

Metal Concentrations in the Groundwater in Birjand Flood Plain, Iran

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Abstract The objective of the present study was to investigate the concentration of metals (cadmium, lead, chromium, zinc, copper, and iron) were measured in groundwater at 30 sites from the Birjand flood plain of eastern Iran during the November 2010; identify any relationships between metals and pH, total hardness. Metal concentrations in the groundwater samples were decreased in sequence of $Zn > Fe > Cu > Cr > Pb > Cd$, respectively. The results showed that the overall mean concentrations of Cd, Pb, and Cr were at 0.000, 0.023, and 0.049 mg l⁻¹, respectively. The mean concentration of Cu, Zn, and Fe were 0.109, 0.192, and 0.174 mg l⁻¹, respectively. Results also indicated that there were correlations among Cd, Cu, and Zn metals.

Keywords Pollution · Cadmium · Lead · Water quality · Birjand flood plain

Today the competition for scarce water resources is intense both in Iran and in many places all over the world.

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Groundwater has long been considered as one of the purest forms of water available in nature and meets the overall demand of rural and semi-urban people. Groundwater is the major source of water supply for agriculture and domestic purposes in urban as well as rural parts of Iran. Among the various reasons, the most important are non-availability of potable surface water and a general belief that groundwater is purer and safer than surface water due to the protective qualities of the soil cover (Shakeri et al. 2009). In the other hands, developments of human societies and industry result in bioenvironmental problems; pollution put the water, air and soil resources at risk. Increasing water pollution causes not only the deterioration of water quality but also threatens human health and the balance of aquatic ecosystems, economic development and social prosperity (Milovanovic 2007).

The studied site is located in East of Iran, Birjand, and the capital city of Southern Khorasan province. It is about 1,490 m above sea level. The climate of the city is semi-arid with cold winter and approximately 8 months dry season (from middle of April to December). Its average rainfall is 171 mm and unevenly distributed throughout the year. The average annual temperature is 16.5°C with the warmest month in July (average 28.5°C) and the coldest in January (average 3.5°C). The sunlight of the year is 255 days.

On the global scale, groundwater contamination is a relatively new problem and increases the stress arising as a result of unprecedented population growth, urbanization, and industrialization since the 1990s (Chen 2002). Pollution of groundwater by metals has been given much attention due to their toxicity, bioaccumulation, and low biodegradability (Ramesh et al. 1995). Some metals present in trace quantity are important for life as it helps and regulates many physiological function of the body. Metals

like Zn, Cu, and Fe, which are required for metabolic activity in organisms, while other metals like Cd, Cr, and Pb have no known physiological activity; they are proved detrimental beyond a certain limit (Marschner 1995; Bruins et al. 2000). The main sources of groundwater pollution are discharge of industrial effluents, agricultural and municipal activities, which contain organic pollutants, chemicals and metals, and run-off from land-based activities (Goldar and Banerjee 2004). Specifically, trace metal contamination of water has emerged as a serious health issue highlighted in published work (Watt et al. 2000). The assessment of water quality can be the first and the most important step toward applying an appropriate quality management plan in order to elimination water pollution (Sanchez et al. 2007). Hence, the objective of this article was to investigate the metal (Cd, Pb, Cr, Cu, Zn, and Fe), pH, and total hardness concentration of groundwater in Birjand flood plain in the eastern Iran.

Materials and Methods

Water samples were collected from 30 sites in the Birjand flood plain in the November 2010. Water samples were collected into acid washed 250-ml plastic bottles. The water samples were filtered using a 0.45 μm nitrocellulose membrane filter. Prior to any analysis, all equipment and containers were soaked in 10 % HNO_3 and rinsed thoroughly with deionized distilled water before use. The determinations of Cd, Pb, Cr, Cu, Zn, and Fe in groundwater were carried out by a GBC (Savant AA Sigma) flame atomic absorption spectrometer. The detection limits for each metal were: Cd (0.0001), Pb (0.001), Cr (0.0001), Cu (0.001), Zn (0.001), and Fe (0.01). Recovery rates ranged from 97 % to 100 % for all investigated elements. The pH measured by a Multi Parameter Analyzer (Consort, Model: C534T& Istek, Model: pdc815), and also total hardness measured by a Photometer (Palintest, Model: 8000). Finally, the resulted data was compared with the national and international standards specified for the maximum rate of metals allowed in drinking water. Statistical analyses were carried out using SPSS ver. 16.0. A Pearson correlation (r) was used to test correlations. All concentrations are reported in mg l^{-1} .

Results and Discussion

The mean concentration of the metals in the groundwater of the Birjand flood plain is given in Table 1. The results showed that the overall mean concentrations of Cd, Pb, and Cr were at 0.000, 0.023, and 0.049 mg l^{-1} , respectively. The mean concentration of Cu, Zn, and Fe were 0.109,

0.192, and 0.174 mg l^{-1} , respectively. Mean concentrations in the groundwater samples were decreased in sequence of $\text{Zn} > \text{Fe} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Cd}$, respectively. Highest heavy metal concentration was found for Zn (0.192 mg l^{-1}) in groundwater sample from Birjand flood plain.

Cd and Pb are the most significant of all the metals because it is both very toxic and very common. Cd concentrations in unpolluted waters are usually below 0.001. Long-term exposure can cause kidney and liver damage, and damage too circulatory and nerve tissue. Groundwater may be contaminated by lead due to enlistment either natural or enriched from anthropogenic activities in the soil and, in some cases, mineral weathering (Buragohain et al. 2010). High doses of Cr cause liver and kidney damage and chromate dust is carcinogenic (Mugica et al. 2002). Cr in excess amounts can be toxic especially the hexavalent form. Essential elements, such as Cu, Zn, and Fe are necessary for the metabolism but can however cause adverse effects when their concentration in the organism becomes excessive. The taste threshold of Cu, Zn, and Fe are about 1–2, 0.1–5, and 0.2–0.3 mg/l , respectively (Table 2). The ideal intake amount of Cu and Zn is 2 and 4–10 mg/day , respectively (Chung et al. 2009). The standard for Cu, Zn, and Fe content in drinking water is 1.3, 5, and 0.3 mg/l in Iran, respectively. Water containing 3 mg copper/l was associated with gastrointestinal disturbance in adults, whereas water containing 1 mg/l was not (Pizarro et al. 1999). When the zinc proportion in water exceeds 4 mg/l , the water will taste bitter; and if the concentration of 5 mg/l lasts for a long time, the wall of the boiling vessel will be covered by a milky white creamy film (Raina and Pollari 1999). Iron is commonly found in gravels and rocks principally in an insoluble form. The results showed that the next to Zn, the Fe accumulated the highest level in the groundwater samples. Presence of high Fe concentration in water can lead to change of color of groundwater (Kerry Rowe et al. 1997).

Applicable international standards for metals in water are presented in Table 2 to determine whether metal concentrations are suitable for drinking water. International guidelines of heavy metals for drinking water conducted according to USEPA (2009), ISIRI (1992), and WHO (2006) standards. Results of this study showed that the groundwater is below guidelines thresholds for drink water with respect to metals (Cd, Cr, Cu, Zn, and Fe). However, the concentration of Pb in groundwater is below the Iranian guidelines for drinking water quality (0.1 mg l^{-1}) and higher than the international guidelines for drinking water quality given by the USEPA (2009) and WHO (2006) which are 0.015 and 0.01 mg l^{-1} , respectively (Table 2).

Measurement of pH and hardness are two of the most important and frequently used tests in water chemistry. pH

Table 1 Levels of metals concentrations, total hardness (mg l^{-1}) and pH in groundwater samples

Station no.	UTM		Metals						pH	Hardness (as CaCO_3)
	Y	X	Cd	Pb	Cr	Cu	Zn	Fe		
1	3636359	712451	0.004	0.035	0.055	1.05	1.69	0.31	7.53	521
2	3636231	711723	0.004	0.031	0.052	0.89	1.12	0.29	7.52	472
3	3638228	698572	0.003	0.045	0.056	0.84	1.78	0.37	7.67	496
4	3637721	703750	0	0.024	0.059	0.012	0.035	0.17	7.86	397
5	3636035	710116	0	0.015	0.055	0.019	0.022	0.12	7.57	520
6	3638324	695950	0	0.021	0.052	0.019	0.041	0.12	8.00	620
7	3639191	689376	0	0.028	0.053	0.031	0.015	0.12	8.01	450
8	3639731	694323	0	0.019	0.057	0.016	0.028	0.22	7.90	460
9	3639110	694028	0	0.028	0.053	0.021	0.017	0.15	7.24	750
10	3642451	711353	0	0.021	0	0	0	0	7.68	440
11	3640640	704880	0	0.19	0.051	0.231	0.11	0.13	8.17	575
12	3639734	706991	0	0.025	0.057	0.017	0.019	0.13	7.34	895
13	3638228	698572	0	0.01	0.059	0.003	0.028	0.15	7.7	440
14	3639141	694863	0	0.015	0.047	0.017	0.079	0.13	7.62	604
15	3638469	695080	0	0.011	0.058	0.011	0.069	0.18	7.62	760
16	3638571	702222	0	0.017	0.081	0.013	0.058	0.13	7.72	404
17	3638571	702916	0	0.014	0.058	0.014	0.04	0.19	7.71	420
18	3637634	705413	0	0.015	0.056	0.005	0.094	0.22	7.71	360
19	3636231	711723	0	0.012	0.057	0.016	0.048	0.18	7.8	424
20	3636359	712451	0	0.015	0.059	0.001	0.022	0.13	7.73	460
21	3637025	712153	0	0.017	0.047	0.003	0.05	0.19	7.7	500
22	3636099	710446	0	0.011	0.086	0.004	0.038	0.22	7.6	620
23	3637024	707658	0	0.013	0.066	0.006	0.035	0.19	7.69	432
24	3642758	724612	0	0.013	0.008	0.002	0.045	0.19	7.56	460
25	3641917	724943	0	0.011	0.009	0.014	0.051	0.15	7.66	308
26	3642898	73713	0	0.015	0.006	0.015	0.074	0.21	7.91	312
27	3641917	724943	0	0.019	0.008	0.015	0.036	0.11	7.66	312
28	3635855	713685	0	0.017	0.061	0.006	0.032	0.21	7.75	464
29	3636688	711345	0	0	0.043	0	0	0.17	7.67	408
30	3637634	705413	0	0.015	0.056	0.005	0.094	0.22	7.71	360
Overall mean			0.000	0.023	0.049	0.109	0.192	0.174	7.69	488

Table 2 Comparison of mean metals concentration (mg l^{-1}) with some national and international water quality standards

Metals	Drinking water*				Present study
	ISIRI	WHO	EU	USEPA	
Cd	0.01	0.003	0.005	0.005	0.000
Pb	0.1	0.01	0.05	0.015	0.023
Cr	0.05	0.05	0.05	0.1	0.049
Cu	1.3	2	0.1–3	1.3	0.109
Zn	5	3	0.1	5	0.189
Fe	0.3	0.3	0.2	0.3	0.174

*Data from WHO (World Health Organization 2006), USA (United States of America 2009), ISIRI (Institute of Standards and Industrial Research of Iran 1992)

is an important factor in determining the chemical and biological properties of water. pH, also influences the degree of ionization, volatility, and toxicity to aquatic life of certain dissolved substances, such as ammonia, hydrogen sulfide, and hydrogen cyanide (Weiner 2007). As the drink water quality should be in the range of 5–9, the study results showed that the pH mean was 7.69 which is in the desirable range. A pH value of 7.69 may be due to the presence of carbonates of calcium and magnesium. The total hardness is sometimes useful as an indicator proportionate to the total dissolved solids present, since Ca^{2+} , Mg^{2+} , and HCO_3^- often represent the largest part of the total dissolved solids (Lin et al. 1996). No human health effects due to hardness have been proven; however, an

Table 3 Correlation coefficient (*r*) between the metal concentrations in water samples from Birjand plan of eastern Iran

	Cd	Pb	Cr	Cu	Zn	Fe	pH	Hardness
Cd	1							
Pb	0.13	1						
Cr	0.07	0.01	1					
Cu	0.98**	0.27	0.08	1				
Zn	0.95**	0.17	0.08	0.97**	1			
Fe	0.71**	0.01	0.27	0.70**	0.76**	1		
pH	0.69**	0.04	0.02	0.52**	0.37*	0.31	1	
Hardness	0.01	0.17	0.35	0.04	0.02	−0.07	−0.02	1

Correlation is significant at the
* $p < 0.05$, ** $p < 0.01$

inverse relation with cardiovascular disease has been reported. Higher levels of drinking water hardness correlate with lower incidence of cardiovascular disease (Weiner 2007). High levels of water hardness may limit the growth of fish; on the other hand, low hardness (soft water) may increase fish sensitivity to toxic metals (Pyle et al. 2002; Ebrahimpour et al. 2010). The investigations in Birjand flood plain showed that the total hardness mean (CaCO_3) is 488 mg l^{-1} , so it may be included in very hard waters. The water of this region is naturally hard due to geological formation of the water.

In order to quantitatively analysis and confirm the relationship among trace element contents in groundwater samples, Pearson's correlation analysis was applied to the data (Table 3). There were a highly positive correlation between Cd and Cu, Zn, Fe, and pH ($p < 0.01$), and, between Cu and Zn, Fe, and pH ($p < 0.01$) also, there was a highly positive correlation between Zn and Fe ($p < 0.01$). Moderately positive correlations were found among between Zn and pH ($p < 0.05$). A significant highly positive correlation was found to exist between Cd and Zn signifying their similar source of geogenic origin and mobility (Haloi and Sarma 2011). Cadmium occurs mostly in association with zinc. It replaces zinc biochemically and causes high blood pressures, kidney damage (Rajappa et al. 2010). Studying on the metals on the groundwater of Brahmaputra flood plain, Haloi and Sarma (2011) showed that the positive correlation were between Cd and Zn. We hypothesize that metals with a high positive correlation are possibly from the same pollution source.

The metal concentration in the groundwater are described in the descending order of $\text{Zn} > \text{Fe} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Cd}$, respectively. Pearson correlation showed that there was significant correlation among Cd, Cu, and Zn metals ($p < 0.05$, $p < 0.01$). All the metals pollutants in the groundwater flood plain are within the national and the international guide lines except for Pb. This study has highlighted the need for further research, in order to determine the permitted levels of metals in groundwater as well as to identify areas of potential toxicity and the drinking water quality.

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