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A survey on fluoride, nitrate, iron, manganese and total hardness in drinking water of Fereidonkenar, Northern Iran during 2008-2013

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Original Article

Abstract
The purpose of present study was to evaluate fluoride, nitrate, iron, manganese and total hardness in drinking water of wells and reservoirs in Fereidonkenar, Mazandaran, Northern Iran and compare the results with national and international standards. This cross-sectional descriptive study was carried out on data during five years from the spring of 2008 until the autumn of 2013. Studies were performed on 430 samples in the different seasons and years taken from water and wastewater company (WWC). The results showed that the average fluoride, nitrate, iron, manganese, total hardness concentrations obtained were 0.42, 10.2, 0.136, 0.03, 382.28 mg/l, respectively. The analysis showed a negative correlation between nitrate and fluoride, iron and manganese and a positive correlation with the hardness. The mean fluoride concentration was less than the standard. Total hardness value was more than recommend standard. Nitrate was below 50 mg/l, in accordance with national and international standards. The amount of iron and manganese in drinking water were acceptable. So, except for low fluoride and high total hardness, there was no any problem in other investigated parameters.

KEYWORDS: Drinking water, Fluoride, Nitrates, Iron, Manganese, Hardness

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Introduction

Water is one of the most vital substances on the earth. The World Health Organization (WHO) declared lack of access to safe drinking water for all is the most important shortage in 20th century. Regardless of its value, its indiscriminate use in various fields continues. This trend causes this resource to be contaminated. The severity of the contamination depends on water management and operation.[1] With rapid population growth and social development in urban and agricultural sections, other needs such as consumption of water sources, energy, industrial production are increasing day by day. On the other hand, contamination of water resources is increasing. In addition to microbial contamination, chemical pollution of water is one of the most important issues in health care debate.[2] Drinking water based on WHO definition, is a water suitable for human

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consumption and domestic use from physical, chemical, bacteriological and radiological aspects.[3] WHO guidelines for drinking water quality was first published in 1984 and 1985, and was revised in 1988. The latest version of the revisions was published in 2003. In Iran, the physical-chemical standards for drinking water was published in 1967 for the first time.[4]

Fluoride is one of the 14 essential elements in animal life, and an important element in the composition of teeth and bones, and drinking water is its most important source in human.[1] Fluoride could cause dental decay and fluorosis lower or higher than the recommended standard amount. Therefore, in each fluoridation program for drinking water based on WHO guideline, some probable disadvantages (fluorosis dental, skeletal, immune system toxicity, genetic toxicity, teratogenicity, nephrotoxicity and gastrointestinal toxicity) must be considered. There is no relation between fluoridation of water and cancer.[5] Fertilizers including nitrogen in agriculture are the main sources of nitrate pollution. Prolonged exposure to high levels of nitrate could cause infertility and bladder cancer. Also the high level of nitric acid increases the acidity of water and drinking water in the distribution system that can increase the corrosive materials.[6-7] Hard water can make some problems in washing soap, hot water pipes, radiators, boilers and other heating units.[8] In 2013, a significant correlation between fluoride in drinking water and the incidence of atherosclerosis and heart disease was found. Yang et al.[9] showed there was no significant association between nitrate in drinking water and colon cancer.

Another study carried out by Alvarez-Bastida et al.[10] in 2013, showed that the average concentration of nitrate in most cases was less than 50 mg/l.[11]

A study done by Tayebi and Sobhanardakani showed that the river Gamasiyab has assimilative capacity, but without monitoring river pollutants, serious problems may occur in future, especially eutrophication.[12] Although iron and manganese do not cause any health problem, high levels of iron and manganese in water could be problematic for consumers.[5,10] Thus, based on the role of water quality in the health of residents as well as the need for continual measurement of various parameters, the aim of this study was to evaluate water quality (fluoride, nitrate, iron, manganese, total hardness) and to compare them with national and WHO standards.

Materials and Methods

This study was a cross-sectional study to evaluate the chemical quality of drinking water including fluoride, nitrate, iron, magnesium, total hardness in Fereidoonkenar, Mazandaran, Northern Iran. Fereidoonkenar is a coastal city about 2300 meters above the sea level. Water resources in Fereidonkenar are wells and ground water. All the information was available in Water and Wastewater Company. In general, changes were evaluated on 430 samples taken seasonally in 5 years during 2008-2013. All samples were analyzed using "standard methods for the examination of water and wastewater, 21st edition eBook".[13] Statistical analysis in this study included descriptive statistics, multiple comparisons between parameters, and Pearson correlation coefficient. Statistical software applied in this study, was GraphPad Prism version 5.0.

Results and Discussion

Fluoride

The results showed that the average concentration of fluoride was 0.416 mg/l in the study period with a standard deviation of 0.035 and a minimum of 0.36 and a maximum of 0.48 mg/l (Table 1).

Table 1. The results of chemical analysis of drinking water in Fereydonkenar city during 2008-2013

	Group	Number of Wells	Mean	Standard Deviation	Standard Error of Mean	Median	Minimum	Maximum	95% Confidence Interval		National standard	WHO standard
									From	to		
Total Analysis	Fe	10	0.136	0.0892	0.0282	0.100	0.052	0.29	0.05	0.29	0.3	0.1
	MN	10	0.030	0.0357	0.0113	0.013	0	0.11	0	0.12	0.4	0.3
	TH	10	382.280	38.8090	12.2730	401.500	303.000	419.76	303.00	419.76	500.0	100
	F	10	0.416	0.0353	0.0112	0.410	0.360	0.48	0.36	0.48	1.5	1.5
	NO_3	10	10.199	3.4520	1.0920	10.445	6.080	17.42	7.73	12.67	50.0	50.0

WHO: World Health Organization; Fe: Iron; Mn: Manganese; NO_3: Nitric oxide; TH: Total hardness; F: Fluoride

Results showed that the highest amount of fluoride was in spring (1.39 mg/l) and the lowest was in winter (0.19 mg/l) in wells No. 2 and No. 5, respectively (Figure 1).

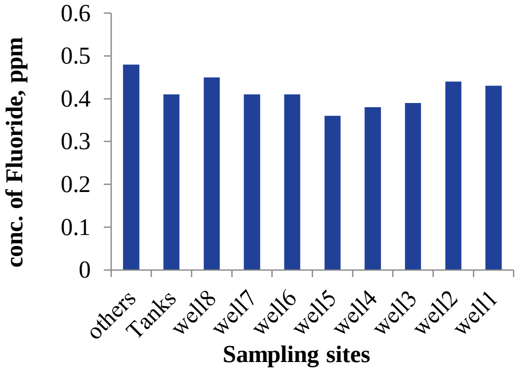

Figure 1. The average of fluoride (mg/l) in well, Tanks and others 2008-2013

In other cases, the amount of fluoride was less than optimal fluoride concentration in warm and cold months. In 334 samples, the fluoride content was less than 0.5 mg/l that was lower than the national standard. There was an increase in the average concentration of (Figure 2). There is a direct correlation between air temperature and water consumption per capita in the warm months. In the other words, drinking water consumption increases in warm months. According to the Iranian standard, the concentration of fluoride is 0.7 mg/l in the warm months, and 1.2 mg/l in the cold months.[14]

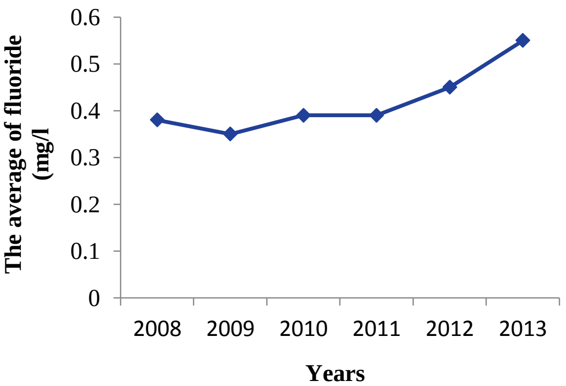

Figure 2. The average of fluoride (mg/l) by year 2008-2013

The level of water fluoride is displayed in figure 3, based on seasonal variation with the lowest levels in summer and in winter. The results of chemical analysis of drinking water are displayed in table 1. Studies done in Shahroud, Iran, showed that the fluoride concentration was between 0.45 to 0.75 mg/l.[15] Fluoride concentration in our study was low and fluoride should be supplemented by other means such as mouth washes, and consumption of fluoride containing foods and water fluoridation are recommended to reduce development of caries. Our results are in line with the reports from Hamadan[16] and Babol[17] that showed the fluoride content was lower than standard in 49% of samples. Mean concentration of fluoride in Ilam water treatment plant was 0.38 mg/l which was lower than WHO and Iran drinking water standard range.[18]

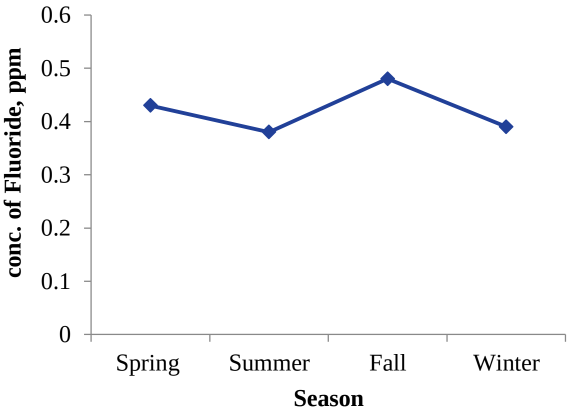

Figure 3. The average concentration of fluoride by season 2008-2013

Nitrate

The mean nitrate concentration in the studied areas was 10.199 mg/l with a standard deviation of 3.452 mg/l. Also data showed that the highest and lowest nitrate concentration were 17.42 (well No. 5) and 6.08 mg/l, respectively. In general, according to the formula proposed by the WHO ($\frac{No_3^-}{50} + \frac{No_2^-}{3} \leq 1$), the total ratio of the measured values was less than the WHO standard recommendation.4 Concentration of nitrate in well No. 5 located in Darvish Kheil was higher than other sampling sites (Figure 4).

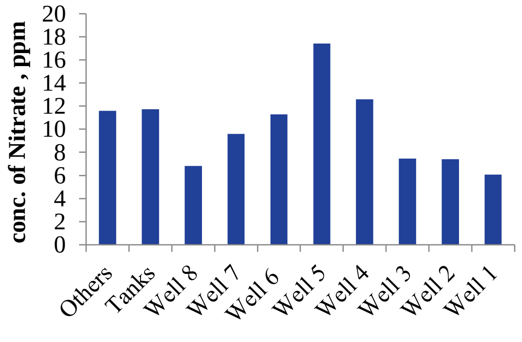

Figure 4. The average of Nitrate (mg/l) in well, Tanks and others 2008-2013

On the other hand, all the nitrate concentrations were less than 50 mg/l. It looks like raw sewage disposal of urban and rural areas was the main source of nitrate ions in municipal water supplies. As figure 5 shows, the concentration of nitrate during these years remained the same.

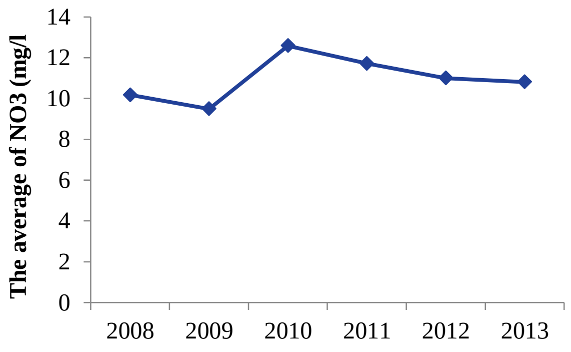

Figure 5. The average of Nitrate (mg/l) by year 2008-2013

The average concentration of nitrate by season is displayed in figure 6. The drinking water resource in this area is underground water and is still the only practical way. Water treatment plant for nitrate removal usually is the suitable way to prevent nitrate problems.[11,19] The average concentration of nitrate in distribution network in Minab was 14.6 ± 7.8 mg/l that was lower than the WHO and the Environmental Protection Agency (EPA) standard amount.[20] In the study done by Ziarati et al. in Gilan and Mazandaran provinces, the average nitrate in most samples were lower than standard amounts (≤ 50 mg/l).[21] The amount of nitrate in Talesh was higher than maximum level 0.01 mg/l and 50 mg/l (29) and the most of the examined samples in Talesh were polluted.[18] The nitrate concentration of examined regions in Ilam was 6.02 mg/l[22] that was lower than Iran[23] and WHO[13] standard which is 500 mg/l and 250 mg/l.

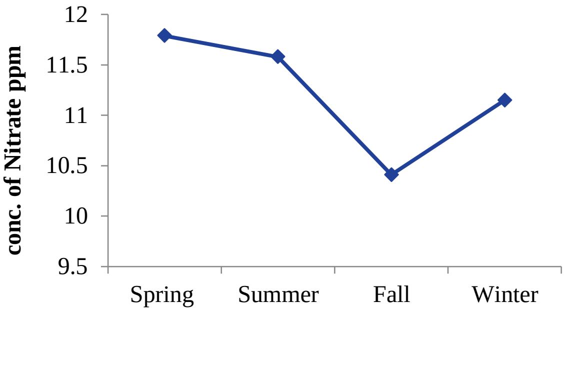

Figure 6. The average concentration of Nitrate by season 2008-2013

Iron

The results indicated that the average iron in the studied areas was 0.1361 mg/l with a standard deviation of 0.089. Therefore, according to figure 7, the concentration of this metal was lower than existing standards.

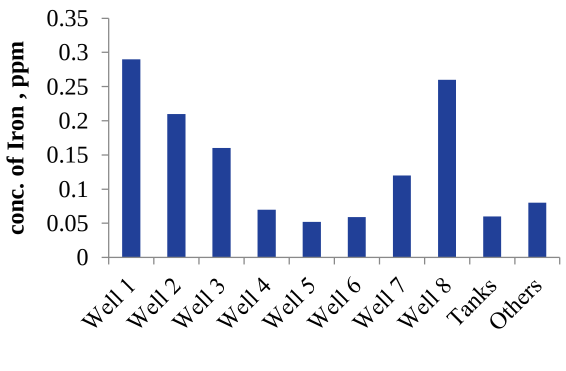

Figure 7. The average of Iron (mg/l) in well, Tanks and others 2008-2013

The average concentration of iron is displayed in figure 8. As this figure shows, minimum iron concentration was in 2012. Seasonal change in iron level in water samples is displayed in figure 9, showing the iron level to be the lowest in fall. Use of fertilizers in agricultural fields and drainage of the most of the leachate into the groundwater can be a reason of this increase. In a study carried out in Qom, Iran, the average concentration of iron in groundwater, reservoirs, and distribution networks was 0.09, 0.07, and 0.07 mg/l, respectively. This study is in line with our results that showed the amount of iron was within limits of EPA[24] and national standards[25] guideline.

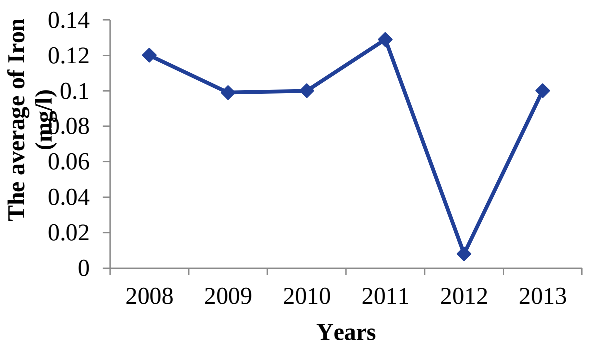

Figure 8. The average of Iron (mg/l) by year 2008-2013

In Birjand and Ghaen, Iran, the average levels of iron and manganese were 0.04 and 0.02 mg/l, respectively.[26] So, the amount of this cation was safe in drinking water in Fereidonkenar as well as Qom,[24] Birjand and Ghaen,[26] Ardebil,[27] Ilam (0.07 mg/l), and Shush and Andimeshk in Khuzestan,[28] Iran. In all of these studies, the average of Fe^{2+} concentration was lower than WHO[13] and Iranian[23] standard (0.3 mg/l for iron).

Manganese

Based on the results, the average amount of manganese was 0.0301 mg/l and in 91% of the samples, the average amount of manganese was very low and in 8%, it was less than the maximum amount of 1.0 mg/l that is desirable. The mean concentration of manganese is displayed in figure 10.

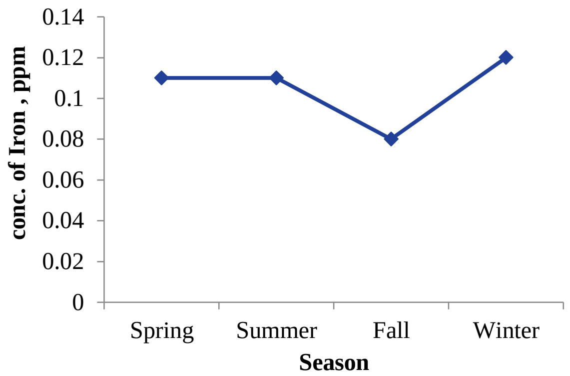

Figure 9. The average concentration of Iron by season 2008-2013

High levels of manganese were obtained from well No. 8 (Figure 10). Besides, as the figure 11 shows, the concentration of manganese in 2008 was significantly higher than the other years. Seasonal manganese level in water samples is displayed in figure 12, showing the highest amount of manganese in spring. The use of fertilizers containing manganese sulfate, that is usual in the rice farming, and the drainage of most of the leachate to the groundwater can be a reason for this increase. These results showed that the amount of manganese was suitable and lower than standard for drinking. Also in another study carried out in Birjand and Ilam, the amount of manganese was reported 0.02 and 0.01 mg/l, respectively[22] that was lower than WHO[13] and Iran[23] drinking water standards which is 0.05 mg/l for manganese.

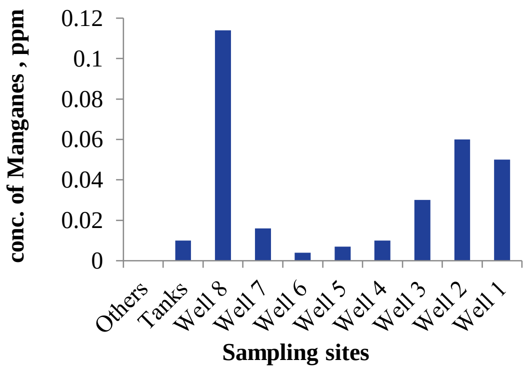

Figure 10. The average of Manganes (mg/l) in well, Tanks and others 2008-2013

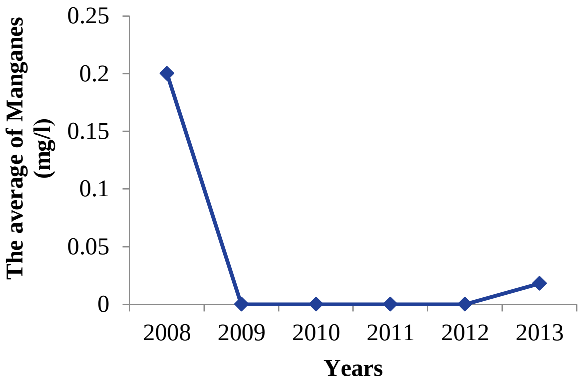

Figure 11. The average of Manganes (mg/l) by year 2008-2013

The average amount of manganese in groundwater, reservoirs, and distribution networks was 0.15, 0.09, and 0.1 mg/l, respectively which was higher than the EPA.[24]

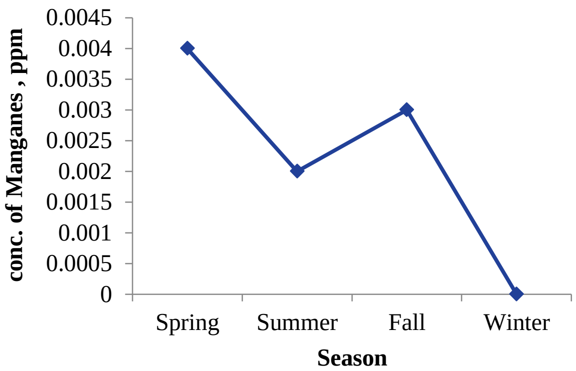

Figure 12. The average concentration of Manganes by season 2008-2013

Total Hardness

Mean, minimum, maximum and standard deviation for hardness in this region were 382.28, 303, 419.76 and 38.809 mg/l, respectively (Figure 13). Ninety-eight percent of water samples were very hard and 2% were hard (Figure 13). WHO reports show any health effects-based guideline value for water hardness, but hardness more than 200 milligrams per liter, can cause scaling in the distribution system and the excessive use of soap and, on the other hand water with a hardness of less than 10 milligrams per liter for the pipes are corrosive.[15] As the figure 14 shows, the total hardness in 2013 was the highest. The hardness of water was also higher in spring and fall (Figure 15).

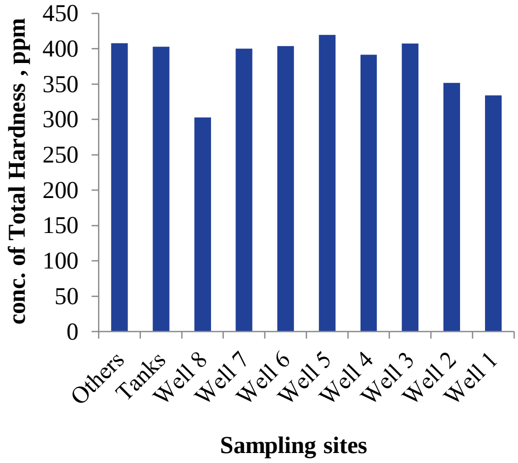

Figure 13. The average of Total Hardness (mg/l) in well, Tanks and others 2008-2013

Fluctuation in the amount of rain and leachate drainage from farming or agricultural fields and using wells water for gardening and farming can affect the total hardness of groundwater. Our result was similar to previous results in Rey which showed medium concentration of total hardness was 375 mg/l.[29] On the other hand, water hardness can decrease cardiovascular diseases (CVD). Mg and Ca in hard water can protect from CVD mortality.[30-32]

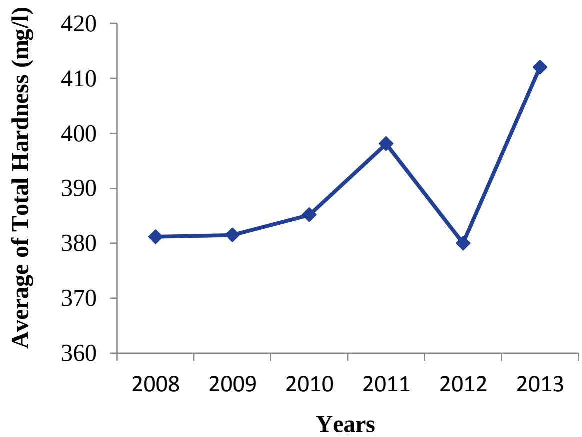

Figure 14. The average of Total Hardness (mg/l) by year 2008-2013

Table 2. Stataistical data for different parameters from 2008-2013

Group	Number of point sampling	Mean	Standard Deviation	Standard Error of Mean	Median	Minimum	Maximum	95% Confidence Interval	
								From	From
Total Analysis									
Fe	10	0.1361	0.0892	0.0282	0.100	0.052	0.290	0.052	0.290
MN	10	0.0301	0.0357	0.0113	0.013	0	0.114	0	0.114
TH	10	382.2800	38.8090	12.2730	401.500	303.000	419.760	303.0000	419.760
F	10	0.4160	0.0353	0.0112	0.410	0.360	0.480	0.360	0.480
NO_3	10	10.1990	3.4520	1.0920	10.445	6.080	17.420	7.7300	12.668
Annual									
NO3	10	10.9600	1.0950	0.4471	10.905	9.490	12.580	9.8110	12.109
F	10	0.4183	0.0722	0.0295	0.390	0.350	0.550	0.3425	0.494
TH	10	389.6600	12.8240	5.2350	383.340	380.000	412.000	376.1900	403.120
Fe	10	0.0927	0.04332	0.0177	0.100	0.008	0.129	0.0472	0.138
MN		0.0363	0.08050	0.0329	0	0	0.200	-0.0482	0.121
Seasonal									
Fe	10	0.1050	0.0173	0.0087	0.110	0.080	0.120	0.0774	0.133
MN	10	0.0022	0.0017	0.0008	0.002	0	-0.004	0.0005	0.005
TH	10	394.7500	6.6520	3.3260	394.500	389.000	401.000	384.1700	405.330
NO_3	10	11.2330	0.6096	0.3048	11.365	10.410	11.790	10.2630	12.202

Fe: Iron; Mn: Manganese; NO_3: Nitric oxide; TH: Total hardness; F: Fluoride

In the study carried out by Momeni et al., as the calcium content in water increased, rate of CVD decreased.[30] On the other hand, there was no relation between urinary calculi and the amount of calcium, bicarbonate, or the total hardness in drinking water. This is leachate drainage good result in different area of Iran with hard and very hard water.[33]

The correlation coefficient parameters

Table 2 shows the data for different parameters from 2008-2013. The analysis showed a negative correlation between nitrate, fluoride, iron and manganese and a positive correlation with the hardness. There was also a positive correlation between manganese and fluoride and total hardness.

As table 3 indicates, P-value between the paired parameters of means is less than the 0.05, stating that we can “reject the null hypothesis” and the difference is “statistically significant”. As shown in table 3, the difference between means of Mn and TH was statistically significant. Also the difference between means of Fe with Mn, TH and NO_3 was statistically significant, but was not significant with Fluoride. Also, the difference between means of NO_3 with Mn, TH and Fe was statistically significant, but is not significant with Fluoride. The table shows there was not any significant difference between fluoride and other parameters.

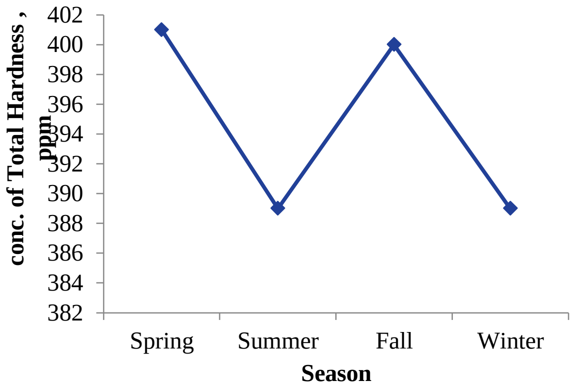

Figure 15. The average concentration of Total Hardness by season 2008-2013

Table 3. Compare of P Value between parameters mean

	Mn	TH	F	NO_3	Fe
Mn		0.0001	0.2797	0.0299	0.0018
TH	0.0001		0.1611	0.0213	0.0006
F	0.2797	0.1611		0.1150	0.2220
NO_3	0.0299	0.0213	0.1150		0.0018
Fe	0.0018	0.0006	0.2220	0.0018	

Fe: Iron; Mn: Manganese; NO_3: Nitric oxide; TH: Total hardness; F: Fluoride

Conclusion

The results showed that fluoride concentrations in most samples were less than the recommended ranges by WHO and Iranian national standards so it is recommend the risk of complications with teeth and bones and filled teeth index (DMFT) in the area should be consider. Our results showed that nitrate concentration was acceptable in all water wells based on WHO standards for drinking water; nitrate concentrations above standard range can cause health problems such as methemogolobinema.[34] Based on analysis of the water, 98% of the drinking water resources in Fereidonkenar was very hard and only 2% was hard indicating a poor quality. The results of studies in Ilam,[35] rural areas of Mazandaran province,[36] Gonbad-e Qabus,[37] Gachsaran,[38] and Amol[39], Iran, was similar to this research in terms of total hardness, fluoride and nitrate. The amount of iron and manganese was within permissible limits of national standards and EPA guidelines. Iron and manganese can cause unfavorable change in color and taste of water. Fereidonkenar drinking water does not have any problem in terms of iron and manganese and their concentration was below the standard level. Analysis showed negative correlation between nitrate and fluoride, iron and manganese and there is a positive correlation with the total hardness. P-value between the paired parameters was less than 0.05, showing that we can "reject the null hypothesis" and the difference was "statistically significant". Therefore, the results of different parameters in this survey showed that the continuous monitoring of the quality of the groundwater area is essential.

Conflict of Interests

Authors have no conflict of interests.

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