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ORIGINAL ARTICLE

Regional distribution pattern of groundwater heavy metals resulting from agricultural activities

J. Nouri · A. H. Mahvi · G. R. Jahed · A. A. Babaei

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Abstract Contaminations of groundwater by heavy metals due to agricultural activities are growing recently. The objective of this study was to evaluate and map regional patterns of heavy metals (Cd, Zn and Cu) in groundwater on a plain with high agricultural activities. The study was conducted to investigate the concentration of heavy metals and distribution in groundwater in regions of Shush Danial and Andimeshk aquifers in the southern part of Iran. Presently, groundwater is the only appropriate and widely used source of drinking water for rural and urban communities in this region. The region covers an area of 1,100 km^2 between the Dez and Karkhe rivers, which lead to the Persian Gulf. For this study, the region was divided into four sub-regions A, B, C and D. Additionally, 168 groundwater samples were collected from 42 water wells during the earlier months of 2004. The flame atomic absorption spectrometry (AAS-Flame) was used to measure the concentration of heavy metals in water samples and the Surfer software was used for determination of the contour map of metal distribution. The results demonstrated that in all of the samples, Cd and Zn concentrations were below the EPA MCLG and EPA secondary standard, respectively. However, the Cu contents of 4.8 % of all samples were higher than EPA MCL. It is also indicated that the concentrations of metals were more pronounced at the southern part of the studied region than at the others. The analysis of fertilizers applied for agricultural activities at this region also indicated that a great majority of the above-mentioned heavy metals were discharged into the environment. Absence of confining layers, proximity to land surface, excess agricultural activities in the southern part and groundwater flow direction that is generally from the north to the southern parts in this area make the southern region of the Shush plain especially vulnerable to pollution by heavy metals than by other contaminants.

Keywords Heavy metals · Groundwater pollution · Distribution · Agricultural activities

J. Nouri · A. H. Mahvi (✉) · G. R. Jahed · A. A. Babaei
Department of Environmental Health Engineering,
School of Public Health, Medical Sciences/University
of Tehran, P. O. Box 14155-6446, Tehran, Iran
e-mail: ahmahvi@yahoo.com

Introduction

More than 50% of the world's population depends on groundwater for drinking (Fry (2005). For many rural and small communities, groundwater is the only source of drinking water (Hani 1990). Since groundwater moves through rocks and subsurface soil, it has a lot of opportunity to dissolve substances as it moves. Furthermore, they are widely distributed as an anthropogenic pollutant (Rangsivek and Jekel 2005). Heavy metals are encountered in various emission sources related to industrial, transportation and urban activities and agricultural practices (Brantley and Townsend 1999; Romic and Romic 2003), which have environmental adverse effects. Land disposal of municipal and industrial wastes and applications of fertilizers and pesticides for agriculture have contributed to a continuous accumulation of heavy metals in soils (Alloway and Jackson 1991). There is an increased concern regarding the environmental impacts of agricultural practices on the bioavailability and leaching of heavy metals. Fertilizers are usually not sufficiently purified during the processes of manufacture; for economic reasons, they usually contain several impurities, among them, heavy metals (Santos et al. 2002; Tanji and Valoppi 1989). Also, heavy metals often form a part of the active compounds of pesticides. Surpluses of heavy metals in soils are frequently caused by the use of fertilizers, metallo-pesticides and sewage sludge. Among the fertilizers that are being used in farmlands, superphosphate contains the highest concentrations of Cd, Cu and Zn as impurities. Copper sulfate and iron sulfate have the highest contents of Pb and Ni (Eugenia et al. 1996). With sufficient surface water infiltration, soil contaminants, such as heavy metals, can leach to underlying groundwater. Unconfined aquifers with shallow water tables overlain by permeable soils are especially vulnerable to various contaminants. The industrial developments and the fact that most contaminants penetrate into soils and eventually groundwater have caused pollution increase, all acting as a threat to today's world. Cd is a heavy metal with chemical properties similar to Zn, but is much less common in the environment than Zn. Cd occurs in igneous rocks and some sedimentary rocks, which is generally associated with Zn ore minerals like sphalerite and with a range of Cu ore minerals (Picker et al. 1992; Pogotto et al. 2001). Cd is often present in artificial fertilizers and this heavy metal may accumulate in soils in areas that have been used for agriculture for long periods (Rattan et al. 2005; Mahvi et al. 2005; Nouri et al. 2006). Concentrations of Cd in water are only likely to be of concern to health, in environments where pH is less than 4.5. Information on the quality of water sources is of great importance in water quality management of water supplied fields. Some countries have set tolerance limits on the addition of heavy metals to soils because of their long-term effects on human, animals and plants. Control on concentrations of heavy metals in fertilizers and sewage sludge and maximum total and annual loading rates to soil have been imposed in some countries (Hani 1990; Muchuweti et al. 2006).

The objective of this study was to evaluate and map regional patterns of heavy metals (Cd, Zn and Cu) in groundwater in a plain with high agricultural activities. The chemical fertilizers, with the different heavy metal contents, which were applied in the Shush and Andimeshk region are shown in Table 1. This study was carried out in Shush and Andimeshk plain regions in the southern part of Iran during 2004–2005.

Table 1 Heavy metal contents of applied chemical fertilizers in the Shush and Andimeshk aquifer (mg/kg)

Applied fertilizers	Cd	Zn	Cu
Urea	0.03	ND	1.0
Super phosphate	12.2	60	22.5
$CuSO_4$	1.5	25.6	255×10^3
$FeSO_4$	0.2	20.5	1.3

ND Not detectable

Materials and methods

The Shush and Andimeshk plains cover an area of approximately 1,100 km^2 in Khozestan, Iran. These plains fall within 35°50′–10°50′N and 23°30′–25°20′E. Figure 1 shows the distribution of the locations of wells in the sampling sites in the studied area. Groundwater levels in the studied area were generally <2 m to more than 88 m below the ground surface. Average water level fluctuations were very low: about 0.5–1 m between dry and wet seasons because of continuous recharges with Dez and Karkhe

Fig. 1 Sampling sites distribution of well locations in the Shush and Andimeshk aquifer

rivers. According to topsoil types, the studied area was divided into four sub-regions A, B, C and D in the flow direction of groundwater. The dominant topsoil overlying the aquifer consisted of sand and gravel with major silt and till content in the sub-region A and with major silt and till and minor clay in the sub-region B. The clay content of topsoil in sub-region C was higher than in sub-region B, and sub-region D had clay topsoil. The soils were generally well drained in the Andimeshk plain, but in the Shush plain they were not. The aquifer was recharged primarily with Dez and Karkhe rivers. Furthermore, in the sub-regions B, C and D, irrigation of farmlands with surface waters (Dez irrigation network) recharged the aquifer during the year.

The water wells used to sample groundwater were selected in such a manner as to represent geographically the whole study area. A total of 168 groundwater samples were taken from 42 water wells. The depth at which water was sampled was around 10 m. below the groundwater table for each well. Sampling and water analyses were completed during the months of April, May, August and September of 2004. Groundwater samples were taken

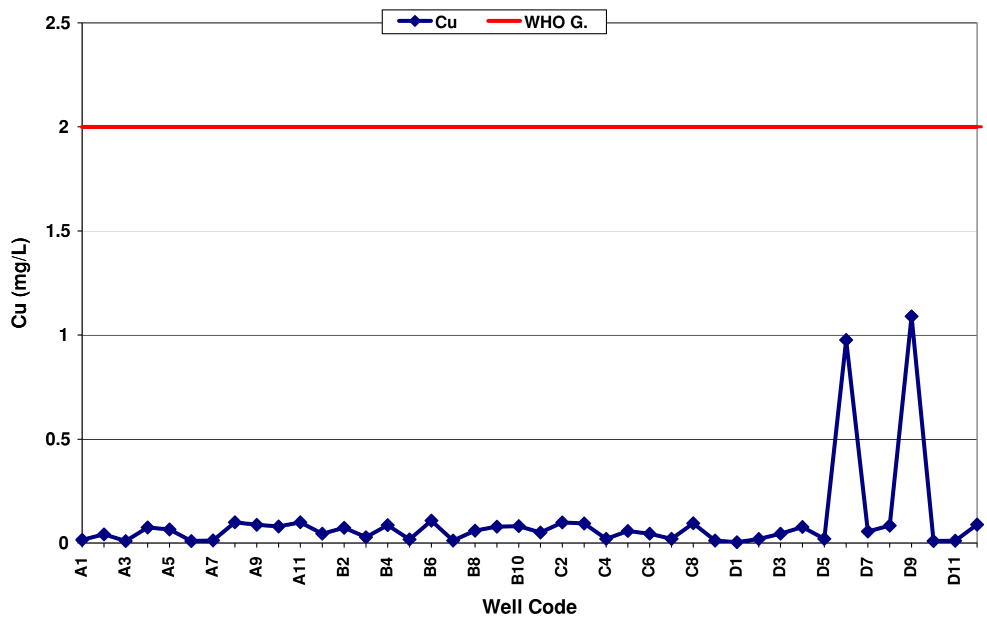

Fig. 2 Comparison of the average concentration of Cu in the Shush and Andimeshk aquifer with WHO guidelines

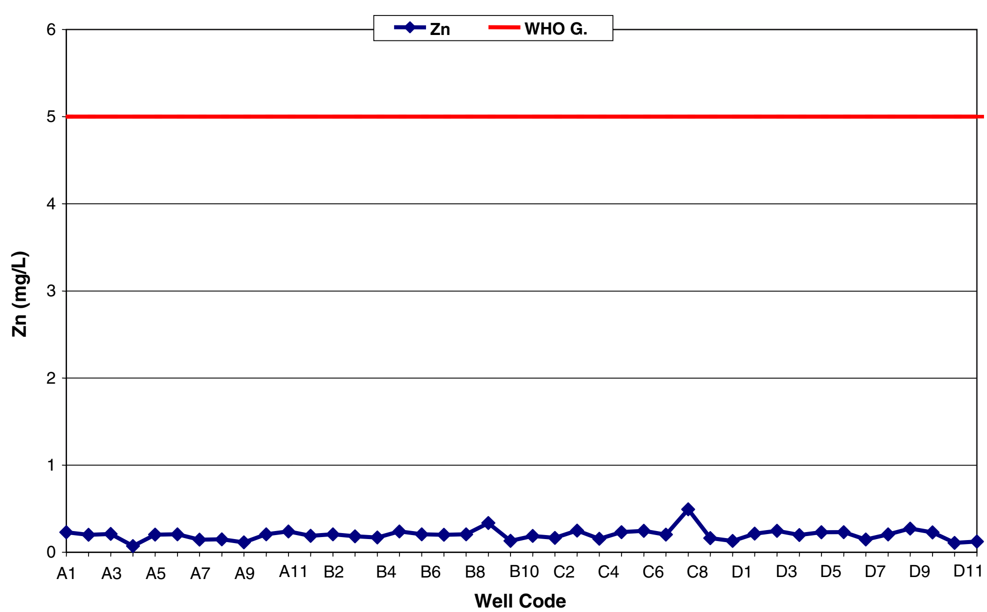

Fig. 3 Comparison of the average concentration of Zn in the Shush and Andimeshk aquifer with WHO guidelines

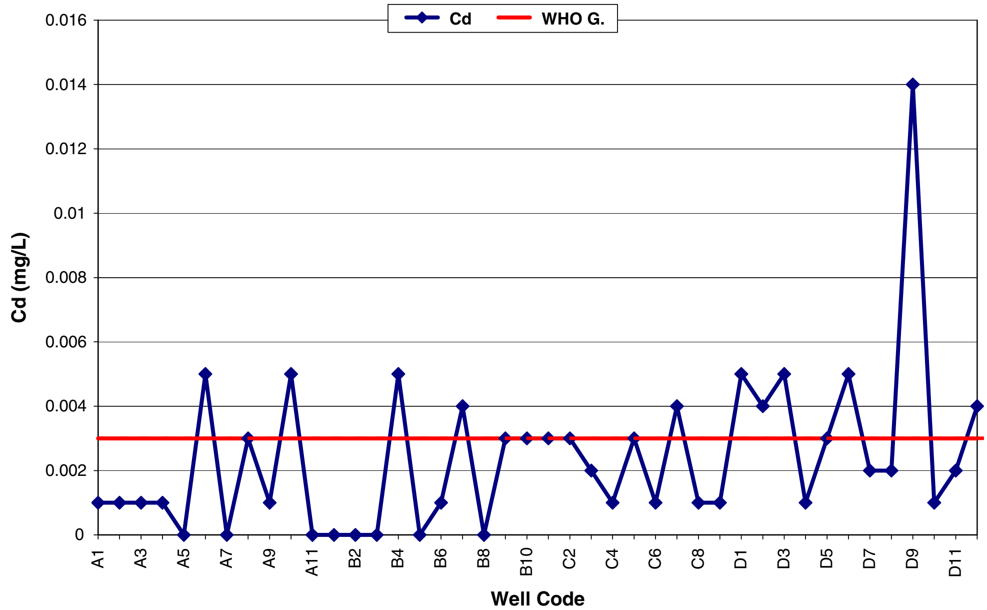

Fig. 4 Comparison of the average concentration of Cd in the Shush and Andimeshk aquifer with WHO guidelines

by means of well pumps after a pumping period of at least 30 min. Each well was sampled four times. The samples were acidified to a pH < 2 with concentration with nitric acid at collection sites, transported to laboratory and then stored in a refrigerator at approximately –20°C to prevent change in volume due to evaporation. According to AAS-flame procedure in standard methods for water and wastewater examination (20th Edn.), the samples were concentrated before analyzing (APHA 1998).

Results and discussion

The results indicated the heavy metal concentrations of groundwater for 42 water wells that were sampled in Shush and Andimeshk plains (Fig. 1). In comparison, sub-regions A, B, C and D showed different amounts of Cu, Zn and Cd content. Figures 2, 3 and 4 compare these with the WHO guidelines. The mean concentrations of heavy metals in groundwater in comparison with EPA standards were as follows: Cd, 0.002–0.005 mg/l; Zn, 0.194–0.233 mg/l and Cu, 0.054–0.207 mg/l (Fig. 5). The results indicated that all of the samples had concentrations that were below the WHO guidelines, except for Cd in the samples. Table 2

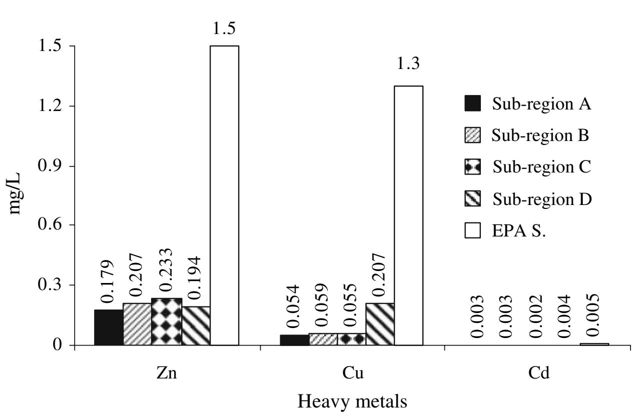

Fig. 5 Comparison of average concentrations of heavy metals in the Shush and Andimeshk aquifer with EPA standards

Fig. 6 Groundwater flow direction in the Shush and Andimeshk aquifer

Table 2 Heavy metals average content of groundwater in the Shush and Andimeshk aquifer

Sub-region	Well code	Depth (m)	Water table (m)	Cd (mg/l)	Zn (mg/l)	Cu (mg/l)
A	A_{1}	130	16	0.001	0.230	0.015
	A_{2}	150	15	0.001	0.200	0.420
	A_{3}	130	72	0.001	0.210	0.010
	A_{4}	150	62	0.001	0.072	0.075
	A_{5}	100	20	ND	0.203	0.065
	A_{6}	100	52	0.005	0.206	0.010
	A_{7}	60	30	ND	0.144	0.013
	A_{8}	120	62	0.003	0.149	0.100
	A_{9}	120	54	0.001	0.114	0.088
	A_{10}	120	39	0.005	0.206	0.080
	A_{11}	90	32	ND	0.239	0.100
B	B_{1}	70	30	ND	0.189	0.045
	B_{2}	100	38	ND	0.207	0.073
	B_{3}	55	15	ND	0.184	0.028
	B_{4}	120	12	0.005	0.169	0.086
	B_{5}	45	27	ND	0.240	0.018
	B_{6}	80	8	0.001	0.206	0.108
	B_{7}	80	10	0.004	0.200	0.012
	B_{8}	50	4	ND	0.200	0.060
	B_{9}	100	8	0.003	0.207	0.079
	B_{10}	70	4	0.003	0.336	0.081
C	C_{1}	80	5	0.003	0.132	0.051
	C_{2}	80	3	0.003	0.166	0.099
	C_{3}	100	6.25	0.002	0.249	0.094
	C_{4}	60	2	0.001	0.154	0.020
	C_{5}	42	8.5	0.003	0.232	0.058
	C_{6}	7	5	0.001	0.246	0.045
	C_{7}	100	6.5	0.004	0.203	0.020
	C_{8}	10	8	0.001	0.494	0.0
	C_{9}	45	4	0.001	0.162	0.012
D	D_{1}	6	3	0.005	0.129	0.004
	D_{2}	100	7	0.004	0.214	0.019
	D_{3}	60	6	0.005	0.247	0.045
	D_{4}	90	4	0.001	0.198	0.077
	D_{5}	70	8	0.003	0.229	0.020
	D_{6}	80	6	0.005	0.231	0.976
	D_{7}	80	4	0.002	0.147	0.056
	D_{8}	100	8	0.002	0.205	0.084
	D_{9}	16	10	0.014	0.272	1.090
	D_{10}	100	3	0.001	0.228	0.011
	D_{11}	120	8	0.002	0.108	0.011
	D_{12}	100	2.5	0.004	0.123	0.089

ND not detectable

shows the depths of wells and water tables in the sub-regions of A, B, C and D, along with the concentrations of heavy metals. Amongst 42 tested water wells, 17 water

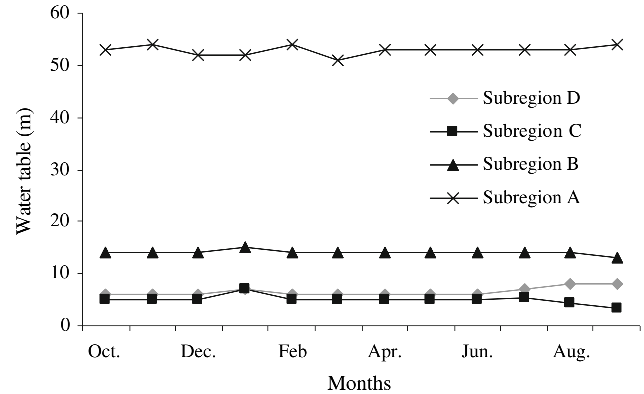

Fig. 7 Water table fluctuations in the Shush and Andimeshk aquifer

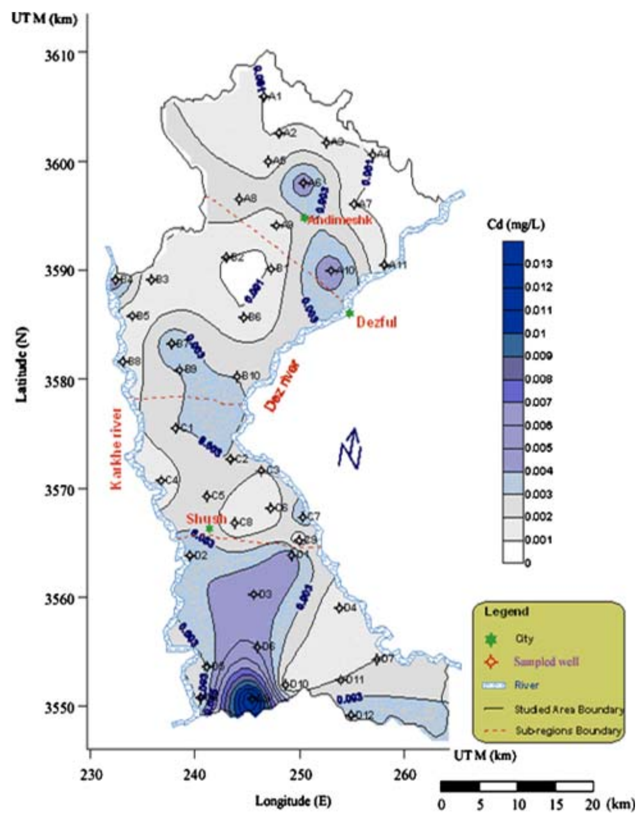

Fig. 8 Distribution of Cd concentration in the Shush and Andimeshk aquifer

wells had lead concentration that exceeded the WHO guidelines (WHO 1997) and were used as follows:

– Ten wells were used for water supply;
– one was used for ice production;
– one was used for aquaculture;
– five were used for other purposes such as poultry, agriculture, household washing, and sand washing industry. Annually, water table fluctuations in the studied region were on average 51.9–53.2 m, 14.1–

14.8 m, 4.6–6.0 m and 4.4–5.6 m in sub-regions A, B, C and D, respectively. Groundwater flow direction in the studied region in the mapping diagram is also shown in Fig. 6. This direction is downward from north to south of the region. The studied region's water table fluctuations are indicated in Fig. 7. This figure indicated that the sub-region A had a bigger fluctuation than the sub-regions B, C and D.

The values of distribution of Cd, Zn and Cu concentrations in groundwater of the studied region are presented in Figs. 8, 9 and 10, which were applied to various maps. These maps provide a basis for making area-wide generalizations concerning the distribution of water quality parameters and serve to isolate water quality problem areas. There were also few differences between the contents of groundwater heavy metals in each sub-region. Cd and Cu were concentrated at the bottom of the region and Zn tended to be present more on the middle part of the studied region, during the spring and summer at the time of study. Meanwhile, it is necessary to mention that there was high Cu and Cd average concentration between wells D6 and D9. It was presumed, during the samplings that this was an unexpected happening which was arisen by the local authority. A chemical fertilizer truck was loaded between wells D6 and D9 for a few days in order to apply fertilizer for the agricultural lands. It was presumed that this notably high Cu and Cd concentration could have arisen due to water leaching into the mentioned wells. However, this loaded bulk was immediately cleaned up a few days after by the local authority.

Conclusion

On the whole, in the studied area, the concentrations of Cd and Zn were below the value of WHO guidelines for drinking water. However, the Cu content of some samples surpassed the above guidelines. The concentration of heavy metals in groundwater was more pronounced in the southern part than in the northern part of the studied area. Absence of confining layers, proximity to land surface, excess agricultural and industrial activities, highest TDS content of groundwater in south part and groundwater flow direction that is generally from north to south in this area makes the southern region of the Shush plain especially vulnerable to pollution by heavy metals and other contaminants. Deeper zones of Shush and Andimeshk aquifers, north of the studied area, had higher Zn concentration than the other areas, due to the anaerobic conditions in the deeper zones and iron influence by macro element fertilizers, such as ferrous sulfate and ferrous nitrate application in permeable agricultural lands. Absence of confining

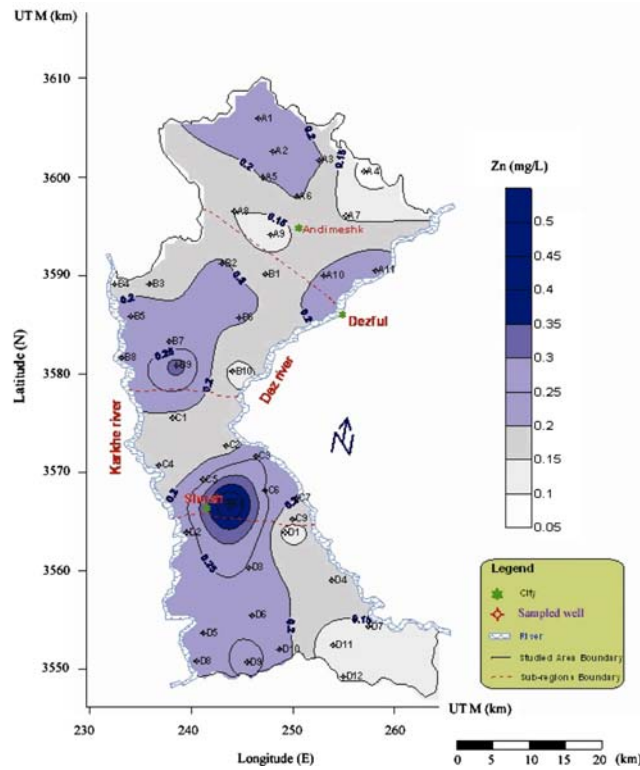

Fig. 9 Distribution of Zn concentration in the Shush and Andimeshk aquifer

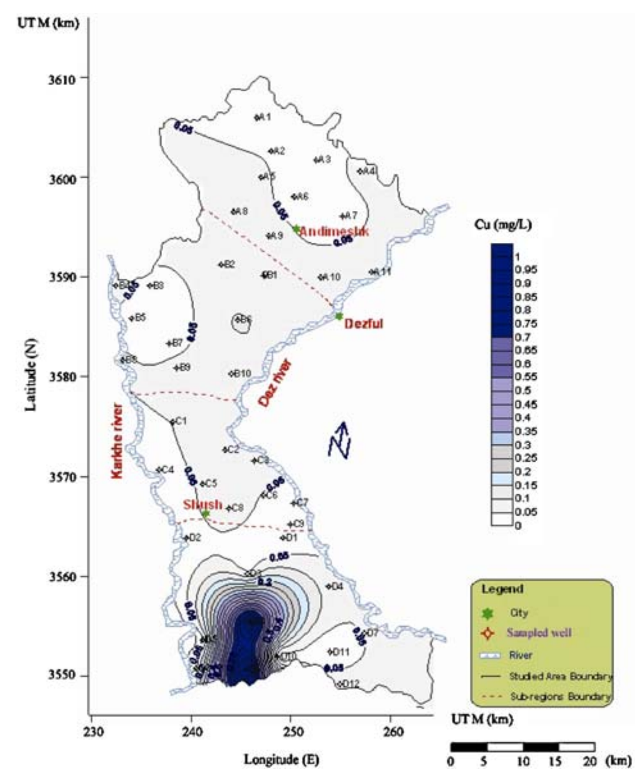

Fig. 10 Distribution of Cu concentration in the Shush and Andimeshk aquifer

layers, proximity to land surface, excess agricultural and industrial activities in south part and groundwater flow direction that is generally from north to south parts in this area makes south region of Shush plain especially vulnerable to pollution by heavy metals and other contaminants. The local economy depends largely on farming. Tourism and manufacturing also contribute to the area's economy. The Shush and Andimeshk aquifer comprise a succession of Dez and Balarood seasonal river deposits interspersed with minor silt in the Andimeshk plain, and Dez and Karkhe rivers sand and gravel deposits interspersed with major clayey silt lenses in the Shush plain. Within the catchment area of the Shush and Andimeshk plains, various lithological units range from the Cenozoic (Pliocene) to Quaternary age. Quaternary age deposits consist of alluvium, which contains loose, interlayer clay, silt, sand and gravel. The thickness of the alluvium is about 200–300 m. The Shush and Andimeshk aquifer is the primary source of groundwater in the study area, supplying approximately 100% of the total drinking water for about 180,000 people who are settled in this area. Groundwater applications in the studied area include municipal and rural water supply, individual household supply, irrigation of farmlands and industrial use. Annual precipitation based on the average of 1961–2000 in the studied area was approximately 270 mm and more than nearly 80% of total precipitation occurred during the December–April period. In comparison, annual potential evaporation is about 1,670 mm, which is six times higher than the annual precipitation (AOKC 2003). Farms occupy over 70% of the studied area, where the main agricultural crops are wheat, corn and sugarcane. Nearly more than 75% of farmlands in the studied area were irrigated with surface waters from the Dez irrigation network and the rest (less than 25%) were irrigated with groundwater (AOKC 2003). The wells that supply water for various purposes have been drilled into the alluvial aquifer. In general, the depths of the wells range from 6 to 150 m. The aquifer has transmissivity and hydraulical conductivity values of 10^{-2}–10^{-5} m^2/s and 10^{-4}–10^{-6} m^2/s, respectively. Application of the best management practices (BMPs) in agricultural regions of the studied areas is necessary for minimizing the chemical contaminants discharge into the groundwater. Investigation of other heavy metals and other chemicals occurrences, on a long-term period at the Shush and Andimeshk plains is also recommended.

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