between (-0.27 to 0.23) to classify the studied water is from the category of clean water to light polluted with nitrates. As for the effects of nitrates' chronic daily intake (CDI) and risk factor (QHI), they fluctuated between (0.081 to 0.876) mg kg^{-1} daily, and (0.548 to 0.050) successively, the highest values were in infants, followed by children aged (6 to 11) years, then elderly females, with values (0.554 and 0.474) mg kg^{-1} daily and (0.346 and 0.296), consecutively. While the age group (16 to 18) years was the least affected by the dangers of nitrates, the chronic daily intake values and the risk quotient ranged between (0.081 to 0.330) mg kg^{-1} daily, and (0.050 to 0.206). Thus, the studied water is considered safe for drinking because it is within the levels recommended by the US. Environmental Protection Agency (QHI=1.0).
Keywords: nitrate; NPI; $HHRNO_3$.

Possíveis riscos à saúde humana por nitratos na água potável: um estudo de caso de água subterrânea no Distrito de Wana, Norte do Iraque

RESUMO: O objetivo desta pesquisa foi determinar a periculosidade para a sáude humana associado aos nitratos ($HHRNO_3$) na água potável do distrito de Wana, a nordeste de Mosul. Foram coletadas 100 amostras de água, de 10 poços em toda a região, entre julho de 2022 e janeiro de 2023, para determinar a concentração média de íons de nitrato, a ingestão crônica média de íons de nitrato e o quociente de risco (QHI) para pessoas de várias idades. De acordo com os resultados do estudo, as concentrações de nitrato variaram de 3,0 a 15 ppm, a uma taxa que não ultrapassou 12,3±0,05 ppm, sendo considerado dentro dos limites recomendados pela Organização Mundial da Saúde. Isso refletiu nos valores do NPI entre -0,27 a 0,23, permitindo classificar a água estudada como da categoria de água limpa para poluição com nitratos. Quanto aos efeitos da ingestão diária crônica de nitratos (CDI) e fator de risco (QHI), esses indices oscilaram de 0,081 a 0,876 mg kg^{-1} diariamente, e de 0,548 a 0,050, respectivamente. Os maiores valores foram obtidos em lactentes, seguidos por crianças com idade de 6 a 11 anos (0,554 e 0,474 mg kg^{-1} diariamente) e idosos do sexo feminino (0,346 e 0,296) consecutivamente. Enquanto a faixa etária (16 a 18) anos foi a menos afetada pelos perigos dos nitratos. Os valores de ingestão diária crônica e o quociente de risco variaram de 0,081 a 0,330 mg kg^{-1} diariamente e de 0,050 a 0,206. Assim, a água estudada é considerada segura para consume, por estar dentro dos níveis recomendados pelos EUA, com QHI=1,0.
Palavras-chave: nitrato; NPI; $HHRNO_3$.

1. INTRODUCTION

Despite the damage caused by high levels of nitrates and nitrites in drinking water, especially groundwater, and foods, low concentrations have health benefits for humans, as studies indicate that nitrate and nitrite ions found in vegetables and drinking water have a beneficial influence on human health because to the interactions they have with biological processes. Nitrates are chemical molecules and the byproducts of physiological processes that make nitrite, which is subsequently converted to nitric oxide., which plays an effective role in preventing cardiovascular diseases such as stroke (ZUCKERBRAUN et. al., 2017; LI et. al., 2020; AL-HAMDANY et. al., 2020; AL-GADI et. al., 2023).

This is due to its important role in regulating blood pressure, such as the pulmonary artery's blood pressure, by expanding the walls of blood vessels and increasing their elasticity (ADIMALLAH; PEIGYUE, 2019; AL-SAFFAWI; AWAD, 2020). However, high concentrations of nitrate and

nitrite ions above the limits allowed by (WHO, 2017) does significant harm to the health of both humans and animals.

Nitrate compounds in the diet are broken down into nitrite ions by anaerobic bacteria living under the tongue. These nitrite ions then react with secondary amines or amides in the stomach to form N-Nitroso compounds (NOC), the most common of which are linked to serious diseases like methemoglobinemia (Blue Baby Syndrome) caused by the oxidation of ferrous in hemoglobin to the ferric form, resulting in a reduction in the blood (BREDA et. al., 2019; ABBASNIA et. al., 2019; AL-BHAR; AL-SAFFAWI, 2020; AL-SAFFAWI; AWAD, 2021).

Figure 1. Blue Baybe syndrome: represented by the blueness of parts of the body such as the lips, face and soles of the feet.
Figura 1. Síndrome Blue Baybe: representada pela coloração azulada de partes do corpo como lábios, face e planta dos pés.

International studies have indicated the prevalence of these health problems in many regions of the world, including the study conducted in the United States of America, which confirmed that the main cause of the Blue Baby Syndrome in infants and even the elderly is the high level of nitrates in drinking water that are greater than the permissible levels (45 ppm); As these symptoms appeared in 80% of infants who were exposed to high levels of nitrates in drinking water (AHMED et. al., 2019). It also increases the risk of thyroid and endocrine disorders, and cancerous diseases such as leukemia, mouth, colon and rectum, stomach and prostate, etc. (TEMKIN et. al., 2019; JUNTAKUT et al, 2020; LIN et. al., 2023; MOTHFER; AL-SAFFAWI, 2023).

For pregnant women, some researchers have indicated that exposure to high levels of nitrates through drinking water is strongly associated with miscarriage, premature births, low birth weights and birth defects in newborns (YU et. al., 2020; SHERRIS et. al., 2021; COFFMAN et. al., 2021; STAYNER et. al., 2022). Reports and studies also indicate that many cases of recurrent miscarriage of pregnant women in the US state of LaGrange, Indiana are because of the widespread usage of nitrate-contaminated wells; excessive nitrate exposure has been linked to an increased risk of birth abnormalities and other adverse outcomes during pregnancy. of the fetuses. It also increases the negative impact on the health of pregnant women and the elderly who suffer from a rare metabolic dehydrogenase deficiency (WHO, 2017).

These risks result from the formation of carcinogenic and mutagenic N-nitroso compounds resulting from the reaction of nitrite derived from the reduction of nitrates in the body with amines and amides. Through experiments and studies, about 300 N-nitroso compounds (NOCs) have been diagnosed, and 85% of 209 nitrosamines and 92% of nitrosamides have a carcinogenic effect (VERMEER et. al., 1998).

By the grace of God on creatures, the presence of ascorbic acid, polyphenols, etc., in high levels in vegetables works to inhibit the formation of NOC compounds to protect humans and animals from dangerous effects. As a result of the importance of nitrate ions, the current study came to assess the health risks of nitrates in the groundwater of the Wana sub-district and its affiliated villages as one of the very limited studies in Iraq.

2. MATERIAL AND METHODS

2.1. Description of the study area:

Ten wells were chosen at random from a range of depths in the Wana sub-district (Deer Umm Tutha and Musharraf Habeit villages) affiliated with the Takleef district in the northeastern part of the city of Mosul, Nineveh Governorate. Their locations were determined using the Global Positioning System (GPS) of Google Earth, as shown in Table 1 and Figure 2 to illustrate the latitude and longitude.

Table 1. Characteristics and specifications of the studied area and wells.
Tabela 1. Características e especificações da área e poços estudados.

Wells No	Coordinates		Depth (m)	Uses
	N	E		
1	36° 31’ 30.821”	42° 45’ 34.182”	45	For drinking, bathing, cooking, watering livestock and poultry, etc.
2	36° 31’ 07.585”	42° 46’ 08.757”	100	
3	36° 51’ 50.938”	42° 47’ 04.600”	27	
4	36° 30’ 50.200”	42° 46’ 14.600”	20	
5	36° 30’ 50.182”	42° 46’ 27.904”	50	
6	36° 30’ 31.410”	42° 46’ 33.801”	17	
7	36° 30’ 46.305”	42° 47’ 51.052”	40	
8	36° 30’ 52.686”	42° 49’ 05.575”	41	
9	36° 30’ 56.819”	42° 49’ 05.067”	117	
10	36° 30’ 53.091”	42° 49’ 21.773”	50	

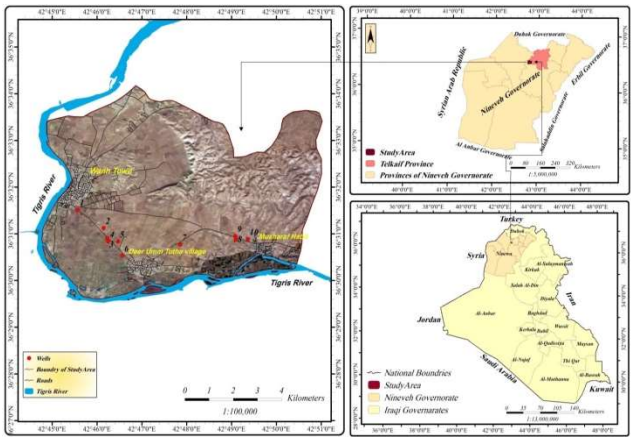

Figure 2. A satellite map of the location of the wells of the town of Wana and its affiliated villages, showing the wells studied.
Figura 2. Mapa de satélite da localização dos poços da cidade de Wana e suas aldeias afiliadas, mostrando os poços estudados.

2.2. Geology of the Study Area:

It is spread in the study area consisting of a flood plain that exists in the form of a strip surrounding the Tigris River and consists of sand, silt, and a little gravel. The area is also characterized by the spread of the Al-Fatha formation belonging to the (Middle Miocene) which is exposed in some locations and contains gypsum $CaSO_4$ H_2O, anhydrite, $CaSO_4$, halite and calcareous salt rocks, clay, and silt, in addition to the formation of Anjana (Upper Miocene) consisting of evaporates and the succession of clay, sand and

marl rocks whose impact is reflected on the groundwater passing through them (AL-SAWAF, 1977; ALYAN, 2010).

2.3. Methodology:

Water samples were collected from ten wells scattered in the study area randomly, starting from July (2022) until January (2023), after operating the well water pump for several minutes, using clean polyethylene bottles, then placed in a refrigerated box and away from light until reaching Environment and pollution laboratory of the College of Education for Pure Sciences, University of Mosul. Nitrate ions were estimated according to the ultraviolet screening method numbered (4500-NO3- B), by taking a known volume from the filtered water sample, then 1 ml of HCl (1N) was added to it, shaken well to homogenize the sample, and then measured using a UV spectrophotometer of the Shimadzu type, of Japanese origin, on the wavelengths are 220 and 275 nm, taking into account the Blank work to correct the readings, and then compared with the standard curve (APHA, 1988; 2017).

2.4. Estimating the damages and risks of nitrate ions:

Two models were used for this purpose:

2.4.1. Nitrate Pollution Index (NPI):

The presence of nitrates is one of the vital factors for assessing the quality of groundwater [15,16]. As a result of its serious effects on human and animal health, the (NPI) was estimated using the following equation (PANNEERSELVAM, 2020; MUHIB et al, 2023)

$$NPI = Ci - HAN / HAN \quad (01)$$

where: NPI = degree of water pollution with nitrates for the study areas, Ci = measured nitrate ion concentration in groundwater, HAN = acceptable nitrate levels for humans (10 ppm) according to (AL-HAMDANY et. al., 2020; MUHIB et. al., 2023).

After finding the value of (NPI) the degree of water pollution with nitrate is classified into five categories as follows: NPI ≤ 0.0 – Clean level., 0.1 -1.0 – Light polluted., 1.1 – 2.0 – Moderate polluted., 2.1-3.0 – Polluted water., NPI > 3.0 - Very Polluted water.

2.4.2. Human Health Risk of Nitrate

The mathematical model was used to evaluate the health risks of nitrate ions in drinking water, which was referred to by the US Environmental Protection Agency (USEPA), as it is considered one of the very few studies of water resources in Iraq, and it is also considered a good method for assessing the health risks of nitrates on the health of consumers for all age groups. Calculated from the following equations (SHALYARI et. al., 2019; ZHANGE et. al., 2019; CHEN et. al., 2021; ALHARBI et. al., 2023):

$$CDI = \frac{Cw * IR * EF * ED}{Bw * AT} \quad (02)$$

$$HQ = HI = \frac{CDI}{RFD} \quad (03)$$

whereas: CDI = chronic daily intake (mg/kg.d).; HQ = Hazard Quotient.; Cw = nitrate concentration measured in water samples.; IR = the daily rate of drinking water (L. day^{-1}).; EF = exposure frequency according to age (day, year).; ED = duration of exposure to nitrate (year).; Bw = body weight by age group (kg).; AT = average time (day).; RfD = measured nitrate reference dose (1.6 mg/kg.daily).

3. RESULTS

The results shown in Table 2 and Figure 3 indicate the values of nitrate ions that ranged between 3.0 and 15.0 ppm, with rates between 3.0 ± 0.26 to 12.3 ± 0.05 ppm, this is the relative increase in the concentrations of nitrate ions in some waters studied, it may be caused by the excessive use of nitrogen fertilizers by farmers, as the remaining quantities are washed away to reach groundwater (DOUNA; YOUSEFI, 2023; GROUT et. al., 2023).

Table 2. Nitrate ion concentration (ppm) for groundwater of Wana Sub-district.
Tabela (2): Concentração de íon nitrato (ppm) para águas subterrâneas do subdistrito de Wana.

Site \ Date	30/7	13/8	27/8	3/9	10/9	17/9	1/10	15/10	5/11	4/12
S1	9.0	10	9.0	9.0	9.0	11	11	10	10	10
S2	12	12	12	12	12	12	12	12	12	12
S3	11	11	15	11	11	12	12	12	12	12
S4	12	12	12	12	12	12	12	12	12	12
S5	12	12	12	12	12	12	12	12	12	12
S6	11	11	11	11	11	12	12	12	12	11
S7	11	12	12	12	12	12	12	12	12	12
S8	12	12	12	12	12	13	12	12	12	12
S9	3.0	3.0	4.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
S10	7.0	7.0	7.0	7.0	7.0	8.0	8.0	8.0	7.0	8.0

Likewise, the improper disposal of agricultural and animal waste, as it is subjected to a series of vital processes by the action of microorganisms, leads to the formation of nitrate compounds; Amino acids are converted to ammonia (NH_3) and then to nitrates by the process of nitrification, as in the following equation (AL-SAFFAWI; AL-BHAR, 2021; AL-MASHHADANY, 2022):

$$\text{Amino acid } (RNH_2) \xrightarrow{Deaminizes\ Enzyme} + NH_4^+$$

$$NH_4^+ \xrightarrow{Nitrosamines} NO_2^- \longrightarrow NO_3^-$$

As for the decrease in concentration in some groundwater, it may be due to self-purification processes and the possibility of nitrate reduction by the denitrification process and its loss in the form of N_2 by different types of

bacteria, including pseudomonas, as in the following equations (AL-MASHHADANY, 2022):

$$6NO_3^- + 2CH_3OH \xrightarrow{Bact} 6NO_2^- + 2CO_2 + 4H_2O$$

$$6NO_2^- + 3CH_3OH \xrightarrow{Bact} 3N_2 + 3CO_2 + 3H_2O + 6OH^-$$

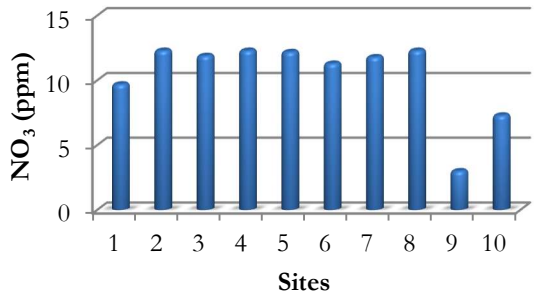

Figure 3. Average concentrations of nitrate ions in the groundwater of Wana Sub-district.
Figura 3. Concentrações médias de iões de nitrato nas águas subterrâneas do subdistrito de Wana.

When comparing the current results with previous studies conducted in Nineveh Governorate, they were higher than the results of Al-Sinjari et. al. (2019) for the village of Jaliukhan, southeast of the city of Mosul, as it amounted to 0.177 ppm, and relatively higher than the results of (Al-Hamdany et. al., 2020), in which rates ranged between 1.23 - 9.66 ppm.

While it was close to the results obtained by Al-Bhar and Al-Saffawi (2021) in their study of Al-Manara village, which amounted to 15.0 ppm, while it was less than the results obtained by Al-Mashhadany (2022) on the groundwater of Sinjar district, which amounted to 48.8 ppm. Generally, the concentrations are high in some regions of the world, as Yu et. al. (2020) indicates a high concentration of nitrates in the well water of rural areas in Yantai, China, reaching 166.4 ppm. This rise in NO_3 concentrations is undesirable because of its negative effects on the health of both humans and animals (TOOLABI et. al., 2021).

3.1. Assessment of Hazard NO3 in water

3.1.1. Nitrate pollution Index (NPI)

The results ruled in Table 3 indicate that the values of the nitrate pollution index of groundwater fluctuated between -0.27 to 0.23, to classify the well water (1, 9, 10) as clean water, while the rest of the studied groundwater was in the category of light pollution. The relative increase is due to agricultural activities and the use of fertilizers and pesticides in the study area (GROUT et. al., 2023).

Table 3. Nitrate pollution index values and classification of the studied water.
Tabela 3. Valores do índice de poluição por nitratos e classificação das águas estudadas.

Sites	NPI	Categories	Sites	NPI	categories
1.	- 0.03	*Clean water*	6.	0.13	*Light Polluted*
2.	0.23	*Light Polluted*	7.	0.18	*Light Polluted*
3.	0.19	*Light Polluted*	8.	0.23	*Light Polluted*
4.	0.23	*Light Polluted*	9.	- 0.70	*Clean water*
5.	0.22	*Light Polluted*	10.	- 0.27	*Clean water*

When comparing the results with other studies, we notice that they are somewhat higher than the results obtained by (Al-Hamadany et al., 2020) for the groundwater of the left side of Mosul city, in which the (NPI) values fluctuated between -0.9 to -0.5, and thus it is classified in the category of water not contaminated with nitrates, while it was consistent with the values that were calculated from the results of Al-Bhar and Al-Saffawi (2021) for the groundwater of Al-Manara village, northeast of Mosul, which ranged between 0.08 to 0.21.

Also, the values of (NPI) are raised in some regions of the world to reach 24.3 and 4.44 in the districts of Satkhira and Manikganj in Bangladesh, to classify the studied water from the category of very polluted water (Muhib et. al., 2023), while the mean values for 77% of the groundwater of rural areas in Yantai County, Shan-dong Province of China 1.46, were to be classified as moderately polluted water (YU et. al., 2020).

3.1.2. Human Health Risk of Nitrate (HHR):

According to Table 4, the HQ values of groundwater in the Wana region were higher for newborns and children 6-11 years, than for the other age groups that were evaluated, ranging between 0.134 to 0.548 and 0.084 to 0.346. This increase is due to the relatively high values of (CDI), which ranged between 0.2137 to 0.87617 and 0.114 to 0.0.550 mg/kg. daily, respectively. As for the age groups 18-21 years and 21-old for females, the values of the risk quotient (HI) fluctuated between 0.065 to 0.266 and 0.072 to 0.296, and with chronic daily intake between 0.084 to 0.425 and 0.116 to 0.474 mg/kg. daily, consecutively.

4. DISCUSSION

As for the age group least affected by the risks of nitrates 16-18 years, in which the values of the risk quotient fluctuated between 0.050 to 0.206, this decrease resulted from the relative decrease in the chronic daily intake (CDI) ranging between 0.081 to 0.330 mg/kg. daily.

When comparing our current results with other studies, we note that they were relatively higher than the results obtained by Al-Saffawi; Awad (2020) for the groundwater of the village of Abu Wajna west of Mosul city, so the chronic daily intake values ranged between 0.235 to 0.180 mg/kg. day, with a risk quotient (QHI) between 0.147 to 0.113, and relatively close to the results obtained by Al-Bhar; Al-Saffawi (2021), so the daily intake ranges between 0.298 to 0.869 mg/kg. day with a hazard quotient between 0.86 to 0.543, while it was less than the results obtained by Al-Gadi et. al. (2023) when studying the groundwater of the villages (Kharsbad, Baybukht, and Abbasiya) north-east of the city of Mosul, in which the values of the hazard quotient reached 1.612, 1.822 and 1.843 and a daily intake of 2.579, 2.916 and 2.948 mg/kg. day, consecutively. These differences in results between studies are due to differences in temporal, spatial, and agricultural practices.

Fortunately, the values of the hazard quotient (HQ) were within the safe limits recommended by the US Environmental Protection Agency (HQ = 1.0), because the high concentration of nitrates in drinking water has serious consequences for consumers (AL-HAMDANY et al., 2020).

Table 4. The results of the chronic daily intake (CDI mg/kg.d) and the hazard quotient (HQ) of groundwater for the Wana region.
Tabela 4. Os resultados da ingestão diária crônica (CDI mg/kg.d) e o quociente de risco (HQ) das águas subterrâneas para a região de Wana.

Site	Cohort	Infant	6-11	11-16	16-18	18-21	21 to Old	
							Females	Males
1	CDI	0.691	0.437	0.319	0.260	0.335	0.374	0.323
	HQI	0.432	0.273	0.199	0.163	0.209	0.234	0.202
2	CDI	0.876	0.554	0.404	0.330	0.425	0.474	0.409
	HQI	0.548	0.346	0.252	0.206	0.266	0.296	0.256
3	CDI	0.848	0.536	0.391	0.319	0.411	0.459	0.396
	HQI	0.530	0.335	0.244	0.200	0.257	0.287	0.255
4	CDI	0.876	0.554	0.404	0.330	0.425	0.474	0.409
	HQI	0.548	0.346	0.252	0.206	0.265	0.296	0.256
5	CDI	0.869	0.550	0.401	0.327	0.421	0.470	0.405
	HQI	0.543	0.344	0.250	0.205	0.263	0.294	0.254
6	CDI	0.805	0.509	0.371	0.303	0.390	0.436	0.376
	HQI	0.503	0.318	0.232	0.190	0.244	0.272	0.235
7	CDI	0.841	0.532	0.388	0.317	0.407	0.455	0.394
	HQI	0.525	0.332	0.242	0.198	0.255	0.284	0.245
8	CDI	0.876	0.554	0.404	0.330	0.425	0.474	0.409
	HQI	0.548	0.346	0.252	0.206	0.266	0.296	0.256
9	CDI	0.214	0.135	0.099	0.081	0.104	0.116	0.100
	HQI	0.134	0.084	0.062	0.050	0.065	0.072	0.062
10	CDI	0.520	0.329	0.240	0.196	0.252	0.281	0.242
	HQI	0.325	0.206	0.150	0.122	0.157	0.176	0.152

5. CONCLUSIONS AND RECOMMENDATIONS

This research is one of a small handful that has assessed HHR in Iraq by factoring in variables such as age, period of exposure, body weight, daily use of drinking water, nitrate levels in drinking water, etc., and nitrate contamination index (NPI). This research shows that:

1. The concentration of nitrates in the groundwater of the Wana sub-district is within the levels allowed by WHO, which is reflected in the values of (NPI) so that the studied water is from the category (unpolluted water to light polluted with nitrates).

2. Fortunately, the nitrate hazard quotient values (HInitrate = HQI) were within the safe levels for drinking according to (US-EPA) for all age groups, especially infants, and there were no health risks to humans and livestock, whether cancerous or non-cancerous.

Therefore, the study recommends periodic follow-ups of the quality of water sources used for drinking, along with educating farmers about the use of scientific fertilization methods to preserve consumers' public health.

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