Hygienic Safety of Nitrates in Locally Bottled Drinking Water in Mosul City Northern Iraq

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Abstract
The current study included evaluating the health safety of nitrates in bottled water on the health of consumers, as water samples were collected from ten shops (for treating bottled water) spread on the left side of Mosul city (eleven replicates from each site) starting from September 2021 until February 2022 to measure the concentration of nitrate ions with the calculation of the human health risks of nitrates (HHR) based on international standard methods. Fortunately, the results of the study indicated that there were no risks of nitrates in bottled drinking water on the health of consumers because the values of the nitrate risk quotient (HInitrate or HQ for all age groups) studied were within the permissible limits (less than 1.0) ranging from (0.00504 to 0.01552) , This decrease in values is due to a decrease in the concentration of nitrate ions, whose rates fluctuated between (0.111±141 to 0.349±0.148) mg. l-1 to reflect on the values of chronic daily nitrate intake (CDI) that ranged between (0.00807 to 0.02482) mg/kg. Day.
Keyword: HHR of NO3, bottled water, Mosul city

1. Introduction

Today, the problem of providing clean and safe water has become one of the biggest challenges facing millions of people in the world, especially in developing countries due to pollution of water sources resulting from indifference and mismanagement of water resources and the failure to implement environmental laws that deter violators and transgressors in dumping waste water into water resources and polluting them because these problems concerning human existence, health, progress, and the economy (Al-Saffawi and Al-Barzanji, 2020). As it is known that the problem of lack of safe water for drinking and civil uses is one of the pillars of national security for any country in the world, especially arid and semi-arid regions whose water sources come from neighboring countries, as is the case in Iraq and Egypt. . Sudan, etc.(Jaafer and Al-Saffawi, 2020) In the current study, we focused on the quality and degree of pollution of bottled water with nitrates, which are among the pollutants dangerous to human health when they are present at high levels (Al-Bhar and Al-Saffawi, 2021). This is the first study conducted in this field in Nineveh Governorate and as a result of the local population's tendency to buy this type of water in abundance for drinking, especially large bottles that are treated locally in small shops spread throughout the city due to their low prices compared to the same bottles of local and international brands. Despite the spread of nitrate compounds in the environment in different concentrations, they are very necessary for plants to manufacture important compounds for plant, animal and human life. However, high concentrations in the soil cause damage to plants, such as deterioration in the quality and quantity of plant production and the possibility of its accumulation in plant tissues that are consumed by humans and animals for nutrition, which causes health risks to consumers. Such as cancerous diseases, as a result of nitrate reduction processes since entering the mouth into nitrite ions, it may react with amines and amides in the digestive system to form nitrosamines or amides (N-nitroso NOCS), compounds, most of them have carcinogenic and mutagenic effects. such as diabetes, irregular thyroid gland functions, ulcers, cancer of the stomach, colon and rectum, lymph nodes, abortion of pregnant women, congenital malformations of fetuses, and sudden death of newborns (Nujić and Habuda-Stanić, 2017 ؛Adimalla and Peiyue, 2019; Al-Saffawi and Awad, 2020).
Let's switch from the dark side to the bright side. When nitrates are present in low concentrations, they play a vital and beneficial role for human health, and this is represented by a reduced risk of heart and blood vessel diseases and stroke due to its transformation into nitrogen monoxide, which leads to the expansion and increase of elasticity of blood vessels and maintains Its balance (, Al-Saffawi and Awad, 2020; Mina et al. 2017), as well as its beneficial importance for patients with stomach ulcers and kidney failure (Anthony et al. 2019). Nitrate ions enter the human body via the diet, which contributes approximately (60-70%) of the nitrate intake to the human body, such as leafy vegetables, frozen meat products and drinking water, which contribute (15-20) %, in addition to internal sources. Nitrate ions are reduced as soon as they enter the mouth to nitrite in the oral cavity (by normal flora) and salivary glands. Fortunately, a large proportion of nitrogen compounds are excreted with urine (Khambata et al. 2015) as shown in Figure 1. Also, eating vegetables containing ascorbic acid, polyphenols and other compounds prevents the formation of NOCs and thus protects humans from its dangerous effects (Ward et al, 2018; Ma et al, 2018). Therefore, this study was conducted to estimate the health risks of nitrates in bottled water, as it is the first study in this field to be conducted on bottled water in Mosul and Iraq.

2. Material and Methods

Description of the Study area

There are many small popular shops to treat water and

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fill it in 18-liter containers in the city of Mosul, and as a result of the conditions that the city went through and the destruction of the infrastructure, many local residents resorted to using bottled water for drinking, especially this type of bottled water because of its cheap prices compared to Similar to local and international brands. Ten popular shops scattered on the left side of

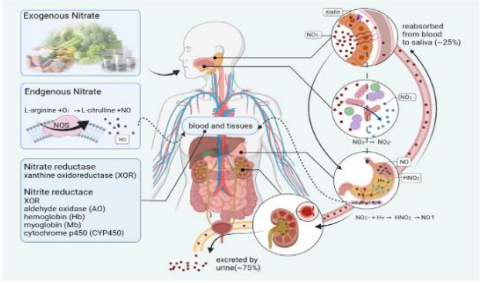

Figure 1. Nitrate pathways in the body: Exogenous nitrate is recycled primarily in the salivary glands, where sialine plays a major role in the active transport and concentration of nitrate.

Part of the nitrate is converted to nitrite by oral bacteria which is subsequently absorbed in the stomach and intestines. The salivary glands absorb up to 25% of the circulating nitrate, and finally the kidneys excrete the majority of nitrogenous compounds. (Ma, et al, 2018).
The city were randomly selected to collect water samples whose locations are shown in the Figure (2) using GPS for Google Earth.

Figure (2) a satellite image showing the locations of the popular bottled water stores on the left side of the city of Mosul.

Sample Collection and Methodology

Water samples were collected from ten stores on the left side of the city of Mosul over a period of six months, three times a month, starting from September (2021) to February 2022. Samples were taken from water containers to measure the concentrations of nitrate ions based on international standard methods (2017, APHA). Nitrate concentrations are measured using the (Ultra violet screening method) by taking a volume of 50 ml of the water sample, then adding to it (1 ml) of HCl (1N) and shaking it well to homogenize, then it is measured using a Japanese UV Spectrophotometer at wavelength 220 and 275 nm, to correct the readings, Blank worked (distilled water) and then compared with the standard curve, to calculate the concentration in units (mg. l-1) (APHA, 1988, 2017)
Estimation of the (HHR) of nitrates from drinking water:
The Human health risk model of nitrate was used according to the US Environmental Protection Agency (US-EPA). This mathematical model is a good tool to assess the health hazards caused by nitrate on consumer health, and it is calculated as follows (Chen et al, 2021; Shaluri et al 2019; Zhange et al, 2019)

$$CDI = \frac{Cw * IR * EF * Ed}{Bw * AT}$$

$$HI = HQ = \frac{CDI}{RFD}$$

Where: CDI: chronic daily intake (mg/ kg/ day), HQ: Hazard Quotient., Cw: nitrate concentration in drinking water (mg. l-1), IR: The daily rate of drinking water for different age groups (liters. day^{-1}), ED represents exposure time) years) . For the local people depend on this water for drinking purposes. Therefore, the exposure frequency (EF) is 365 days per year. Bw: body weight (kg), ET: mean time values (in days), RfD: the reference dose of nitrate (1.6 mg/kg/day). The values of these factors were obtained from the indicated health risk tables of US.EPA (Zhang et al, 2019). If the HI value (HQ) is less than 1.0, the water is considered within the permissible levels and does not pose a health risk to consumers (Adimalla and Wu, 2019).

3. Results and Disscutions

The results shown in the table (2) indicate that the values of the risk quotient) HQ= HI) of nitrates in the bottled water of the popular stores spread in Mosul city and for all age groups were within the safe limits because it did not exceed the danger limits (1.0) recommended by the US Environmental Protection Agency (Chen et al, 2o21), where the values ranged between (66E-4 to 248E-4). It also notes the relative increase in the values of the risk quotient for infants compared to the rest of the age groups studied, ranging from (110E-4 to 158E-4). This increase in values is due to the increase in the daily intake of nitrates (CDI), which ranged between (175E-4 to 254E-4) mg/kg. Day.
As for the age group (21-old), it is noted from the table (2) the relative increase in the values of chronic intake of nitrates (CDI), especially for females compared to males.

Ranging between (95E-4 to 137E-4) mg/kg. day, and the values of the hazard quotient (HQ) amounted to (857E-4), while the rest of the age groups, the values of the risk quotient fluctuated between (0.01001 to 0.00982), and it is noted that the age group (6-11) years is more affected by nitrate problems, as the values of (HQ, CDI) were relatively high, ranging from (111E-4 to 160E-4) mg/kg. Day, and (69E-4 to 100E-4) consecutively compared to other age groups (11-21) years,
From the grace of God, the values of the risk quotient for the studied water are within the safe limits for drinking, because the rise of these values outside the recommended limits has serious negative effects on the health of consumers, such as Blue baby syndrome in children, and even the elderly can suffer from this syndrome in addition to cancerous diseases, abortions for pregnant women, sudden death of newborns, etc. (Al-Hamdany et al., 2020). When comparing the current results, we note that they are less than the results obtained by (Al-Saffawi and Awad, 2020) when they studied the health risks of nitrates in the water sources of Abu Wajna village, west of Mosul, in which CDI values fluctuated between (225E-4 to 1800E-4) mg/kg. Day, and HQ values between (142E-4 to 1125E-4),

Table (2): Results values of chronic daily intake (CDI) in (mg/kg/day), and hazard Quotient (HQ) for bottled water in the studied popular stores.								
Cohorts Sites		Infants	6-11	11-16	16-18	18-21	21 to Old	
							Males	Females
BS1	CDI HI:QI	248e-4 155E-4	157E-4 98.2E-4	115E-4 71.5E-4	93.6E-4 58.5E-4	120E-4 75E-4	116E-4 72 E-4	134E-4 84 E-4
BS2	CDI HI:QI	246E-4 154E-4	156E-4 98 E-4	114E-4 71 E-4	93 E-4 58 E-4	120E-4 75 E-4	115E-4 72 E-4	134E-4 84 E-4
BS3	CDI HI:QI	241E-4 150E-4	152E-4 95 E-4	111E-4 69 E-4	91 E-4 57 E-4	117E-4 73 E-4	112E-4 70 E-4	130E-4 81 E-4
BS4	CDI HI:QI	191E-4 120E-4	121E-4 76 E-4	88 E-4 55 E-4	72 E-4 45 E-4	93 E-4 58 E-4	89 E-4 56 E-4	104E-4 65 E-4
BS5	CDI HI:QI	175E-4 120E-4	111E-4 69 E-4	81 E-4 51 E-4	66 E-4 41 E-4	85 E-4 53 E-4	82 E-4 51 E-4	95 E-4 65 E-4
6BS	CDI HI:QI	230E-4 144E-4	145E-4 91 E-4	106E-4 66 E-4	87 E-4 54 E-4	111E-4 70 E-4	107E-4 67 E-4	124E-4 78 E-4
BS7	CDI HI:QI	208E-4 130E-4	132E-4 82 E-4	96 E-4 60 E-4	78 E-4 49 E-4	101E-4 63 E-4	97 E-4 61 E-4	113E-4 70 E-4
BS8	CDI HI:QI	214E-4 134E-4	135E-4 85 E-4	99 E-4 62 E-4	81 E-4 50 E-4	104E-4 65 E-4	100E-4 63 E-4	116E-4 72 E-4
BS9	CDI HI:QI	253E-4 158E-4	160E-4 100E-4	117E-4 73 E-4	117E-4 73 E-4	123E-4 77 E-4	118E-4 74 E-4	137E-4 86 E-4
BS10	CDI HI:QI	226E-4 141E-4	143E-4 89 E-4	104E-4 65 E-4	85 E-4 53 E-4	109E-4 68 E-4	105E-4 66 E-4	122E-4 76 E-4

Likewise with the results of the study of Al-Bhar1 and Al-Saffawi (2021) of the health risks of nitrates in the water sources of Al-Manara village, northeast of Mosul, where the CDI and HQ values fluctuated between (8691E-4 to 2980E-4) mg/kg. Day, and (5432E-4 to 1862E-4) consecutively. It is much lower than the results of Hassan (2021) study of the human health risks (HHRNitrate) in water sources for some villages in Kirkuk governorate in northern Iraq, where the HInitrate or HQ Hazard Quotient values ranged between (4.215 to 116E-3) and attributed this to high values of chronic daily intake (CDI) that fluctuated between (6.744 to185E-3) mg.kg. Day, where 50% of the studied water samples exceeded the international permissible limits, which poses a danger to consumers of all age groups.

In general, the decrease in the chronic daily intake and the risk quotient of nitrates in the studied bottled water is due to the low levels of nitrates in it, as the results show in Table (3) and Figure (2) that the values ranged between (0.053 to 0.987) mg. l-1, and at fluctuating values rates between (0.246 to 0.356) mg. l-1, It is also noted from the table

that the concentrations fluctuated significantly between the bottled water of the studied stores, but the matter came to a noticeable change for the same stores in different periods, which may be attributed to the different treatment processes and the quality of reverse osmosis filters and maintenance operations, as well as the lack of efficiency of the owners of these stores, as the water source for these shops is the water of Alsahirun water supply plant in Mosul city, where the concentration of nitrate ions ranges between (0.44 to 1.39) mg. l-1 (Al-Hamadany et al, 2021a).

Fortunately, the results of nitrate concentration in the studied water are significantly less than its concentration in the water sources of Al-Manara village and some areas of eastern Mosul city, fluctuating between (10.8 to 19.1) and (10.9 to 11.2) mg. l-1 respectively (Al-Bhar and Al-Saffawi, 2020; Al-Hamadany et al, 2020). But when compared with other regions of the world, nitrate levels were recorded in the waters of southern India, reaching (160) mg. l-1 (Karunanidhi et al., 2019) and (348) mg. l-1 in the region of Siddipet, southern India (Adimalla and Wu , 2019) to reach concentrations of 1063 mg. l-1 in parts of Manitoba and Columbia; (Ward et al, 2018).

Table (3): Results of nitrate ions concentration in the studied bottled water (mg. l-1)											
Repl Sites	26/9	20/10	26/10	31/10	7/11	14/11	17/11	21/11	27/11	12/5	2/12
BS1	0.273	0.415	0.108	0.631	0.400	0.594	0.277	0.311	0.315	0.316	0.197
BS2	0.213	0.586	0.551	0.124	0.108	0.665	0.604	0.251	0.101	0.278	0.333
BS3	0.182	0.495	0.533	0.526	0.232	0.432	0.255	0.590	0.198	0.101	0.173
BS4	0.182	0.349	0.365	0.071	0.193	0.316	0.191	0.671	0.175	0.105	0.337
BS5	0.173	0.515	0.140	0.053	0.211	0.418	0.180	0.172	0.363	0.101	0.382
BS6	0.156	0.448	0.389	0.420	0.277	0.582	0.073	0.140	0.455	0.110	0.497
BS	0.160	0.491	0.302	0.062	0.260	0.084	0.946	0.212	0.272	0.115	0.311
BS8	0.111	0.601	0.365	0.065	0.290	0.288	0.116	0.304	0.600	0.312	0.257
BS9	0.162	0.557	0.987	0.123	0.187	0.302	0.433	0.151	0.300	0.302	0.162
BS10	0.113	0.617	0.405	0.210	0.358	0.395	0.480	0.120	0.156	0.45	0.120

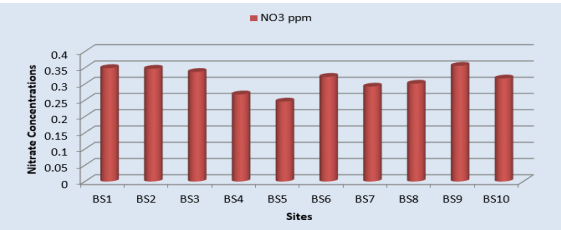

Figure (2) Concentration rates of nitrate ions in bottled water) mg. l-1).

4. Conclusions and Recommendations

The studied bottled water is safe in terms of the risks of nitrates because the values of the risk quotient (QH) are within the permissible limits (less than 1). On the other hand, these low concentrations of nitrates have health benefits for consumers, including the prevention of cardiovascular diseases such as heart

attack and stroke. Therefore, we recommend the necessity of periodic follow-up of nitrate concentrations in drinking water of all kinds to know the daily intake and the risk quotient.

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