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Article Health Risk Assessment of Nitrate and Fluoride in the Groundwater of Central Saudi Arabia

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Abstract: High nitrate and fluoride contamination in groundwater cause a variety of disorders, including methemoglobinemia, teratogenesis, and dental and skeletal fluorosis. The present work assesses the non-carcinogenic health risks posed by nitrate and fluoride in infants, children, and adults using the USEPA method. Groundwater samples were collected from 36 wells and boreholes in three central Saudi Arabia study areas. Nitrate concentrations varied from 0.70 to 47.00 mg/L. None of the 36 studied boreholes had nitrate levels that exceeded WHO guidelines (50.00 mg/L). Fluoride ranged from 0.63 to 2.00 mg/L, and 30.55% of the fluoride samples (11 out of 36) exceeded the WHO recommendations for acceptable drinking water (1.5 mg/L). The average hazard index (HI) values for adults, children, and infants were 0.99, 2.59, and 2.77, respectively. Water samples surpassed the safety level of 1 for adults, children, and infants at 44.44, 97.22, and 100%, respectively. Accordingly, water samples from Jubailah and a few from Wadi Nisah may expose infants, children, and adults to non-cancer health concerns. Infants and children are more vulnerable to non-carcinogenic health risks than adults, possibly due to their lower body weight.

Keywords: nitrate; fluoride; hazard index; groundwater; Saudi Arabia

1. Introduction

Groundwater is an important resource for drinking and irrigation, especially in dry and semi-arid regions [1,2]. However, shallow groundwater is vulnerable to contamination from various geogenic and anthropogenic sources, such as rock weathering, cation exchange during oxidation or reduction, rapid industrialization, urbanization, and excessive fertilizer use [3,4]. Recently, there has been a growing concern about groundwater quality and its influence on human health due to water consumption with high concentrations of nitrate and fluoride. Nitrate and fluoride concentrations in groundwater can negatively affect human health. These two toxic ions are listed as non-carcinogens by the US Environmental Protection Agency (USEPA) and have received worldwide attention for their devastating effects on human health [2].

Nitrate is an inorganic ion (NO_3^-) that naturally occurs in the nitrogen cycle and is widely found in nitrogen-containing fertilizers. Nitrate can enter groundwater through different natural and anthropogenic sources, e.g., rock-water interaction from the weathering of nitrite-bearing rocks, septic tanks, dairy lagoons, wastewater effluents, livestock waste, agricultural land, landfill leachate, fertilizers, pesticides, and manure application [5,6]. High levels of NO_3 in water bodies and drinking water create eutrophication, toxic algal blooms, and various diseases, including blue infant disorder (methemoglobinemia), thyroid disorders, teratogenesis, and mutagenesis [2,7,8]. Pregnant women, infants, and young children are most susceptible to the harmful effects of NO_3 [9].

The USEPA lists fluorine as a potentially harmful chemical pollutant [10,11]. Fluoride enters water bodies through natural and artificial sources, e.g., weathering of fluoride-bearing minerals, aluminum smelters, coal-based power stations, phosphatic fertilizer plants, brick manufacturing, steel production, coal combustion, sewerage, over-withdrawal of groundwater, and electroplating industries [12,13]. Drinking water with excessive fluoride can cause side effects including tooth decay (0.50 mg/L), fluorosis (1.50–5 mg/L), and skeletal fluorosis (5–40 mg/L) [14,15]. Arthritis, neurological problems, thyroid disease, cancer, infertility, hypertension, and a low fetus-to-sperm ratio are all

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linked to high fluoride concentrations (> 10 mg/L). Moreover, fluoride alters DNA structure, which impacts teeth and bones [14,16].

The groundwater in central Saudi Arabia has been subjected to intense study in the last two decades regarding water resources, groundwater quality for drinking and agricultural usage, and general hydrochemical evaluations ([e.g., 17–23]. Previous studies in the Northwest Riyadh area indicated that average concentrations of TDS, Ca^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, and F^- exceeded the WHO's permissible limits for drinking water. The evaluation of groundwater quality from Wasia and Biyadh aquifers in Wasia Well Field (Northeast Riyadh) concluded the suitability of Wasia samples for drinking and agricultural purposes but not for industrial ones. Conversely, water samples from Biyadh are unsuitable for drinking, industrial, or agricultural purposes. Furthermore, the groundwater quality in Wadi Nisah, south of Riyadh, is unsuitable for drinking. Previous studies concluded that extensive and repeated irrigation could increase ion levels in general. They attributed the higher NO_3^- and F^- values to the widespread application of fertilizers and pesticides in the study area. None of the studies on groundwater in central Saudi Arabia treated the impacts of nitrate and fluoride on human health. Therefore, we aimed to examine the distribution of NO_3^- and F^- in the groundwater of three areas in central Saudi Arabia and document the role of geology, aquifer depths, and agriculture activity on NO_3^- and F^- levels. Moreover, we sought to determine the impact of NO_3^- and F^- contamination on adults, children, and infants' health using a methodology suggested by the USEPA. The results of this investigation will benefit risk management, safeguarding groundwater quality, and health professionals' decision-making.

2. Geological Setting

The exposed sedimentary succession in central Saudi Arabia is represented mainly by Triassic–Cretaceous rocks and subdivided into the following formations from older to younger: Minjur, Marrat, Dhruma, Tuwaiq Mountain Limestone, Hanifa, Jubaila, Arab, Hith, Wasia, and Aruma formations. The Jurassic and Cretaceous rocks in central Saudi Arabia have been described from many points of view, such as stratigraphy, paleontology, sedimentology, and depositional history ([e.g., 24–38].

The major aquifer systems identified in the Wasia Well Field are Wasia (Middle Cretaceous) and Biyadh (Lower Cretaceous). Both Biyadh and Wasia have a primarily continental origin. The Biyadh aquifer has mainly cross-bedded quartzite and sandstone with some thin shale, marl, dolomite, and ironstone. The Wasia aquifer comprises medium- to coarse-grained, well-sorted, non-cemented, and poorly cemented rock. The Wadi Nisah area consists of sedimentary formations ranging from the Upper Triassic to the Quaternary period, with outcrops decreasing in age from west to east. Hydrogeologically, the study area consists of a multi-layered aquifer system with the Manjur, Biyadh, and Jurassic Limestone Formations, Cretaceous Wasia, and Quaternary alluvial deposits forming the main water supply sources.

3. Material and Methods

Groundwater samples were collected from 36 groundwater wells, mainly used for agricultural water supply in central Saudi Arabia: 12 from Wadi Nisah, 14 from the Al Jubailah area, and 10 from the Wasia Well Field (Figure 1). The Al Jubailah area is located 40–55 km northwest of Riyadh, at 24°53′14.4″ to 24°54′59.4″ N and 46°20′41.5″ to 46°25′47.2″ E in Wadi Hanifa, which runs south through Riyadh. The Wasia Well Field is located some 110 km northeast of Riyadh between latitudes 25°09′ and 25°14′N and longitudes 47°28′–47°33′ E. The samples were collected in pre-rinsed plastic bottles and filtered through 0.45-mm pore-size filters. Nitric acid was added to the samples for preservation, and the bottles were stored in cooling boxes at temperatures below 5 °C. F^- and NO_3^- levels were analyzed using standard analytical procedures in the laboratories of King Saud University.

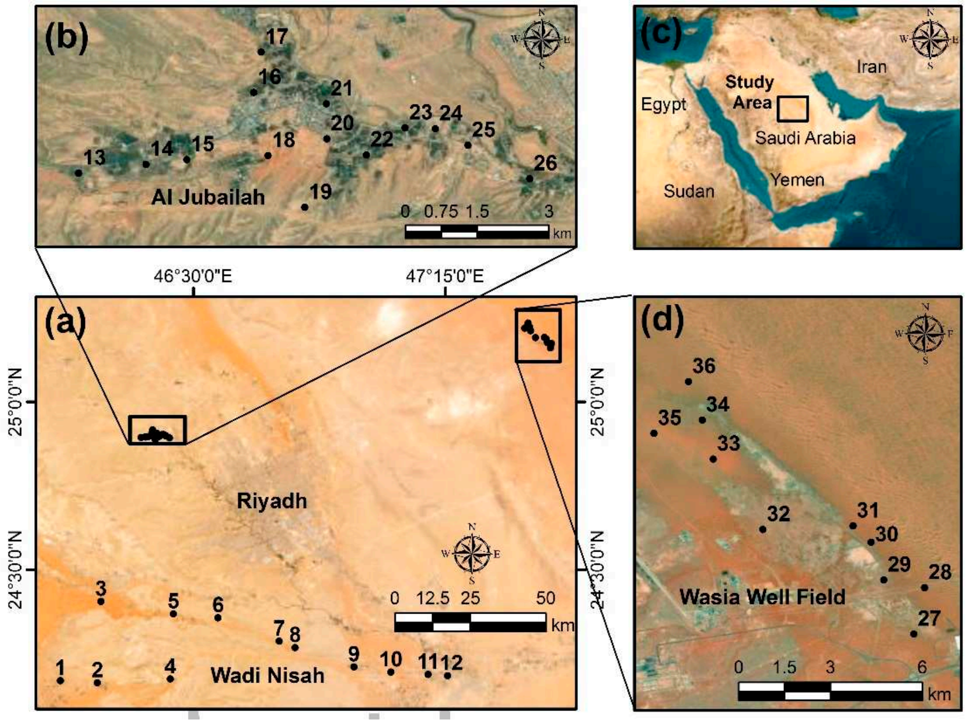

Figure 1. Locations of the groundwater samples in central Saudi Arabia. a. Wadi Nisah, b. Al Jubaillah, C. Location of study in Saudi Arabia, d. Wasia Well Field.

In this study, we assessed the danger that NO_3^- and F^- pose to human health for adults, children, and infants via the oral channel. The following equations calculate the daily water intake (CDI), hazard quotient (HQ), and non-carcinogenic hazard index (HI) associated with drinking water [39,40].

$$CDI = (C \times DI \times F \times ED)/(BW \times AT)$$

$$HQ = CDI/RfD$$

$$HI = \Sigma\ (HQfluoride + HQnitrate)$$

where C is the concentration of nitrate and fluoride in the water in milligrams per liter; DI is the amount of water consumed daily in liters; F is the number of days per year of exposure; ED is the number of years of exposure; BW is the weight of the age group under consideration in kilograms; AT is the average timing in days; and RfD is the reference dose (NO_3^- = 1.6 and F^- = 0.06 mg/kg/day) [41]. Table 1 describes the parameter values applied to health exposure assessment.

Table 1. Parameters applied for health exposure assessment through drinking water and hazard index classification of in this work.

Risk Exposure Factors	Unit	Adults	Children	Infants
DI	L/d	2	1.5	0.8
F	d/year	365	365	365
ED	years	40	10	1
BW	kg	70	20	10
AT	d	14,600	3650	365
HI ≤1	no health risk to humans			
HI >1	higher level of hazard			

4. Results and Discussion

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4.1. Concentration and Distribution of Nitrate and Flouride

The nitrate concentration in the study areas varied from 0.70 mg/L in borehole 33 (Wasia Well Field) to 47.0 mg/L in borehole 22 (Jubailah), with an average of 22.59 mg/L (Table 2). None of the 36 boreholes studied had nitrate levels exceeding WHO guidelines (50.0 mg/L). However, by comparing these three study areas, we noticed that the lowest nitrate levels were recorded in Wasia Well Field, averaging 2.79 mg/L. By contrast, the highest concentrations were recorded in Jubailah, averaging 37.93 mg/L. The Wadi Nisah levels fell in between, averaging 21 mg/L (Figure 2). Similarly, fluoride ranged from 0.63 mg/L in borehole 31 from Wasia Well Field to 2.00 mg/L in borehole 25 from Jubailah, averaging 1.23 mg/L. Eleven out of thirty-six fluoride samples (30.55%) exceeded the WHO's acceptable limit for drinking water (1.5 mg/L). The lowest nitrate levels were recorded in Wasia Well Field, averaging 0.82 mg/L, whereas the highest concentrations were recorded in Jubailah, averaging 1.70 mg/L. Wadi Nisah fell in between, averaging 1.00 mg/L (Figure 3).

The Al Jubailah area is a valley that consists primarily of palm farms alongside vegetables and fruits. The region's irrigation source is shallow groundwater (25–100 m) resulting from flood waters. This region's increased nitrate and fluoride concentrations may be due to intensive farming conditions and pollutants from heavy fertilizer use and sanitation. Some of these pollutants may also be due to the region's rocky origin. On the contrary, the Wasia Well Field region is quite far from agricultural areas, and the groundwater is deeper (180–300 m), which is fossil water to some extent. The rocks in the aquifer are fine sandstones. Therefore, nitrate and fluoride concentrations are the lowest in these study areas. The Wadi Nisah area is a valley that collects water from other valleys. The valley has many palm farms and renewable groundwater, which decreases nitrate and fluoride levels. Compared to the Wadi Al Jubailah area, the farming area in the Wasia Well Field is significantly lower.

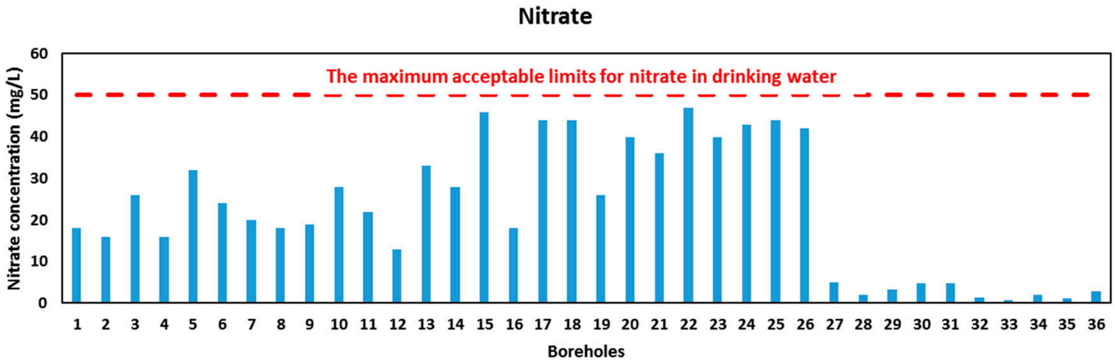

Figure 2. Distribution of nitrate concentrations (mg/L) in the groundwater of the study areas.

Table 2. Concentrations of nitrate and fluorite in the study areas.

S.N.	Lat.	Long.	Nitrates	Fluoride	S.N.	Lat.	Long.	Nitrates	Fluoride
1	24.16958	46.10469	18	0.92	21	24.90678	46.39139	36	1.3
2	24.16344	46.21425	16	0.86	22	24.89717	46.39886	47	1.8
3	24.40542	46.22508	26	0.86	23	24.90225	46.40614	40	1.5
4	24.17483	46.43194	16	1.1	24	24.90211	46.41181	43	1.7
5	24.36869	46.44094	32	1.32	25	24.899	46.41792	44	2
6	24.35672	46.57375	24	0.87	26	24.89272	46.42953	42	1.8
7	24.28703	46.75603	20	0.91	27	25.16055	47.5633	5.1	1.12
8	24.26814	46.80336	18	0.95	28	25.17417	47.56645	2.1	1.05
9	24.21053	46.97817	19	1.05	29	25.17642	47.55445	3.2	0.7
10	24.19528	47.08814	28	1.11	30	25.18752	47.55073	4.7	0.65
11	24.1885	47.19881	22	1.12	31	25.19228	47.54542	4.8	0.63
12	24.18442	47.25731	13	0.88	32	25.19123	47.51897	1.3	0.87

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13	24.89375	46.34486	33	1.5	33	25.21192	47.50437	0.7	0.76
14	24.89539	46.3575	28	2	34	25.2234	47.50117	2.1	0.88
15	24.89628	46.36517	46	1.7	35	25.2195	47.487	1.1	0.78
16	24.90889	46.37775	18	2	36	25.23465	47.49712	2.8	0.79
17	24.9165	46.37911	44	1.3		Min.		0.7	0.63
18	24.89706	46.38039	44	1.9		Max.		47	2
19	24.88733	46.38731	26	1.8		Aver.		22.59	1.23
20	24.90019	46.39144	40	1.5					

1–12 (Wadi Nisah); 13–26 (Jubailah); 27–36 (Wasia Well Field).

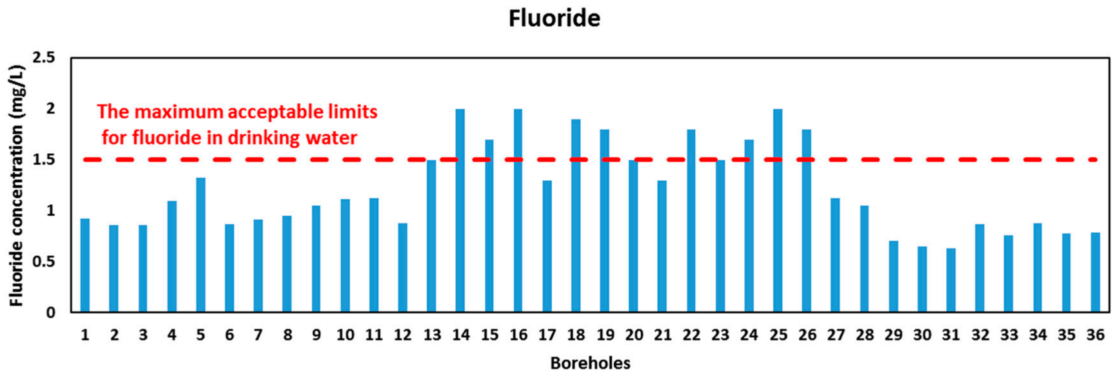

Figure 3. Distribution of fluoride concentrations (mg/L) in groundwater of the study areas.

4.2. Human Health Risk

Fluoride and nitrate are two of the most frequent and pervasive contaminants in many groundwater supplies, making water contamination a major environmental problem. Excessive nitrate levels in drinking water have been linked to various human health issues, including gastrointestinal cancers, methemoglobinemia, Alzheimer's disease, vascular dementia, and multiple sclerosis [42]. Furthermore, high and low fluoride doses in water can be dangerous [43]. Nitrate's chronic daily intake (CDI) values (mg/kg/d) for adults, children, and infants ranged from 0.020 to 1.343 (average of 0.646), 0.053 to 3.525 (average of 1.695), and 0.056 to 3.76 (average of 1.808), respectively. The CDI values for fluoride in adults, children, and infants varied from 0.018 to 0.057 (average of 0.035), 0.047 to 0.150 (average of 0.092), and 0.050 to 0.160 (average of 0.098), respectively (Table 3). The average HQ values of nitrate and fluoride for adults, children, and infants were 0.40 and 0.58; 1.06 and 1.53; and 1.13 and 1.64, respectively (Table 4).

Table 3. Chronic daily intake (CDI) (mg/kg/d) of nitrate and fluoride for adults, children, and infants.

S.N.	NO_3^-	CDI			F^-	CDI		
		Infants	Children	Adults		Infants	Children	Adults
1	18	1.44	1.35	0.514	0.92	0.074	0.069	0.026
2	16	1.28	1.2	0.457	0.86	0.069	0.065	0.025
3	26	2.08	1.95	0.743	0.86	0.069	0.065	0.025
4	16	1.28	1.2	0.457	1.1	0.088	0.083	0.031
5	32	2.56	2.4	0.914	1.32	0.106	0.099	0.038
6	24	1.92	1.8	0.686	0.87	0.07	0.065	0.025
7	20	1.6	1.5	0.571	0.91	0.073	0.068	0.026
8	18	1.44	1.35	0.514	0.95	0.076	0.071	0.027
9	19	1.52	1.43	0.543	1.05	0.084	0.079	0.03
10	28	2.24	2.1	0.8	1.11	0.089	0.083	0.032

11	22	1.76	1.65	0.629	1.12	0.09	0.084	0.032
12	13	1.04	0.98	0.371	0.88	0.07	0.066	0.025
13	33	2.64	2.48	0.943	1.5	0.12	0.113	0.043
14	28	2.24	2.1	0.8	2	0.16	0.15	0.057
15	46	3.68	3.45	1.314	1.7	0.136	0.128	0.049
16	18	1.44	1.35	0.514	2	0.16	0.15	0.057
17	44	3.52	3.3	1.257	1.3	0.104	0.098	0.037
18	44	3.52	3.3	1.257	1.9	0.152	0.143	0.054
19	26	2.08	1.95	0.743	1.8	0.144	0.135	0.051
20	40	3.2	3	1.143	1.5	0.12	0.113	0.043
21	36	2.88	2.7	1.029	1.3	0.104	0.098	0.037
22	47	3.76	3.53	1.343	1.8	0.144	0.135	0.051
23	40	3.2	3	1.143	1.5	0.12	0.113	0.043
24	43	3.44	3.23	1.229	1.7	0.136	0.128	0.049
25	44	3.52	3.3	1.257	2	0.16	0.15	0.057
26	42	3.36	3.15	1.2	1.8	0.144	0.135	0.051
27	5.1	0.408	0.38	0.146	1.12	0.09	0.084	0.032
28	2.1	0.168	0.16	0.06	1.05	0.084	0.079	0.03
29	3.2	0.256	0.24	0.091	0.7	0.056	0.053	0.02
30	4.7	0.376	0.35	0.134	0.65	0.052	0.049	0.019
31	4.8	0.384	0.36	0.137	0.63	0.05	0.047	0.018
32	1.3	0.104	0.1	0.037	0.87	0.07	0.065	0.025
33	0.7	0.056	0.05	0.02	0.76	0.061	0.057	0.022
34	2.1	0.168	0.16	0.06	0.88	0.07	0.066	0.025
35	1.1	0.088	0.08	0.031	0.78	0.062	0.059	0.022
36	2.8	0.224	0.21	0.08	0.79	0.063	0.059	0.023

Table 4. The Hazard Quotient (HQ) and Hazard Index (HI) for fluoride and nitrate in adults, children, and infants.

S.N.	HQ Nitrates			HQ Fluoride			HI		
	Infants	Children	Adults	Infants	Children	Adults	Infants	Children	Adults
1	0.9	0.844	0.321	1.227	1.15	0.438	2.127	1.994	0.76
2	0.8	0.75	0.286	1.147	1.075	0.41	1.947	1.825	0.695
3	1.3	1.219	0.464	1.147	1.075	0.41	2.447	2.294	0.874
4	0.8	0.75	0.286	1.467	1.375	0.524	2.267	2.125	0.81
5	1.6	1.5	0.571	1.76	1.65	0.629	3.36	3.15	1.2
6	1.2	1.125	0.429	1.16	1.088	0.414	2.36	2.213	0.843
7	1	0.938	0.357	1.213	1.138	0.433	2.213	2.075	0.79
8	0.9	0.844	0.321	1.267	1.188	0.452	2.167	2.031	0.774
9	0.95	0.891	0.339	1.4	1.313	0.5	2.35	2.203	0.839
10	1.4	1.313	0.5	1.48	1.388	0.529	2.88	2.7	1.029
11	1.1	1.031	0.393	1.493	1.4	0.533	2.593	2.431	0.926
12	0.65	0.609	0.232	1.173	1.1	0.419	1.823	1.709	0.651
13	1.65	1.547	0.589	2	1.875	0.714	3.65	3.422	1.304
14	1.4	1.313	0.5	2.667	2.5	0.952	4.067	3.813	1.452
15	2.3	2.156	0.821	2.267	2.125	0.81	4.567	4.281	1.631
16	0.9	0.844	0.321	2.667	2.5	0.952	3.567	3.344	1.274
17	2.2	2.063	0.786	1.733	1.625	0.619	3.933	3.688	1.405
18	2.2	2.063	0.786	2.533	2.375	0.905	4.733	4.438	1.69
19	1.3	1.219	0.464	2.4	2.25	0.857	3.7	3.469	1.321
20	2	1.875	0.714	2	1.875	0.714	4	3.75	1.429

21	1.8	1.688	0.643	1.733	1.625	0.619	3.533	3.313	1.262
22	2.35	2.203	0.839	2.4	2.25	0.857	4.75	4.453	1.696
23	2	1.875	0.714	2	1.875	0.714	4	3.75	1.429
24	2.15	2.016	0.768	2.267	2.125	0.81	4.417	4.141	1.577
25	2.2	2.063	0.786	2.667	2.5	0.952	4.867	4.563	1.738
26	2.1	1.969	0.75	2.4	2.25	0.857	4.5	4.219	1.607
27	0.255	0.239	0.091	1.493	1.4	0.533	1.748	1.639	0.624
28	0.105	0.098	0.038	1.4	1.313	0.5	1.505	1.411	0.538
29	0.16	0.15	0.057	0.933	0.875	0.333	1.093	1.025	0.39
30	0.235	0.22	0.084	0.867	0.813	0.31	1.102	1.033	0.393
31	0.24	0.225	0.086	0.84	0.788	0.3	1.08	1.013	0.386
32	0.065	0.061	0.023	1.16	1.088	0.414	1.225	1.148	0.438
33	0.035	0.033	0.013	1.013	0.95	0.362	1.048	0.983	0.374
34	0.105	0.098	0.038	1.173	1.1	0.419	1.278	1.198	0.457
35	0.055	0.052	0.02	1.04	0.975	0.371	1.095	1.027	0.391
36	0.14	0.131	0.05	1.053	0.988	0.376	1.193	1.119	0.426

The hazard index (HI) ranged from 0.37 to 1.74 (average of 0.99) for adults, 0.98 to 4.56 (average of 2.59) for children, and 1.05 to 4.87 (average of 2.77) for infants (Table 4, Figure 4). Groundwater samples surpassed the safety level of 1 by 44.44 (16 out of 36), 97.22 (35 out of 36), and 100% for adults, children, and infants, respectively (Figure 4). According to the study's findings, drinking water in most of the study areas, particularly in water samples from Jubailah (boreholes 13–26) and a few from Wadi Nisah (boreholes 5 and 10), could expose infants, children, and adults to non-cancer health concerns. Additionally, our findings show that infants and children are more vulnerable to non-carcinogenic health risks than adults, possibly due to their lower body weights. Many researchers worldwide obtained similar results assessing health risks caused by nitrate and fluoride in groundwater, e.g., in Northwest China [44] (Chen et al., 2016); Western Khorasan Razavi, Iran [45] (Qasemi et al., 2019); Medchal area, South India [11] (Duvva et al., 2022); and Noyyal basin, India [2] (Kom et al., 2022).

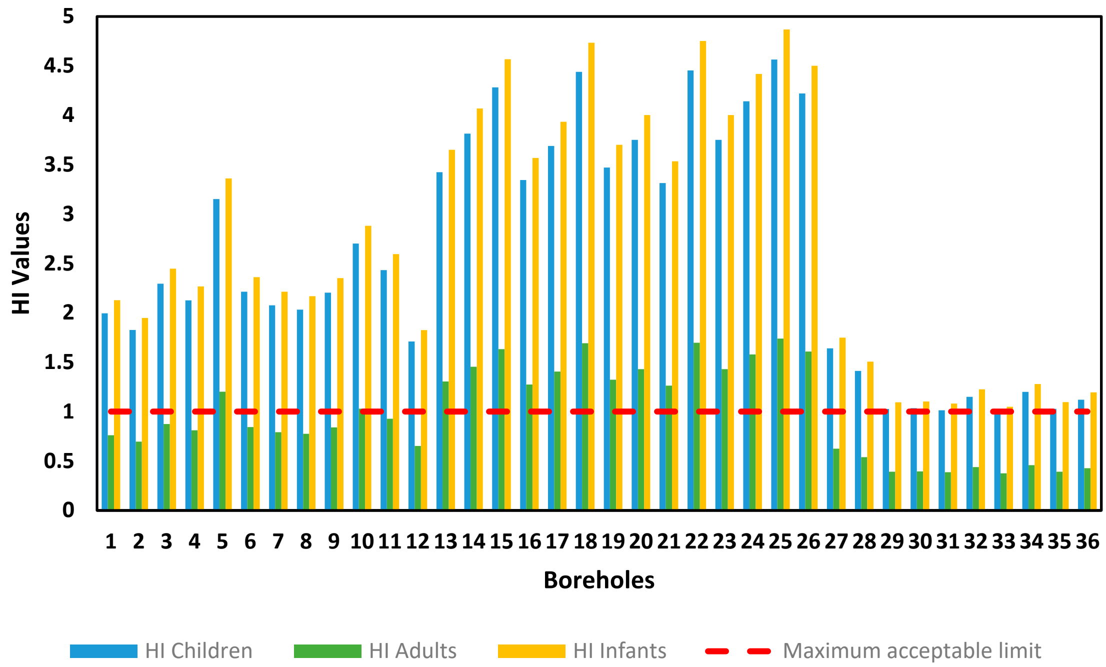

Figure 4. Non-carcinogenic risks induced by fluoride and nitrate in drinking water.

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5. Conclusions

We evaluated the health effects of nitrate and fluoride in central Saudi Arabia. Our findings indicated that none of the 36 studied boreholes had nitrate levels above WHO guidelines (50.00 mg/L). By contrast, 11 out of 36 areas had fluoride levels exceeding the acceptable limit for drinking water (1.5 mg/L). The lowest nitrate and fluoride levels were recorded in the Wasia Well Field area, whereas the highest concentrations were recorded in the Jubailah area. The increased nitrate and fluoride concentrations in Jubailah may be attributed to intensive palm farms and the region's heavy use of fertilizers and sanitation. The water samples had HI values exceeding the safety level for adults, children, and infants at 44.44, 97.22, and 100%, respectively. Infants and children are more vulnerable to non-carcinogenic health risks than adults due to their lower body weight.

Author Contributions: Conceptualization, T.A. and A.S.E.-S.; methodology, T.A. and A.S.E.-S.; software, T.A. and A.S.E.-S.; writing—original draft preparation, T.A. and A.S.E.-S.; writing—review and editing, T.A. and A.S.E.-S. All authors have read and agreed to the published version of the manuscript.

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