



Assessment of Multi-trace Elements Level in Drinking Water Based on Ground Water Sources

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The heavy metal trace elements and their concentrations in drinking water were determined at 7 sampling stations in north Tehran suburbs during fall and winter of year 2008-2009. The level of elemental concentration of each metal was determined by an inductively coupled plasma atomic emission spectrometry instrument (ICP-AES) according to standard sampling and measurement methods. The results showed that the concentration range of Al, Ni and B in drinking water was in the given order of 119-210, 2.8-20.40 and 123-1000 $\mu\text{g/L}$, which are above WHO standards guideline. The concentrations of other metals such as zinc, copper, vanadium and manganese were below the critical values. The phosphate and nitrogen fertilizers could be the major sources of heavy metals' presence in drinking water of the areas under water pollution assessment.

Key Words: Drinking water, Heavy metals, Inductively coupled plasma atomic emission spectrometry, Pollution.

INTRODUCTION

Water is one of the most important substances on earth. The research shows that although 70 % of earth's surface is water, but freshwater comprises 3 % of the total water on earth. Only a small percentage (0.01 %) of this freshwater is available for human use and about three-quarters of all fresh water is in the form of ice caps and glaciers located in polar areas far from most human habitation¹. Due to rapid population growth and vast urbanizations of the world during the last century, irregular consumption of water in agriculture, industry and economic development and improved living standards even such small proportion of freshwater is under severe stress^{2,3}. The demand for water is expected to increase in the next few years, while the capabilities for developing fresh water resources are declined. Using other non-conventional sources such as the use of reclaimed water for irrigation, groundwater and its recharge, the desalting of brackish water, the shifting of agriculture into low water-demanding crops, the efficient use of available water including the better use of pricing and water conservation measures and the preservation of the water quality^{4,5}, adapting improved farm irrigation systems and deficient irrigation⁶, minimizing soil evaporation, optimal water allocation to different fields or crops and optimizing irrigation time and amount based on rainfall and water resource availability⁷, controlled alternative partial root-zone irrigation^{8,9} are alternative solutions for the whole world.

The land of Iran is located in the west part of Asia, known as Middle East. The land is covered by arid and semi-arid areas with an average annual precipitation less than one third of that of the world¹⁰. Islamic Republic of Iran is also facing critical water shortage and pollution. The water precipitation rate is lower than its evaporation. This causes continuous fall in water quantity in the rivers, lakes and the groundwater as well. The water demand in Iran is supplied by surface and underground water sources. In most parts of the country, the scarcity of fresh water resources is noticeable. Groundwater supplies provide over half of the total annual water demand in Iran and are used as drinking water and agricultural irrigation. The importance of groundwater resources as an alternative water supply is increasingly realized, due to higher costs and diminishing quality of surface waters in face of increasing water shortage problem¹¹⁻¹³.

Monitoring of the quality and quantity of groundwater resources would be indispensable for improvements of population's health in some areas, which are the only available source of drinking water, cooking, agricultural irrigation and for protection of valuable fresh water resources^{3,14}.

The expansion of industries leads to the pollution of ecosystems. Unfortunately, industrial or household waste discharges directly or indirectly into water sources cause excessive pollution of the surface and underground water. Consequently, the water quality and irrigation level are decreased¹⁵.

Most of the monitoring efforts started in the 1960s and since then the research programs have been focused on the detection of undesirable and deleterious effects of chemical pollutants¹⁶. Surface and underground water sources are known to contain trace elements. Toxic elements are discharged into rivers and lakes and leach into the soil and groundwater. Chemicals of high health risk are widespread but their presence is unexplored because their long term health effect appears by chronic exposure opposed to acute exposure. Besides, heavy metals are not biodegradable and enter global ecological cycles via natural water which is the main pathway¹⁷⁻¹⁹. These metals can be intensified easily along the food chain, cause toxicity to plants and accumulate in human tissues^{20,21}. Therefore, the measurement of heavy metals concentrations in various water supplies in Iran or other neighboring countries is important for proper evaluation of the hazards associated with their intake.

The pollution of drinking water sources in many parts of Iran and its consequent effects on human health and the environment is an issue of great concern. Toxic metals are posing major threats to water quality in Iran.

In this study, concentrations of heavy metals have been determined at 7 different sampling stations in the north Tehran suburbs, during two seasons, fall and winter 2008-2009. The importance of the groundwater in the area should not be underestimated because they are the only water source for drinking, agricultural and gardening purposes for the people living in these areas. Despite the lack of alternative water sources, the groundwater geohydrology of the region remains poorly studied.

EXPERIMENTAL

Areas under study: The Greater Tehran Province is one of the 31 provinces of Iran. It covers an area of 18,909 square kilometers and is located in the north of the central plateau of Iran. Tehran Province borders Provinces of Mazandaran in the north, Qom in the south, Semnan in the east and Qazvin in the west. This province includes 13 townships, 43 municipalities and 1358 villages. This province has a semi-arid, steppe climate in the south and an Alpine climate in the north.

Selected seven sampling stations were: Lavasan-e-Bozorg, which is situated in the city of Tehran and its geographical coordinates are 35° 49' 30" North, 51° 46' 58" East, Barg-e-Jahan with geographical coordinates: 35° 50' 37" North, 51° 44' 2" East, Zard Band-e-Lashgarak in 35° 49' 0" North, 51° 34' 0" East, Niknam Deh, with geographical coordinates: 35° 49' 7" North, 51° 43' 52" East, Kond-e-sofla (Kond-e-pa'in) 35° 51' 53" North and 51° 38' 49" East with approximate population of 7 km radius from this point is 1814, Rahatabad with geographical coordinates: 35° 53' 48" North, 51° 37' 1" East and Rasanan in 35° 48' 8" North, 51° 45' 21" East. The area of the sites under study was 274.78 km² (Fig. 1).

Sampling technique: First, essential information on geohydrology of the district was obtained and groundwater resources were identified. For the determination of heavy metals, the samples of water were collected from all the stations. Prior to sample collection, the flasks were rinsed with tap water and then kept overnight with 1:1 HNO₃-H₂O and finally rinsed

with double-distilled water. Collected samples were stored in pure polyethylene vials for analysis. The samples were acidified with (0.2 vol %) nitric acid ultrapure (Merck, Germany) for obtaining pH less than 2. Acidification minimizes the adsorption of metals onto the walls of the container. The samples were stored at approximately 3-4 °C in a refrigerator before analysis. Sampling was performed twelve times in each station; with total 84 samplings. The stations and the order of sampling from each spot are shown in Tables 1 and 2.



Fig. 1. Iran map and the sampling stations

TABLE-1
DESIGNATION NUMBERS OF THE STATIONS

Number of the station	Name
1	Barg-e-Jahan
2	Rasanan
3	Lavasane-Bozorg
4	Zard Band-e Lashgarak
5	Niknam Deh
6	Kond sofla (Kond-e-pain)
7	Rahatabad

Analytical methods: Elemental concentrations were determined by an instrument of inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin -Yvon 138 Ultrace, France) equipped with VGA (vapour generation accessory). The operating parameters were as follows:

Forward power: 800 W; RF frequency: 16 MHz; plasma gas (Ar): 12 L/min; aerosol gas (Ar): 0.29 L/min; flow rate of sheath gas (Ar): 0.18 L/min; nebulizer type: mein hard. The procedural method was followed by standard method EPA

TABLE-2
ORDER OF SAMPLING AT THE DETERMINED STATIONS FROM THE 1ST WEEK TO THE 12TH WEEK

Day	Number of the station											
Saturday	1	7	6	5	4	3	2	1	7	6	5	4
Sunday	2	1	7	6	5	4	3	2	1	7	6	5
Monday	3	2	1	7	6	5	4	3	2	1	7	6
Tuesday	4	3	2	1	7	6	5	4	3	2	1	7
Wednesday	5	4	3	2	1	7	6	5	4	3	2	1
Thursday	6	5	4	3	2	1	7	6	5	4	3	2
Friday	7	6	5	4	3	2	1	7	6	5	4	3
The number of the week	1 st	2 nd	3 rd	4 th	5 th	6 th	7 th	8 th	9 th	10 th	11 th	12 th

TABLE-3
AVERAGE CONCENTRATIONS AND RSD % OF DETERMINED HEAVY METALS

Station No.	Al		Ni		Zn		V		B		Cu		Mn	
	Mean (µg/L)	RSD (%)	Mean (µg/L)	RSD (%)	Mean (µg/L)	RSD (%)	Mean (µg/L)	RSD (%)	Mean (µg/L)	RSD (%)	Mean (µg/L)	RSD (%)	Mean (µg/L)	RSD (%)
1	205.19 ± 16.00	7.79	16.60 ± 2.00	12.05	3.90 ± 0.71	17.95	2.50 ± 0.35	14.00	123.48 ± 18.00	14.58	8.80 ± 0.80	9.09	52.01 ± 10.00	19.23
2	119.54 ± 18.00	15.05	7.20 ± 0.60	8.33	2.30 ± 0.30	13.04	2.90 ± 0.40	13.79	147.06 ± 17.00	11.56	10.00 ± 1.04	10.4	55.10 ± 10.00	18.18
3	165.31 ± 17.20	10.28	2.80 ± 0.40	14.28	2.60 ± 0.42	16.15	2.70 ± 0.50	18.52	771.16 ± 30.00	3.89	6.80 ± 1.06	15.59	48.02 ± 5.60	11.66
4	174.65 ± 16.00	9.16	20.40 ± 2.20	10.78	3.70 ± 0.20	5.40	3.50 ± 0.40	11.43	1000.31 ± 55.00	5.49	15.60 ± 2.10	13.46	78.00 ± 12.01	15.38
5	210.03 ± 18.00	8.57	3.40 ± 0.30	8.82	2.10 ± 0.32	14.28	1.40 ± 0.18	12.86	366.31 ± 28.00	7.64	13.00 ± 1.10	8.46	65.42 ± 10.00	15.29
6	142.78 ± 22.00	15.40	5.60 ± 0.60	10.71	2.20 ± 0.20	9.09	2.65 ± 0.25	9.43	599.17 ± 46.00	7.68	5.20 ± 0.60	18.75	68.00 ± 8.00	11.76
7	132.16 ± 23.00	17.40	9.60 ± 0.70	7.29	4.52 ± 0.61	13.49	2.10 ± 0.30	14.28	482.19 ± 16.00	3.32	12.20 ± 0.80	6.56	61.00 ± 7.30	11.97

200.7 for concentration determinations of aluminum, zinc, copper, vanadium, boron, manganese and nickel in water and wastewaters. All standard and sample solutions were prepared with deionized triplet distilled water obtained by Aquamax Ultra 370, Young Lin Instrument Co., Korea. Before starting the tests, all glasswares were soaked in 15 % HNO₃ solution for at least 48 h and then rinsed with deionized water²². Calibration curves for ICP-AES were determined using different sets of standard solutions. The sets consisted of standards containing 0, 25, 50, 100, 200, 500 and 1000 µg/L of metals in ultrapure HNO₃ (Merck).

For preparing the samples, 200 mL of each well-mixed sample was transferred to a beaker. Four mL of HNO₃ 1:1 (v/v) was added in each sample. Watch glasses were used to cover the containers, to prevent them from contamination. Then, samples were heated to 80-85 °C using hot plates to obtain the final volume of about 10-20 mL before metal precipitation²³. The above procedure was repeated twice. The beaker walls and the covers were washed carefully with ultra pure deionized water and then the rinse water was filtered. The filtrate was transferred to a 100 mL volumetric flask with the addition of about 10 mL of water. All samples were prepared in duplicate. Following the metal concentration determinations, the mean values of elemental concentration and the relative standard deviations (R.S.D.) were also calculated. The statistical analysis was performed using ANOVA.

Statistical analysis: Statistical analysis was performed using MiniTab software (release 11.12, Minitab Inc., State College, PA, USA). Data were reported as mean ± standard

deviation at significance level of $p < 0.05$. Differences were considered statistically significant when the p value was < 0.05 .

RESULTS AND DISCUSSION

There are seven stations allocated for this study as shown in Table-1. These villages are located in the north of Tehran, the capital of Iran. The sampling from wells was carried out every alternate week according to Table-2 for two seasons (fall and winter); therefore the sampling was performed for 12 weeks on a rotational schedule according to which most of the stations would be sampled at least once every alternate week. This implies that in every consecutive week of sampling, all stations were tested in different days from the last sampling for a proper random sampling of every station. The concentrations of heavy metals in the drinking water, collected in two seasons from specified stations are given in Table-3.

Heavy metals are the cause of more environmental pollution than organic chemicals. These metals are entered into both surface and groundwater through human activities like large scale use of chemicals in agriculture, unsuitable disposal of industrial and municipal wastes. Many of these metals are considered essential for humans, animals and plants normal growth but when present at high concentrations they can be toxic and lead to adverse health consequences. The concentration of different trace metals such as, aluminum, zinc, copper, vanadium, boron, manganese and nickel were measured in the areas under investigation. The WHO and Iranian national standard guideline have recommendation limits in concentration values for different metals as depicted in Table-4^{24,25}.

Element	WHO guideline values (mg/L)	Iranian national standard (mg/L)
Aluminum	0.2	0.2
Zinc	3.0	15
Copper	2.0	1.0
Vanadium	-	0.1
Boron	0.5	1.0
Manganese	0.4	0.5
Nickel	0.02	1.0

As it is evident in Tables 3 and 4, the level of Zn, V, Cu and Mn in sources under investigation are within the limits of both standard guidelines and safe limits, although the concentrations of Al, B and Ni in drinking water samples of some places are higher than the WHO guideline. As can be seen in Fig. 2, nickel concentration is a little higher than WHO standard in one station, *i.e.* station number 4 and in station number 1 is near to the safe limit. Nickel, is a widely distributed element in the environment and can be found in air, water and soil²⁶.

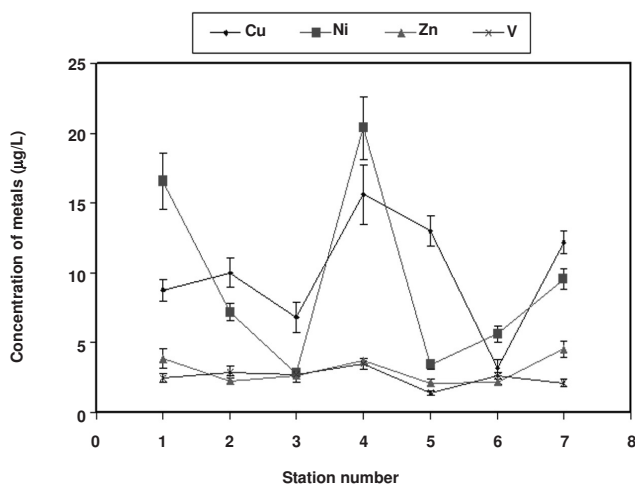


Fig. 2. Comparison of 4 elemental concentrations in different stations

Nickel is a compound which occurs in the environment only at very low levels. Foodstuffs naturally contain small amounts of nickel. When people intake consists of large quantities of vegetables from polluted soils, nickel uptake will increase. Plants are known to accumulate nickel and as a result the nickel uptake from vegetables would be boosted. In small quantities nickel is essential, but when the uptake is very high it can be a danger to human health. Development of lung, nose, larynx and prostate cancer, birth defects, heart disorders could be the results of an uptake of too large quantities of nickel²⁷. The local population of the areas like station 4 can be at risk of exposure to high doses of nickel with food and water being the two main sources. Fig. 3 shows that the concentrations of Al in stations designated as numbers 1 and 5 were a little above the Iranian National Standard and for B the concentration of this metal in station numbered as 2, 4 was above the Iranian National Standard, which it is twice the WHO standard value for boron.

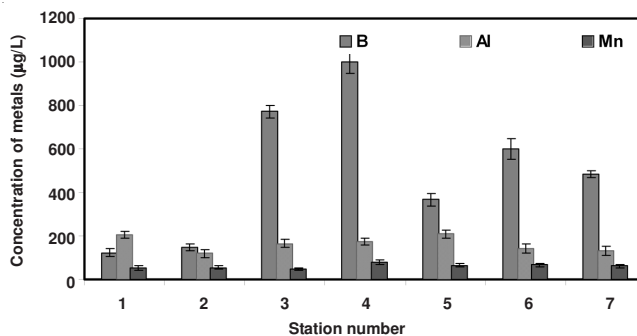


Fig. 3. Comparison of 3 elements with highest concentration in different stations

It is observed that among all the metals present in drinking water of all the stations, Zn and V were at the lowest while, B and Al were at highest concentration levels. According to WHO reports long-term exposure of humans to boron compounds cause mild gastrointestinal irritation and in some studies, aluminum is reported to be associated with the brain lesions characteristic of Alzheimer disease. In several ecological epidemiological studies the incidence of Alzheimer disease has been associated with aluminum in drinking-water²⁸. The concentration range of Al, Ni and B in drinking water was in the given order of 119-210, 2.8-20.40 and 123-1000 µg/L. The variations of heavy metal concentration in the drinking water were not significant in two seasons of fall and winter or days ($p > 0.05$) and were relatively stable throughout the 6 months of the year in all the villages. However, it is revealed that there is a slight increase in concentration levels during the winter months when the ground is covered with snow and there is more intensive percolation of water into the soil and as a result water absorbs and dissolves more metals and their salts. Such trend has been observed in the investigation of arsenic element in drinking water of 8 villages in Kurdistan Province²⁹ and Ni, Cr and Cu in Khuzestan Province²¹. Heavy metals enter the living environment by natural and anthropogenic routes. Increased anthropogenic input of toxic metals in soils may result in the transport of an increased content of metals in the groundwater or surface water. Hazardous metals input include those from commercial fertilizers, phosphate industry waste and mining and water processing³⁰. In these regions, agricultural waste water is the major source of water pollution. Chemical fertilizers, containing heavy metals such as Ni, Al and B are used in agriculture-related industries of the villages. The phosphate and nitrogen fertilizers are major sources of heavy metals in soil and transfer of Ni, Zn, Al and other heavy metals in soil-plant systems³¹⁻³³. From these sources heavy metals may leach into the water. Phosphate fertilizers increase the concentration levels of metals and phosphorous (P) in solvated soil and they therefore, lower the pH of the soil. The increase in solution of such metals could be due to desorption of heavy metals from the soil³⁴. Uptakes of such elements by plants, which are consumed directly or indirectly by humans, originate from heavy metal contaminants in phosphate fertilizers and need to be of serious concern. Also the municipal wastewater from villages is directly discharged into the soil where there is no wastewater and sewage treatment plant currently active in this area³⁵. Station number 4 with more

land for agricultural activities compared to other stations and as it is observed in Figs. 2 and 3, the concentration of boron and aluminum are higher than other metals, which is probably due to the concentration of these metals in the fertilizers being used. Because these villages are close to each other and using almost the same fertilizers, the trends of the elemental concentrations are more or less similar in all.

The chemical analysis of the drinking water of these stations and the concentration of other metals has been reported elsewhere³⁶ and the results indicated that the level of metals in sources under investigation were within the limits of both standard guidelines.

Conclusion

The purpose of this study was to assess the heavy metal pollution level in and their concentrations in the drinking water of 7 stations in the suburbs of Tehran, the capital of Iran. Boron is reported as the highest concentration, with aluminum and nickel standing next. The concentrations of these metals are higher than the official safe recommended values and the concentrations of zinc, copper, vanadium and manganese are below the guideline values. In this area, agricultural waste water and using phosphate and nitrogen fertilizers are the major sources of water pollution by heavy metals. Therefore, the use of such fertilizers should be of serious concern.

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