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Chromium, Nickel and Manganese in the Groundwater Resources of Asadabad Plain, Iran

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Background & Aims of the Study: Heavy metals are one of the most important environmental pollutants which agricultural and industrial activities and urban development increased their entry rate to the underground resources. This study aimed to investigate the concentration of chromium, nickel and manganese in groundwater resources in Asadabad plain.

Materials & Methods: Sampling of groundwater done in 2015 autumn. In this study, according to the Cochran's sample size formula, tote formula, totally 60 samples of groundwater of Asadabad plain were collected from 20 wells and after preparation stage with atomic device, elements concentration of samples is read. To analysis of data SPSS 19 with significant level of 0.50 is used.

Results: The concentration average of Chromium, Nickel and Manganese equal to 0.044¬ ±0.016, 70.42±10.83 and 2.64±0.83 ppb. The comparison results of the concentration average of elements based on WHO and ISIRI standard shows the concentration average of elements is lower than standard level.

Conclusions: Currently the groundwater resources of Asadabad plain are not polluted with heavy metals, but long-term excessive use of agricultural inputs and construction of polluting industries can cause a threat to groundwater resources in this area.

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Background

By rapid growth of population and development of societies, in addition to urban and agricultural water needs, other needs such as industry and power generation are increasing everyday (1). Water is vital for life and is the most important natural resources in the world. All living organisms, such as plants, animals and humans are depended on it and live in a place where water may exist (2). On the other hand, the contamination of water resources is expanding today. In addition to microbial contamination, chemical contamination of water is also one of the important issues which was discussed in the meantime and heavy metals have particular importance (1). Ground water contamination by pollutants such as heavy metals like chromium, nickel and manganese reduce the quality of this resource and make it unusable in some areas (3). Heavy metal pollution of water resources is due to agricultural activities, industrial and urban development in the last decade and has been one of the serious environmental problems (4). Studies on the crops that are irrigated with contaminated water showed heavy metals of contaminated water build up in these crops and through this enter in human food chain (3). The most fundamental question in relation to heavy metals is their metabolism in the body. In fact, heavy metal after entering the body, have not excreted from the body but accumulate in tissues such as fat, muscles, bones and joints.

This can result in a number of diseases and conditions in the body. Heavy metals as well as other alternatives salts and minerals are needed for body. For example, if zinc is deficient in food, cadmium will replaced. The accumulative property of heavy metals in plants and entering the food chain increases the risks of them (5). According to the dangers of heavy metal, the measurement of these metals in water resources should permanently be taken for monitoring of their concentration. Stability of metal ions in the environment creates many problems. Metals such as organic pollutants cannot be decomposed by chemical or biological method in nature (6-8). In fact, these metals at high concentrations, because of their tendency to accumulation, showed toxic effects with biological and bio-magnification consequences in the food chain (9). The research results on water resources in the plain of Ali Abad Katool showed a significant difference between the concentrations of heavy metals in samples and national and international standards (10). Piri in a research (2010), had been measured the concentration of nickel, aluminum, copper and manganese which were found in the water supplies of the Zabol city of Iran. It indicated the concentrations of elements- except for Ni- measured at all stations were less than standard (11). In another study, to determine the concentration of manganese in groundwater of Scotland, results showed that in 30 percent of sites, manganese concentration in groundwater was above the limit which is set by the World Health Organization (12).

Assuming the development of agriculture in the study area, over use of agricultural inputs by farmers and the lack of monitoring of groundwater resources in the Asadabad plain, may results in accumulation of heavy metals in groundwater resources and damaging effects on the health of residents.

Aims of the study:

This study aimed to investigate the concentration of chromium, nickel and manganese in groundwater resources in Asadabad plain of Hamedan, Iran.

Materials & Methods

Research area: Asadabad plain with an area of 962 square km in catchment area of upper Karkhe. Asadabad city is between 37:34- 34:50 north latitude and 9:47- 51:47 East meridian of Greenwich, its political position is in western Iran and the northern margin of the eastern Asadabad plain and its height from sea level is 1650 meters. Plain limited area is 295 square kilometers. Highest point of the watershed is Almoblagh Mountain with higher than 2,900 meters and the lowest point is the departure station near the village of Khosroo-Abad with the height of 1400 meters. The maximum area of the basin is at altitude of 1500 to 1700 meters and the slope of plains is of North East to the South West. Drinking water for residents of Asadabad city supplied through 1398 wells, 323 springs and 41 aqueduct of groundwater aquifers in Asadabad plain (13).

Sampling Method: In this study, to evaluate heavy metal pollution of water resources in Asadabad plain, after conducting preliminary field studies and taking into consideration uniform dispersion stations in parts of the plain that the wells dug, using the equation N=Z2S2/D2 (14), 20 wells for drinking and agriculture selected after recording the geographical coordinates of the Global Positioning System device (GPS) samples. Sampling of wells performed in autumn 2015 with half-liter polyethylene containers that were already washed in the laboratory by nitric acid, and sampling method of water resources was in accordance with the standard instructions (15). Also we waited a few minutes before sampling to ensure that the water is pumped directly from the water resources (16). Afterward, in order to avoid exposure to sunlight, samples were placed in a suitable container at low temperature until transportation to the laboratory. In the laboratory, to stabilize and preventing sedimentation of elements in the sample solution, by adding concentrated nitric acid, pH samples reduced to 2 (17). To analyze the samples for measuring the concentration of the studied heavy metals, 1ml of concentrated nitric acid added to 25 ml of water and heated for 10 minutes at 50 ° C under the vacuum hood. Then, the samples shook for 10 minutes at moderate speed (85 rpm) and after passing through the Wattman filter (42) concentration of heavy metals like chromium, Nickel and manganese read by ICP in the laboratory (ICP-710 Varian, Australia) in terms of parts per billion with 3 iteration (18). According to the obtained concentrations, target indices calculated and the results were compared with the water standards.

Data analysis method

Data processing package was SPSS19 and Kolmogorov-Smirnov test run for ensuring data normality. Deviated data were analyzed by box plot. To compare the concentration average of studied elements between stations one-way variance test (Duncan test) was used. To compare the average concentration of studied elements based on WHO & ISIRI standard we used single sample t-test. To determine the correlation between heavy metals parameters (If the data be normal), we used Pearson correlation test.

Results

Results of reading the average concentration of investigated elements in samples are presented in Table 1.

Table 1) The average concentration of elements investigated in groundwater samples of Asadabad plain (Part/billion)

	SD± The concentration average of element		
Stations	**Chromium**	**Nickel**	**Manganese**
1	0.051 ±0.002 defg	55.95 ±10.46 a	1.69 ±0.19 abc
2	0.088 ±0.005 h	65.82 ±8.93 b	2.80±0.51 fgh
3	0.059 ±0.007 g	75.96 ±1.62 c	1.82 ±0.043 abcd
4	0.045 ±0.003 de	67.76 ±1.66 d	2.22 ±0.29 bcdef
5	0.048 ±0.004 def	81.70 ±1.99 cde	2.25 ±0.041 bcdefg
6	0.059 ±0.003 g	66.58 ±1.51 b	3.12 ±0.48 h
7	0.031 ±0.006 b	56.47 ±2.24 a	2.71 ±0.42 efgh
8	0.058 ±0.008 g	65.81 ±2.86 b	3.20 ±0.28 h
9	0.027 ±0.003 ab	88.09 ±4.38 e	2.14 ±0.78 bcde
10	0.028 ±0.001 ab	86.35±3.07 de	1.48 ±0.44 a
11	0.036 ±0.003 bc	79.04 ±2.65 cd	2.23 ±0.10 bcdefg
12	0.052 ±0.009 efg	60.55 ±0.84 ab	1.65 ±0.13 ab
13	0.021 ±0.003 a	79.10 ±2.69 cd	2.43 ±0.34 defg
14	0.020 ±0.002 a	59.89±3.01 ab	2.86 ±0.40 gh
15	0.030 ±0.001 b	65.61 ±3.06 b	3.29 ±0.47 h
16	0.044 ±0.003 de	78.89 ±6.02 cd	2.29 ±0.41 cdefg
17	0.049 ±0.003 def	81.64±5.24 cde	4.06 ±0.23 i
18	0.051 ±0.003 fg	74.80 ±3.41 c	2.29±0.26 cdefg
19	0.043 ±0.015 cd	62.33±1.90 ab	4.24 ±0.53 i
20	0.035 ±0.002 bc	56.00 ±2.87 a	3.99 ±0.55 i
Total average	0.044 ±0.016	70.42 ±10.83	2.64 ±0.83

Non-common letters (a, b, c, etc.) in each column showed a significant difference (p-0<α-0.0005) in the mean concentrations of groundwater samples between stations, based on one-way analysis of variance (Duncan test).

Table 2 shows the statistical comparison results of the heavy metals (chromium, Nickel and manganese) concentration in Asadabad plain samples, based on the World Health

Organization (WHO) standard (19) and national standard (ISIRI) (20).

Table 2) Statistical comparison of the investigated elements concentration based on WHO and ISIRI standard (Part/billion).

Parameters	Standard		Standard Deviation	t	df	p-value	Confidence Interval (%95)	
							Down	Top
Chromium	WHO	50	-49.95	-23441.1	59	0.000	-49.959	-49.951
	ISIRI	50	-49.95	-23441.1	59	0.000	-49.959	-49.951
Nickel	WHO	50	-47.35	-436.87	59	0.000	-47.57	-47.14
	ISIRI	40	-47.35	-344.62	59	0.000	-37.57	-37.14
Manganese	WHO	100	-29.57	-21.14	59	0.000	-32.37	-26.77
	ISIRI	70	0.42	0.30	59	0.7	-2.37	3.22

Table 3 shows the correlation coefficient of heavy metals concentration for studied samples.

Table 3) The correlation between the amounts of heavy metals in groundwater samples of Asadabad plain (part/billion)

	Heavy metal		
heavy metal	**Chromium**	**Nickel**	**Manganese**
Chromium	1	-0.139	0.005
Sig		0.28	0.97
Nickel		1	-0.281*
Sig			0.03
Manganese			1
Sig			

The significance level 0.05

Discussion

Existence of heavy metals in contemporary industrial world led to a great problem that enters to human body via different ways. Heavy metals play two fundamental roles in live creatures that first one is contribution in structure of vital molecules and other is coenzyme role that acts as an activator in acceleration of reactions. Thus, availability of certain heavy metals in specific and desired quantity is necessary, and if variation occurs, natural reactions of body will be disrupted or delayed and lead to undesired responses in live creatures organs. Changing of metals quantity occurs in different ecosystems, under different conditions. Metals can enter into groundwater via natural factors such as soil erosion, flooding or artificial factors such as human activities including municipal, industrial or agricultural sewage (21). Average accumulated concentration of studied elements in samples showed that minimum and maximum concentration of chromium element with 0.020±0.002 and 0.088±0.005 parts per billion are for no.14 and no.12 stations respectively. Chromium is a toxic element and its toxicity depends on its chemical forms; 6-valence chromium is more toxic than 3-valence chromium. Biotic and abiotic factors that led to increasing 6-valence chromium can lead to increasing of its toxicity in water. Chromium mainly enters water via advanced industries swages including aero-plane industry, pesticides, dyes and plating industry; probably in addition to geological features, agricultural activity around well is one of high level of chromium in no.2 station. In other hand, minimum and maximum concentration of Ni element with 55.95±10.46 and 88.09±4.38 parts per billion relates to no.1 and no.9 stations. Because of direct and long exposure of groundwater with stones, there is sufficient time for influencing from environment and groundwater tables often solve much materials so, groundwater is naturally vulnerable (22). Ni, also, found in Pentlandite and Pyrrhotite minerals. Ni may enter in environment via fossil fuels in power plants, mines, refineries, blasting of surpluses and sanitary sewages (23). Assuming absence of these parameters in the study, probably high levels of Ni in no.9 station relates to geologic factors of studied zone. Ni is one of heavy metals that have maximum mobility and transmission in watery environments. Also, minimum and maximum average concentration of Manganese was

1.48±0.44 and 4.24±0.53 part per billion relates to no.10 and no.19 stations. Manganese quantities in natural waters usually are very small and Manganese carbonate is seldom soluble and high levels of anhydride carbonic in water which leads to formation of Manganese bicarbonate (24). Availability of heavy metals in groundwater depends on multiple factors, including level and method of fertilizing or used pesticides, climatic factors, time of sampling, level of groundwater and geology of area (25); On the other hand, Manganese found in carbonated minerals like Dolomite. Accordingly, high levels of Ni in no.19 station in addition to geological features of area may be related to climatology and sampling time (table1). Because one of the probable factors is geological structure of area, we can't propose a definite view about role of plain geological structure in pollution and availability of studied elements in groundwater. Statistical results showed that average concentration of studied materials in ground water of Asadabad plain is lower than W.H.E and national standards. So, with 95% probability, groundwater sources in Asadabad plain are clean of Chromium, Ni and Manganese metals and have no problem for short time health (table 2). Availability of heavy metals in groundwater resources can be attributed to geological structure and climatology of area that due to rainfall can led to solution of elements available in stones and minerals found in area and entering elements to groundwater resources (26). On the other hand, one of the reasons of significant difference between average concentration of studied metals in groundwater resources is type and using method of agricultural complements including chemical fertilizers and fungicides in fields around of wells. Also, correlation results between chromium, Ni and Manganese in groundwater resources of studied area showed significant relation in level 0.05 between Ni and Manganese. This correlation points to common resources for entering of these metals to water resources of the area (table 3). Actually, nowadays, due to severe droughts, decreasing of rainfall and increasing of population from one hand and human activities from the other hand, water resources underwent variations that with intensification of this variations, Asadabad plain is not exempt from these variations. Results of this study are compatible with those of Rajaei et al that measured health hazards of heavy metals in Aliabad Katoul groundwater resources and showed a significant difference between heavy metals concentration with national and international standards (15). Also, Sharafi et al study of Pb, Arsenic, Zinc and Cu elements in Zanjan groundwater showed that the concentration of these elements is lower than W.H.O standards (27). Also, the results of Sobhanardakani et al study's, showed mean concentrations of As, Zn, Pb, Cd and Cu were significantly lower than the permissible limits (13). In another study, Yari and Sobhanardakani showed that the water resources of QaleehShahin plain, Kermanshah Province, are not polluted by heavy metals and are suitable for drinking (28). Also, this study is compatible with findings of Assubaie et al on the concentration of some heavy metals in water of Al-hassa field of Saudi Arabia showed that average concentration of heavy metals in groundwater is suitable for irrigation purposes (29).

Conclusion

Finally, we can say that groundwater resources in Asadabad plain due to absence of affecting industries are not vulnerable to pollution. On the other hand, we can't put a definite point about local effect of geological structure for entering heavy metals. But as the cultivation of wheat, alfalfa, potato, corn and beet in Asadabad plain, an important point is the application of chemical fertilizers and pesticides that may infiltrate gradually in ground water due to rainfall and lead to groundwater pollution in long run. Thus, more emphasis is on the point that harms of uncontrolled using of chemical fertilizers and materials in agricultural fields and resulting bioaccumulation can lead to unrecoverable consequences.

Footnotes

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Conflict of Interest:
The authors stated no conflict of interest.

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