Original Article

Health Risk Assessment of Fe, Mn, Cu, Cr in Drinking Water in some Wells and Springs of Shush and Andimeshk, Khuzestan Province, Southern Iran

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Received: 13.09.2015 *Accepted: 19.10.2015*

ABSTRACT

Background: In the current study,the hazard quotient, the hazard index (HI) and spatial variations of Fe,Mn,Cu and Cr in drinking water sources of Andimesk-Shush, Khuzestan Province, Southern Iranaquifer were assessed.

Methods: We compared theconcentrations of aforementioned heavy metals in wells and springs inAndimeshk and Shush regions. The non-carcinogenic risk assessment of heavy metals was implemented usingUnited States Environmental Protection Agency (USEPA) index.The spatial maps in the area were developed by geostatistical methods.

Results: Mean concentrations of heavy metals in groundwater sources of the study area in decreasing order was as follows: Cu >Mn> Fe> Cr. Except for iron,mean heavy metal concentrations were higher than the standard levels. Manganese concentration in 41.5% of the samples exceeded the permissible limits. Copper was higher than the safety limit in 74% of the samples, and chromium in 54% of the cases. The spatial pattern of heavy metals concentrations indicated higher concentrations in the southern parts of the region. The mean hazard quotients of most samples for the four heavy metals were lower than one, indicating that there was no immediate threat due to the exposure to these heavy metals. The calculated accumulated hazards of these heavy metals produced different results, with hazard indices of higher than one.

Conclusion: The accumulated hazard indicesfor the evaluated metals were higher than one, indicating that chronic ingestion of these waters threatens the health of local consumers on the long run.

Keywords: Chemical Water Pollution, Heavy Metals, Risk Assessment.

IJT 2016 (2): 29-35

INTRODUCTION

Heavy metal pollution of soil and water has become one of the main concerns of human beingsrecently [1]. Next to industrial, agricultural and other anthropogenic sources, soil weathering also influence leaching and bioavailability of trace elements [2]. In arid and semi-arid areas with water shortage, dependence on groundwater resources is more common and evaluation of these water sources used for drinking purposes is of utmost importance.

Because of health effects of heavy metals, they have attracted attention in water quality studies. Among them, iron and manganese are naturally available in many geological formations and can change the taste and odor of water according to the reports published by the United States Environmental Protection Agency (USEPA), thus they can restrict domestic and industrial usage of waters [3]. Iron is the second most common metal in the earth crust and has a tendency to bind to oxygen and sulfur; therefore, iron is mostly seen as oxidized form in the environment [4]. In drinking water sources, salts of Fe (II) are unstable and typically precipitate as iron hydroxide, but ground waters, which are kept in anaerobic conditions, may contain some iron when discharged out [5]. Manganese is also a trace element in the earth crust which mainly originates from weathering. There are different oxidation states for this element in nature, among them Mn (II) as the reduced form and Mn

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(VI) in the oxidized form. Health impacts and side effects of water contaminated with manganese, such as neurological symptoms, have been proved [6].

Chromium is available in various oxidation states, mainly Cr (III) and Cr (VI).Depending on the oxidation, its biological activity is different. The toxicity of Cr (VI) is about 100 to 1000 times higher than that of Cr (III) [7]. Chromium in the sixth oxidation state, as CrO_4^{2-} and $HCrO_4^-$, has high mobility in the environment [8]. On the other hand, Cr (VI) is a carcinogenic substance as well. In reduced condition, Cr (VI) is converted to Cr (III) that is insoluble in the aquifers and bind to solid particles, thusit has low toxicity [9].

Copper is an essential element for life, however at higher levels can cause anemia and destroys kidney and liver tissues [10]. The copper content of the earth crust ranges from 25 to 75 mg/kg. Organic matters in the soil have a high affinity for copper and can reduce the binding of copper to solid particles [11]. High concentrations of copper have been found in groundwater in area with mining or metal smelting activities. Since this element has low mobility in soil, it may reach high levels in some regions [12].

Andimeshk and Shush are two cities located in the southern parts of Iran, north of Khuzestan Province. This study area has arid environment. According the precipitation statistics in the recent past 40 yr, more than 80% of the precipitation happens between December to March. On the other hand, the amount of evaporation is about 1670mm, which is more than six times higher than that of precipitation in the region. About 70% of the total land used in the area is used for agriculture. The dominant agricultural products are wheat, sugar cane and cereals. Nearly 75% of the water requirements in the agricultural sector are provided through surface sources and the rest is catered by the ground waters [13]. Since the area is arid, all of the drinking water in the rural regions is provided by groundwater resources and assessment of the groundwater quality is of great importance.

With respect to the groundwater quality, some studies have been conducted earlier. Babaei et al [13]. Evaluated the amounts of heavy metals including Cr, Fe, Mn and lead in ground waters using samples from 42 wells in Shush-Andimeshk aquifer and concluded that the amounts of Cr and Fe were lower than permissible values, while the values of Mn and lead were higher than standard levels in some samples. Nouri et al [14]. Studied the levels of Cd, Zn and Cu in Shush-Andimeshk aquifer and found that Cd was lower than USEPA standards, whereas in 4.8% of the samples copper was higher than the standards. In addition, the amount of heavy metals in the southern part of the study area was higher than that of the northern parts [14].

Given the above-mentioned explanations, the main objectives of the current research was to verify the spatial variations of Fe, Mn, Cr and Cu in some wells and springs in Shush-Andimeshk aquifer, and to study its health risk. In our study, the quality of water in springs is presented for the first time in this region.

MATERIAL AND METHODS

The data set associated with this study was collected from 89 wells and springs (79 wells and 10 springs) in in Andimeshk-Shush aquifer, northern part of Khuzestan Province, southern Iran. Using acidified poly ethylene bottles, samples were collected in the field. Nitricacid was added to the samples and was kept in 4°C until transportation to the laboratory. In the laboratory, atomic absorption spectrometry was utilized to analyze the levels of Fe, Mn, Cu and Cr. Spatial variation of heavy metals was assessed by Mann-Whitney U test.

The non-carcinogenic health risk of heavy metals in the wells and springs that exceeded the standard values was evaluated by the following equations [15]:

$$D_i = \frac{C_W * IR * EF * ED}{B_W * AT} \quad (1)$$

$$HQ = \frac{D_i}{RfD} \quad (2)$$

$$HI = \sum_{i=1}^{n} HQ_i \quad (3)$$

In equation (1), D_i is the daily dose of heavy metals (μgkg^{-1}d^{-1}) to which consumers might be exposed. C_w (μgl^{-1}) is the concentration of heavy metals in the water, IR (Lday^{-1}) is the absorption rate of heavy metals which was 2.2 in the current study, EF (day year^{-1}) is the frequency of exposure to heavy metals which is

365 d/yr, ED (yr) is the total duration of exposure to heavy metals which was considered 70 yr, B_w (kg) is the body weight which we used 60kg for both men and women. Finally, AT (day) wasthe average time to which the consumers were exposed to heavy metals and was equal to 2550 in the current study. Moreover, in equation(2), RfD ($\mu g kg^{-1} day^{-1}$) is the reference dose for each heavy metal which were 3,40 and 140 for Mn, Cu and Cr based on USEPA[16], respectively. HQ in equation (3) is the hazard quotient of heavy metals and if exceeds one, the health risk of heavy metals will be high. To assess the accumulated impacts of heavy metals for the consumers, the hazard index (HI) was calculated. It is the sum of the hazard quotients for heavy metals, and if it is higher than one, the risk of heavy metals in the water would be high [17].

Geostatistics usessemivariogram method to quantify thespatial variation of a regionalized variable. Semivariogram functions are based on the assumption that things nearby, tend to bemore similar than things that are further apart. The semivariogramis half the expected squared difference between paired data valuesz (x) and z(x + h) to the lag distance h [18]. For discrete sampling sites, the usual equation for the variogram is:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (4)$$

Where z (x_i) represents the value of the variable z at location of x_i , h isthe lag distance, and N(h) is the number of sample pairs separated by h. It is rare for the distance between the pairs of sample points tobe exactly equal to h. Therefore, the lag distance h is often represented by a distance band. The experimental variogram is calculated for several lag distances. This is then generally fitted with atheoretical model, such as the spherical, exponential, linear or Gaussian models. These models provide information onthestructure of the spatial variations and the input parameters for Kriging interpolation. Semivariogram analysis is used to explore the autocorrelation range of the concentration data. When fitting a model, the nugget (Co), sill (Co + C), and range (A) are the important characteristics for exploring directional autocorrelation. Co is the nugget value caused by the experimental error and random factors that are within the sampling scales; C is the structure value, which originates from the heterogeneity of soil parent material, terrain, climate and some other factors; (Co + C) is the sill value, which shows total variation within the system; and Co/(Co + C) is the nugget coefficient. This ratio represents the degree of spatial variation dominated by random or structural factors. The distance at which the semivariogram levels off to the sill is the range (A). Sample locations further apart from the range are not spatially auto correlated [19].

RESULTS

The descriptive statistics of heavy metals in the wells and springs of the study area are demonstrated in Table1. The mean concentration of Fe, Mn, Cu, and Cr in the springs of the region was0.03,0.80,8.17 and 0.07 mg/l, respectively. The overall mean copper level was influenced due to high levels of this element in one of the stations (KohnabBalarural area). The mean concentration of Fe, Mn, Cu and Cr in the wells' waters was0.11,0.20,0.42 and 0.05 mg/l, respectively. The spatial variations of heavy metals (Table2) showed that except for the chromium, there was significant difference between Fe, Mn and Cu at 1%significance. With respect to Fe, the mean concentration in Shush (0.16 mg/l) was significantly higher than that of Andimeshk (0.04 mg/l). The levels of Mn were 0.32 mg/l in Shush and 0.11 mg/l in Andimeshk. The mean concentration of Cu in Andimeshk (0.69mg/l) was comparable to Shush (0.66mg/l). Finally, for chromim there was no significant difference between Shush and Animeshk and the value in both regions was 0.05 mg/l.

Assessment of the health risk of heavy metals in groundwater, showed that the levels of Fe in none of the samples was higher than the standard value of 0.3 mg/l, while for Mn in 37 samples (41.5%) the values were higher than the safe level(0.1 mg/l). This value for copper was higher in 74% of the samples (66samples) and its concentrations exceeded the standard level of 0.05mg/l. As for chromium, in 48 samples (54%) the values were higher than the permissible level of 0.05 mg/l.

The non-carcinogenic health risks of heavy metals in stations for which the values were higher than the standard levels are presented in Figure1-3. The mean non-carcinogenic health risk of Cr, Cu and Mnwas0.62,0.38 and 0.05,respectively.These results illustrated that as a whole the mean of non-carcinogenic risk was not higher than one, however copper in 10 stations (11%) and chromium in one station(1%) had higher than one risks. Accordingly, the lowest health risk was associated with manganese for which the highest hazard quotient was 0.7 and the highest value belonged to copper with a hazard quotient of higher than 2.5 in some stations. With respect to chromium, except for one of the stations, the hazard quotient fluctuated between 0.5 and 1.0.

The geostatistical methods were utilized to illustrate the spatial variations of the considered heavy metals, resulting in the maps (Figure4). The similarity among these maps is that the concentration of metals in the southern parts of the study area (around Shush) is higher than that of the northern parts (around Andimeshk).

Table1. Descriptive statistics of iron, manganese, copper and chromium in the wells and springs of the study area.

Heavy metals	Springs				Wells			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Iron	0.01	0.09	0.04*	0.03	0.01	0.3	0.11*	0.08
Manganese	0.02	2.58	0.3	0.8	Nd	2.67	0.20	0.37
Copper	0.02	25.95	2.72	8.17	0.02	2.90	0.42	0.60
Chromium	Nd	0.24	0.06	0.07	Nd	0.08	0.05	0.02

*:Significant at 5% level

Table2. The descriptive statistics of heavy metals in groundwater in Shush and Andimeshk.

Heavy Metal	Andimeshk				Shush			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Iron	0.01	0.13	0.04**	0.03	0.05	0.3	0.16**	0.07
Manganese	ND	2.58	0.11**	0.37	0.07	2.67	0.32**	0.48
Copper	0.02	25.95	0.69**	3.81	0.04	2.91	0.66**	0.71
Chromium	ND	0.24	0.05	0.04	0.03	0.08	0.05	0.01

**:Significant at 1% level
SD:Standard deviation

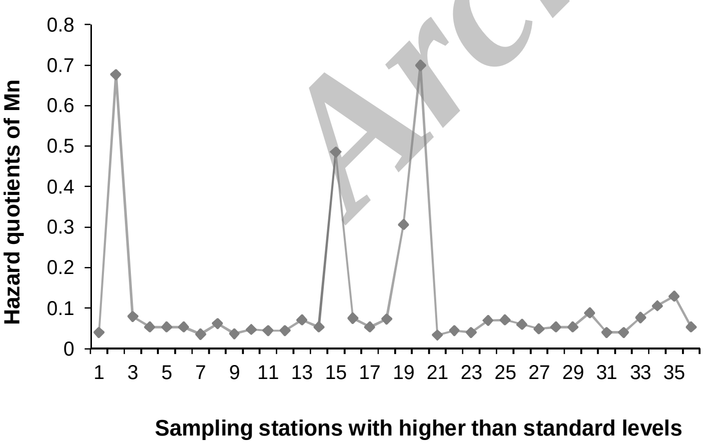

Figure 1. The variations of hazard quotients of Mn in sampling stations with higher than standard levels.

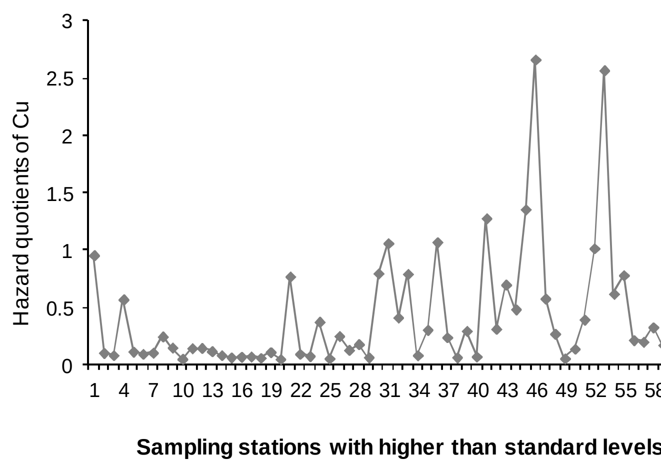

Figure 2. The variations of hazard quotients of Cu in sampling stations with higher than standard levels.

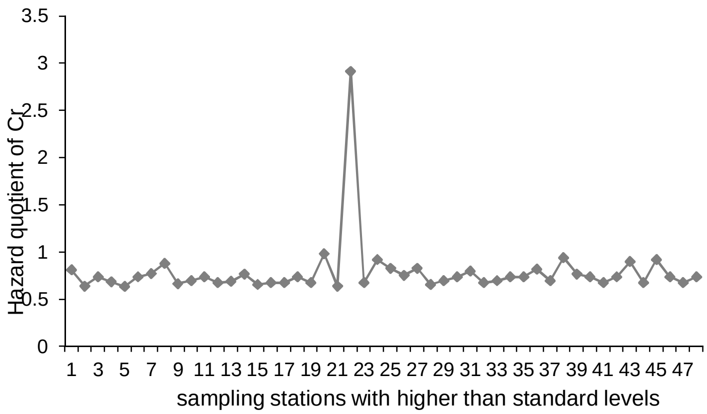

Figure 3. The variations of hazard quotients of Cr in sampling stations with higher than standard levels.

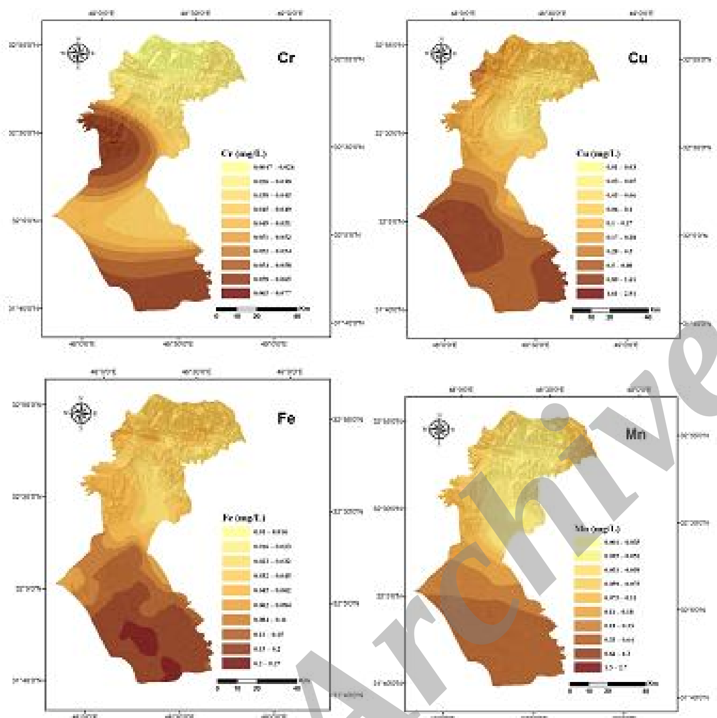

Figure 4. Spatial pattern of Cr, Cu, Fe, Mn in the groundwater resources Andimeshk-Shush aquifer.

DISCUSSION

The results of Mann-Whitney U test showed that there was significant difference between the levels of Fe in the wells and springs (Table1) at 5%significance, which could be because the erosion of the iron tubes in the wells [20].

As it was mentioned earlier, the prevalent land use in Shush-Andimeshk region is for agriculture and industrial activities are rare. Therefore, next to geological formations which are the main sources of Fe and Mn in the groundwater, agricultural activities play a significant role as well. According to the statistics provided from the Andimeshk Agricultural Office, about 51670 tons of manure has been applied in agricultural fields, in 2013. The application of animal waste and poultry manures in agricultural soils is a source of Cu in these areas [21]. Copper is usually used as an additive to the diet of livestock and poultry to improve the growth and prevent diseases [22]. As copper intake by farm animals is almost entirely excreted, the subsequent application of these manures in agricultural fields results in the contamination of soil with this heavy metal [23]. Copper levels in this study ranged from 0.02 to 2.9 mg/l, which was higher than a previous study [24], showing the increasing trend of pollution the area in recent years. Heavy metals are also one of the impurities of agricultural fertilizers resulting in pollution of agricultural lands and the subsequent contamination of ground waters. For instance, the levels of heavy metals in agricultural fertilizers applied in the study area indicated superphosphate with 22.5 mg/kg of copper impurity and CuSo4 with 255000 mg/kg copper [24], were one of the most influential contaminants of ground waters.

The reducing anaerobic conditions in deep groundwater sources release the more soluble Mn (II) from mineral formations [25]. Chromium is mostly available in the environment in two oxidation states, and Cr (VI) has a higher solubility and toxicity with carcinogenic and mutagenic potentials [26]. To consider the accumulated impacts of these four heavy metals on the health of consumers the hazard index was calculated as 1.37. Since this level was higher than one, it indicates that the health of consumers of these water sources is endangered on the long run. The spatial maps of our study confirm the result of Nouri et al. [24], illustrating that the southern parts of the studied region were more contaminated. However, the spatial pattern of chromium in the region is unique, meaning that next to the southern part, in the southwest of Andimeshk, high values of chromium were detected as well.

A study on the risk assessments of heavy metals in the groundwater sources of Ali Abad

Katol [27], showed that Zn and Pb had the highest and lowest influence, respectively. Moreover, the non-carcinogenic hazard index was reported to be 10×10-4 in the autumn and 6.48×10^{-5} for the spring months [27]. The health risk of heavy metals in Kohistan region in the northern part of Pakistan was evaluated and concluded that the hazard quotient of all of the assessed heavy metals were lower than one, implying that there was no health risk associated with heavy metals at the time of the study [28]. The mean hazard quotient reported for Cr, Cu and Mnwas4×10^{-4}, 3.8×10^{-2}, 2.6×10^{-3},respectively, which were lower than the results of the current research[28]. In another research [29], the health risk of heavy metals in the groundwater sources in Swat, in the northern part of Pakistan, was investigated and the hazard quotient of all heavy metals was lower than one. In that study, the health risk of heavy metals in decreasing order was Mn >Cr >Cu, which was dissimilar to our findings [29]. In summary, the hazard quotient in our research was higher than that of previous studies [27-29].

CONCLUSION

Mean concentrations of heavy metals in groundwater sources of the study area in decreasing order was as follows: Cu> Mn> Fe> Cr. Except for iron, mean heavy metal concentration was higher than the standard levels. Manganese concentration in 41.5% of the samples exceeded the permissible limits. Copper was higher than the safety limit in 74% of the samples, and chromium in 54% of the cases. The spatial pattern of heavy metals in the groundwater sources in the region indicated that the patterns in Andimeshk and Shush were different and higher concentrations were mainly detected in Shush area. The mean hazard quotients of most samples for the four heavy metals were lower than one, indicating that there was no immediate threat due to the exposure to these heavy metals. The calculated accumulated hazards of these heavy metals produced different results, with hazard indices of higher than one, indicating that chronic ingestion of these waters threatens the health of local consumers on the long run.

ACKNOWLEDGEMENT

The authors of this paper are grateful to Mr. Eisa Ahmadpour for his cooperation in field activities. The authors declare that there is no conflict of interests.

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