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Investigation of Heavy Metals in Groundwater

J. Nouri, A.H. Mahvi, A.A. Babaei, G.R. Jahed and E. Ahmadpour
Department of Environmental Health Engineering, Center for Environmental Research,
School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

Abstract: The objective of this study was to evaluate and map regional patterns of heavy metals (Cu, Cd, Ni and Zn) occurrence in south of Iran. The study was performed in Shush and Andimeshk plains in the south part of Iran, with high agricultural activities that cover an area of 1100 km^2 between the Dez and Karkhe rivers. This region was divided into four sub-regions A, B, C and D. Additionally 168 groundwater samples were collected from 42 water wells during the months April, May, August and September of 2004. The Flame Atomic Absorption Spectrometry (AAS-Flame) was used to measure the heavy metals concentration in water samples. The results demonstrated that all of the samples, Cu, Zn and Ni concentrations have been shown below the EPA MCLG, EPA secondary standard and EPA MCL, respectively, but Cd, contents of 4.8% of all samples was higher than EPA MCL. The heavy metals concentration is more pronounced in south part than northern part of the studied area. Absent confining 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 heavy metals pollution and other contaminants.

Key words: Heavy metals, groundwater, aquifer, Shush, Andimeshk and Iran

INTRODUCTION

Only a small fraction (about 2.5%) of earth's water is fresh and suitable for human consumption. Approximately 13% of this fraction is groundwater; an important source of drinking water for many people worldwide (Bachmat, 1994). For example, more than 50% of the world's population depends on groundwater for drinking water. For many rural and small communities, groundwater is the only source of drinking water (Canter, 1987). Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic or industrial application (Petrus *et al*., 2005). Natural heavy metals concentrations in soils are due to erosion and weathering of parent rocks. Some trace elements, such as Cu and Zn, are necessary in low concentrations for all living organisms while most of them present toxicity hazards at high concentrations (Merian, 1991). Urbanization (Harrison and Wilson, 1985; Garcia *et al*., 1996; Pitt, 1996; Pagotto *et al*., 2001; Rangsivek and Jekel, 2005), industrial activities (Brantley and Townsend, 1999) and agricultural practices (fertilizers and pesticides application to farmlands) have environmental adverse effects (e.g., groundwater contamination with heavy metals). Because fertilizers are usually not sufficiently purified during the processes of manufacture, for economic reasons, they usually contain several impurities, among them heavy metals. Also, heavy metals often form a part of the active compounds of pesticides. A surplus of heavy metals in soils is frequently caused by using fertilizers, metallo-pesticides and sewage sludge. Among the fertilizers that used in farmlands, superphosphate contains the highest concentrations of Cd, Co, Cu and Zn as impurities. Copper sulfate and iron sulfate have the highest contents in Pb and Ni (Eugnia *et al*., 1995), urban runoff (Allen *et al*., 2002) and industrial activities that can be transport to groundwater with recharged waters. 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 development and the fact that most contaminants penetrates into soils and eventually groundwater have caused pollution increase, all acting as a threat to today's world. Information on the water sources quality is of great importance in the water quality management and water supplies field. Some countries have set tolerance limits on heavy metals additions to soils because their long-term effects on human, animals and plants. Control on heavy metals concentrations in fertilizers and sewage sludge and maximum total and annual loading rates to soil have been imposed in some countries (Hani, 1990).

Corresponding Author: J. Nouri, Department of Environmental Health Engineering, Center for Environmental Research, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

The objective of this present study was to investigate the heavy metals contamination of groundwater in Shush and Andimeshk plains in the south of Iran, with high agricultural activities in these areas.

MATERIALS AND METHODS

The Shush and Andimeshk plains cover an area of approximately 1100 km^2 in Khozestan-Iran. These plains are located north of Khozestan (32°, 00'-32°, 35' N 48°, 10'-48°, 25'E). The local economy depends largely upon farming. Tourism and manufacturing also contribute to the area's economy. The Shush and Andimeshk aquifer is comprised of a succession of Dez and Balarood seasonal river deposits interspersed with minor silt in Andimeshk plain and Dez and Karkhe rivers sand and gravel deposits interspersed with major clayey silt lenses in Shush plain. Within the catchments area of the Shush and Andimeshk plains, various lithological units ranges from Cenozoic (Pliocene) to Quaternary in age. Quaternary-age deposits consist of alluvium, which is contains of 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 180000 people that settlement in this area. Groundwater applications in the study area are municipal and rural water supply, individual household supply, irrigation of farmlands and industrial. Annual precipitation in based on the average of 1961-2000 in the study area is approximately 270 mm that nearly more than 80% of total precipitation occurred during the December-April period. In comparison, annual potential evaporation is about 1670 mm that it is 6 times higher than annual precipitation (Water and Electric Organization of Khozestan County, 2000). Farms occupy over 70% of the study area, that the main agricultural crops are wheat, corn and sugar-cane. Nearly more than 75% of farmlands in studied area irrigated with surface waters from Dez irrigation network and the rest (less than 25%) irrigated with groundwater (Agriculture Organization of Khozestan County, 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 6-150 m. The aquifer has transmissivity and hydraulical conductivity values mostly 10^{-2}-10^{-5} m^2 sec^{-1} and 10^{-4}-10^{-6} m sec^{-1}, respectively. Groundwater levels, in study area, are generally <2 m to more than 88 m below the ground surface. Average water-level fluctuations are very low; about 0.5-1 m between dry and wet seasons because of continues recharge with Dez and Karkhe rivers. The general direction of groundwater flow is southward.

According to topsoil type we divided the studied area to four sub-regions A, B, C and D in groundwater flow direction. The dominant topsoil overlaying the aquifer consist sand and gravel with major silt and till in sub-region A and with major silt and till and minor clay in sub-region B. The clay content of topsoil in sub-region C is higher than sub-region B and sub-region D has clayey topsoil. The soils are generally well drained in Andimeshk plain but in Shush plain are not. The aquifer is recharges primarily with Dez and Karkhe rivers. Furthermore, in sub-regions B, C and D irrigation of farmlands with surface waters (Dez irrigation network) recharges the aquifer during the year (Water and Electric Organization of Khozestan County, 2000).

The water wells used to sample groundwater were selected in such a manner to represent geographically the whole study area. From 42 water wells, 168 groundwater samples were taken. Sampling and water analyses were completed during the months of April, May, August and September of 2004. Each well was sampled four times and 4 heavy metals (Cu, Cd, Ni and Zn) were analyzed in these waters. The procedures recommended by APHA *et al.* (1998) were followed during the field and laboratory work. Groundwater samples were taken by means of well pumps after a pumping period of at least 30 minutes. Samples acidified to pH<2 with conc. Nitric acid on collection sites, transport to laboratory and then stored in a refrigerator at approximately 4°C to prevent change in volume due to evaporation. According to AAS-Flame procedure in standard methods for water and wastewater examination (20th Ed.), we concentrate the samples before analyzing (APHA *et al.*, 1998).

RESULTS AND DISCUSSION

Table 1 shows the heavy metals concentrations of groundwater at 42 water wells that were sampled in Shush and Andimeshk plains. In comparison, sub-regions A, B, C and D show different means in each heavy metals contents, which shows in Fig. 1. Regarding to the four sub-regions, the sub-region D had highest average Cu, Cd and Ni concentrations in groundwater. According to results the highest Zn concentrations was observed in sub-region C. Concentrations of heavy metals in groundwater are as follows: Cu, 0.003-1.2 mg L^{-1}, Zn, 0.065-0.51 mg L^{-1}, Cd and it was to 0.015 mg L^{-1} and Ni, 0.009-0.083 mg L^{-1}. The average groundwater Cu, Zn, Cd and Ni concentrations for the studied area showed 0.1, 0.2, 0.003 and 0.025 mg L^{-1}, respectively. The results indicated that all of samples Cu, Zn and Ni concentrations were below the EPA drinking water standards, but in 4.8% of samples Cd concentration was more than EPA MCL (0.005 mg L^{-1}).

Figure 2-5, maps provide a basis for making area-wide generalizations concerning the distribution of water-quality parameters and they serve to isolate water-quality

Table 1: Heavy metals contents of groundwater in studied area

Sub-region	Well code	Depth (m)	Water table (m)	Cu (mg L^{-1})	Cd (mg L^{-1})	Ni mg L^{-1})	Zn (mg L^{-1})
A	A_1	130	16	0.015	0.001	0.022	0.23
	A_2	150	15	0.042	0.001	0.026	0.2
	A_3	130	72	0.01	0.001	0.017	0.21
	A_4	150	62	0.075	0.001	0.022	0.072
	A_5	100	20	0.065	ND*	0.031	0.203
	A_6	100	52	0.01	0.005	0.021	0.206
	A_7	60	30	0.013	ND	0.024	0.144
	A_8	120	62	0.1	0.003	0.019	0.149
	A_9	120	54	0.088	0.001	0.019	0.114
	A_{10}	120	39	0.08	0.005	0.018	0.206
	A_{11}	90	32	0.1	ND	0.012	0.239
B	B_1	70	30	0.045	ND	0.022	0.189
	B_2	100	38	0.073	ND	0.028	0.207
	B_3	55	15	0.028	ND	0.017	0.184
	B_4	120	12	0.086	0.005	0.019	0.169
	B_5	45	27	0.018	ND	0.021	0.24
	B_6	80	8	0.108	0.001	0.021	0.206
	B_7	80	10	0.012	0.004	0.024	0.2
	B_8	50	4	0.06	ND	0.029	0.207
	B_9	100	8	0.079	0.003	0.041	0.336
	B_{10}	70	4	0.081	0.003	0.025	0.132
C	C_1	80	5	0.051	0.003	0.026	0.187
	C_2	80	3	0.099	0.003	0.049	0.166
	C_3	100	6.25	0.094	0.002	0.029	0.249
	C_4	60	2	0.02	0.001	0.017	0.154
	C_5	42	8.5	0.058	0.003	0.019	0.232
	C_6	7	5	0.045	0.001	0.016	0.246
	C_7	100	6.5	0.02	0.004	0.019	0.203
	C_8	10	8	0.095	0.001	0.021	0.494
	C_9	45	4	0.012	0.001	0.017	0.162
D	D_1	6	3	0.004	0.005	0.02	0.129
	D_2	100	7	0.019	0.004	0.014	0.214
	D_3	60	6	0.045	0.005	0.02	0.247
	D_4	90	4	0.077	0.001	0.024	0.198
	D_5	70	8	0.02	0.003	0.029	0.229
	D_6	80	6	0.976	0.005	0.074	0.231
	D_7	80	4	0.056	0.002	0.031	0.147
	D_8	100	8	0.084	0.002	0.038	0.205
	D_9	16	10	1.09	0.014	0.049	0.272
	D_{10}	100	3	0.01	0.001	0.024	0.228
	D_{11}	120	8	0.011	0.002	0.011	0.108
	D_{12}	100	2.5	0.089	0.004	0.047	0.123

*ND = Not Detectable

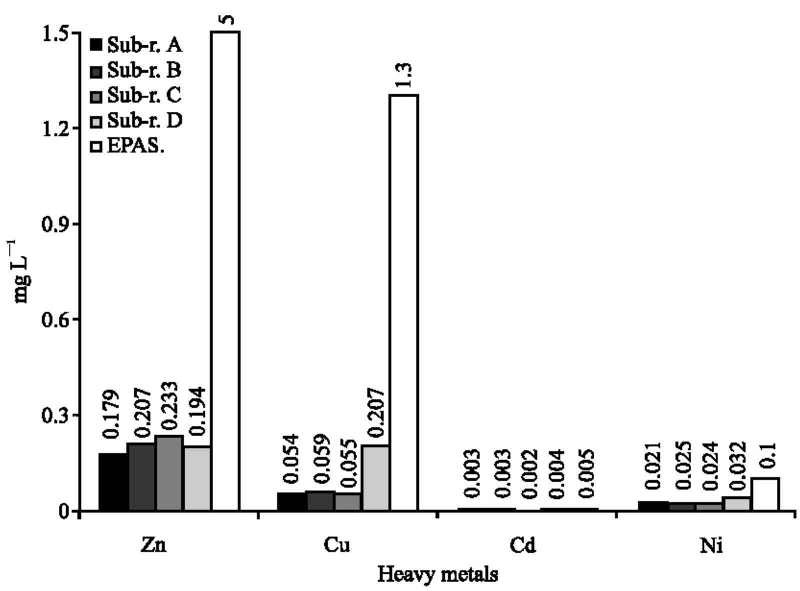

Fig. 1: Comparison of heavy metals average concentrations in studied area with EPA standards

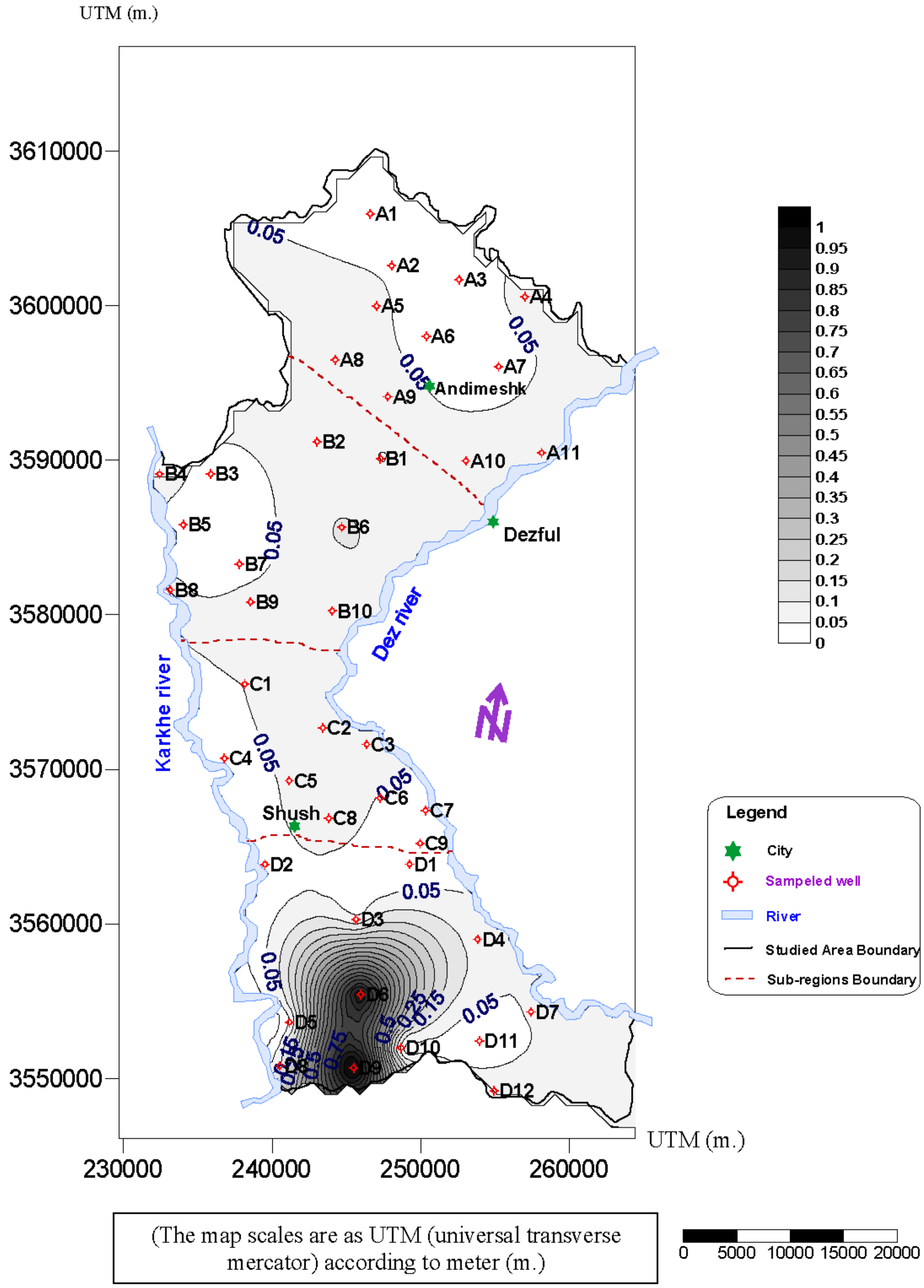

Fig. 2: Distribution of Cu (mg L^{-1}) in Shush and Andimeshk aquifer

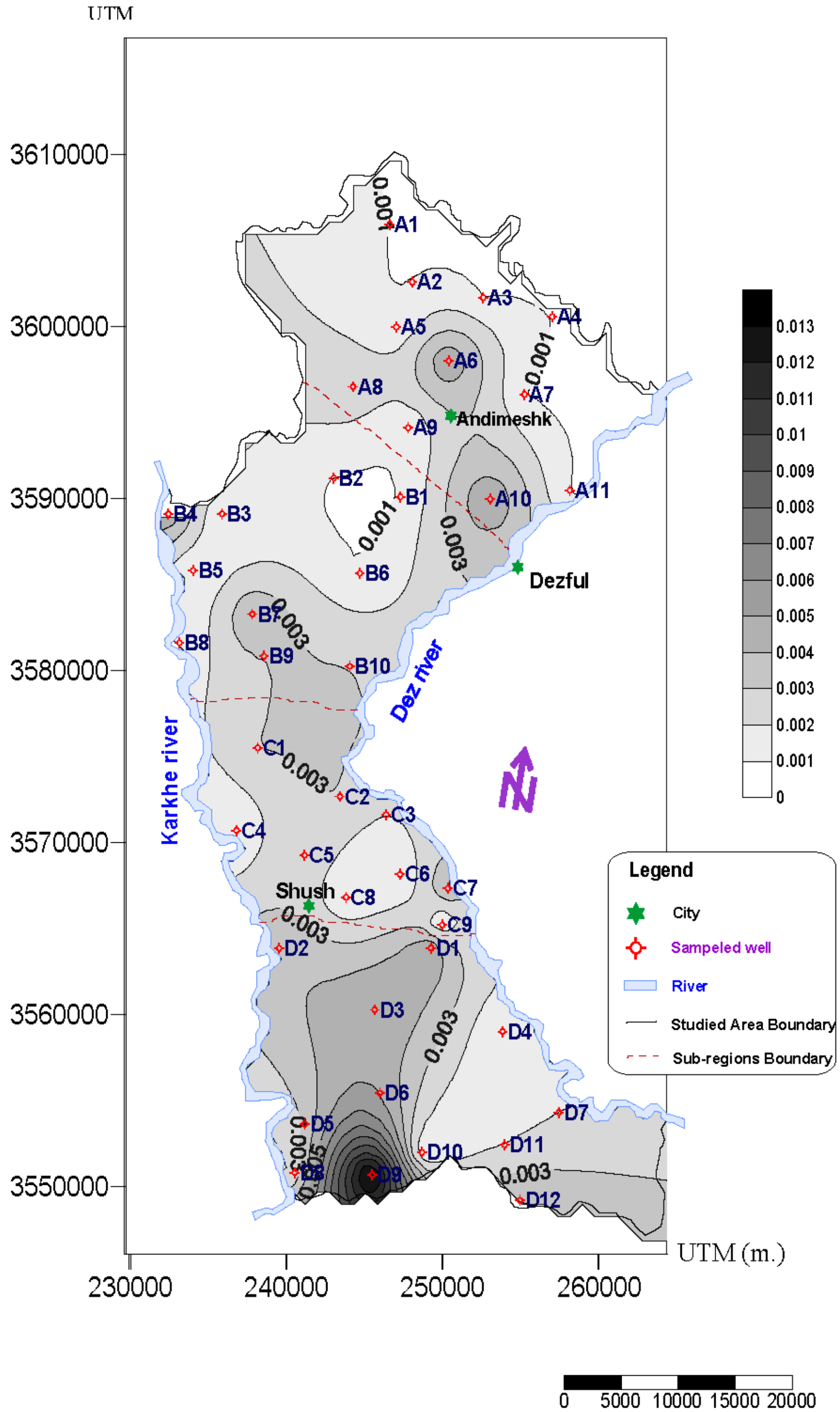

Fig. 3: Distribution of Cd (mg L^{-1}) in Shush and Andimeshk aquifer

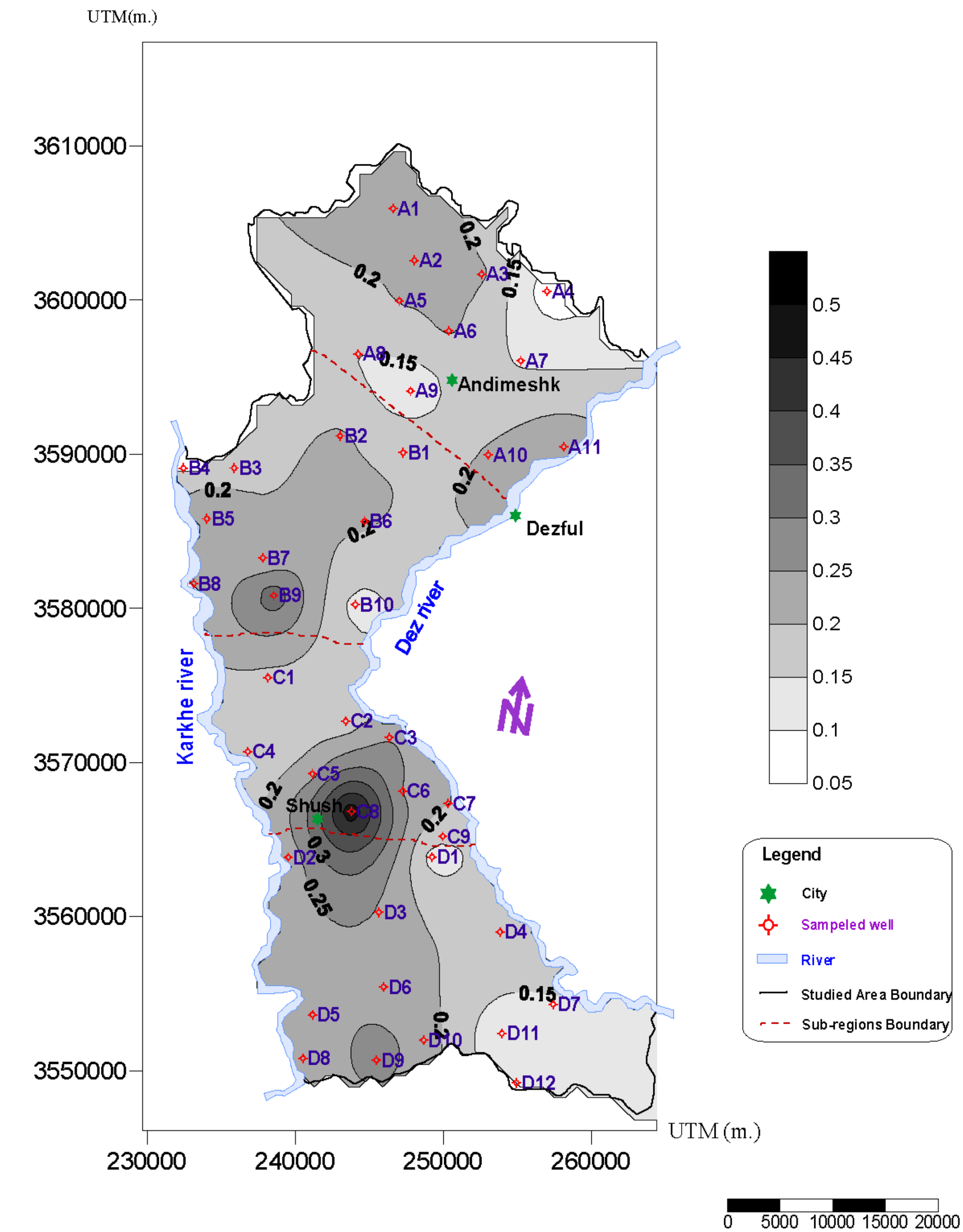

Fig. 4: Distribution of Zn (mg L^{-1}) in Shush and Andimeshk aquifer

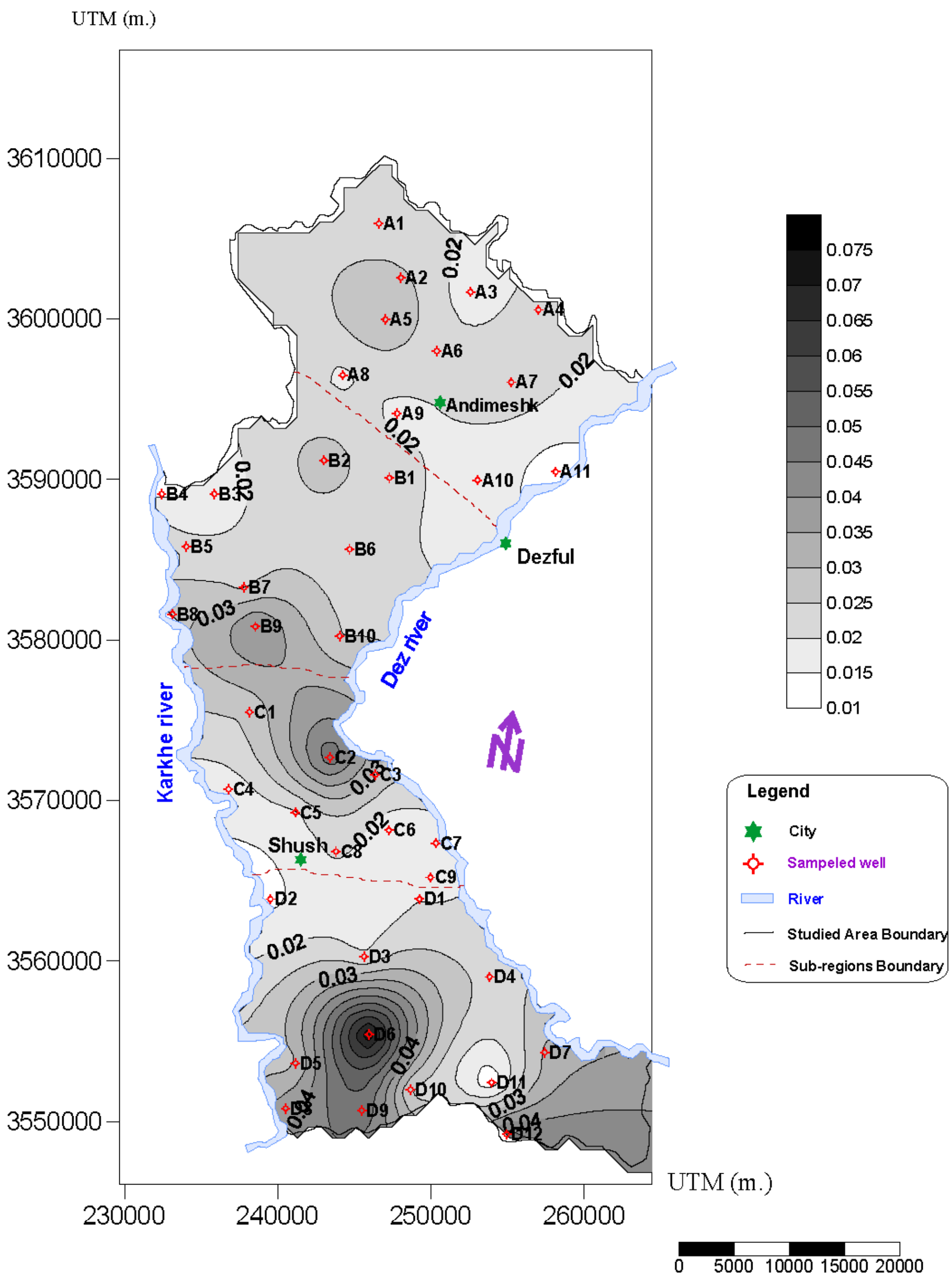

Fig. 5: Distribution of Ni (mg L^{-1}) in Shush and Andimeshk aquifer

problem areas. As shown in Fig. 3, high Cd concentrations occurred at the sites of 5 water wells (A_6, B_4, D_1, D_3 and D_9).

Annually water table fluctuations in the studied area are averagely 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. There are a few differences between groundwater mean heavy metals contents, during spring and summer 2004, in each sub-regions of the studied area.

CONCLUSIONS

In overall the studied area concentration of Cu, Zn and Ni were below the drinking water standards, but Cd content of some samples surpassed the drinking water standard. The heavy metals concentration is more pronounced in South part than Northern part of studied area. Absent 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 south region of Shush plain especially vulnerable to heavy metals pollution and other contaminant. Deeper zones of Shush and Andimeshk aquifer at the North of Andimeshk city had lower heavy metals concentration than other area. Agricultural practices, especially cultivation, fertilization and pesticides application in farm lands are principal causes of heavy metals contamination over a regional scale. The principal significance of this research is that shows which Shush and Andimeshk regions has been impacted by heavy metals. Heavy metals concentrations in the Eastern and Western parts of Shush and Andimeshk plains were lower compared to other parts of these plains, because of continues discharge of Dez and Karkhe rivers to this aquifer.

It is therefore proposed that application of BMPs (Best Management Practices) in agricultural regions of studied areas to minimize the chemical contaminants discharge into the groundwater. Investigation of other heavy metals and other chemicals occurrences, in long term period at Shush and Andimeshk plains is offered.

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