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An Experimental Study of Macro and Micro Elements in Groundwater

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Abstract: The objective of this study was to evaluate and map regional patterns of two macro elements (Fe and Mn) and two micro elements (Pb and Cr), that all of these grouped as heavy metals, occurrence in ground water. 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, Fe and Cr concentrations have been shown below the WHO guidelines, but Mn and Pb contents of 7.1 and 40.5% of all samples was higher than WHO guidelines respectively. The Fe concentration is more pronounced in north part than southern part but groundwater Mn and Pb contents in south part is higher than northern part of studied area. The Cr contents of groundwater in studied area not follow particular pattern but its concentration was higher in sub-regions B and D compared to sub-regions A and C. 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: Macro and micro elements, Groundwater, Shush and Andimeshk, 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. Since groundwater moves through rocks and subsurface soil, it has a lot of opportunity to dissolve substances as it moves. Iron and manganese are common metallic elements found in the earth's crust (Oram, 1995), that water percolating through soil and rock can dissolve minerals containing iron and manganese and hold them in solution (Spellman, 2001). It is well known that Cr (VI) compounds are toxic and carcinogenic. Furthermore, they are widely distributed as an anthropogenic pollutant (Kim *et al*., 2001). Heavy metals are encountered in various emission source related to automobiles. Vehicle exhaust had provided the main source of lead (Nriagu, 1990) due to the use of leaded gasoline. Urbanization (Harrison and Wilson 1985; Garcia *et al*., 1996; Pitt, 1996; Pagotto *et al*., 2001; Rangsivek, 2005), industrial activities and agricultural practices (fertilizers and pesticides application to farmlands) (Brantley and Townsend, 1999; Spellman, 2001) have environmental adverse effects (e.g., groundwater contamination with heavy metals). In urban runoff samples, copper, lead and zinc are detected over 90% frequency, cadmium and chromium to a lesser extent (Pitt, 1996). 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

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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. Some macro elements, such as Fe and Mn, are necessary in low concentrations for all living organisms while most of them present toxicity hazards at high concentrations. 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).

The objective of this present study is to investigate and map the macro and micro elements 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^{-z}, respectively. Groundwater levels, in study area, are generally <2m to more than 88m 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 2 macro elements (Fe and Mn) and 2 micro elements (Pb and Cr) 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, we concentrate the samples before analyzing.

RESULTS AND DISCUSSION

The results show the macro and micro elements concentrations of groundwater at 42 water wells that were

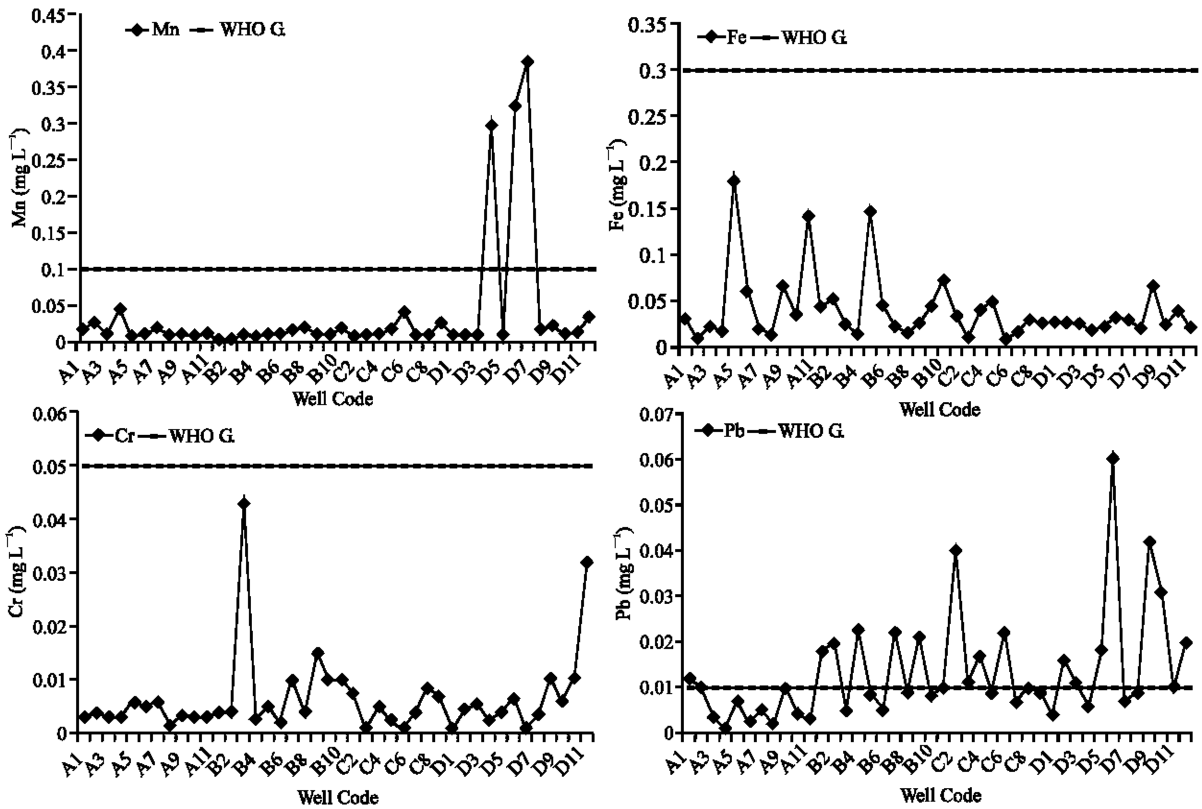

Fig. 1: Comparison of macro and micro elements aversge concentrations in the studied area with WHO

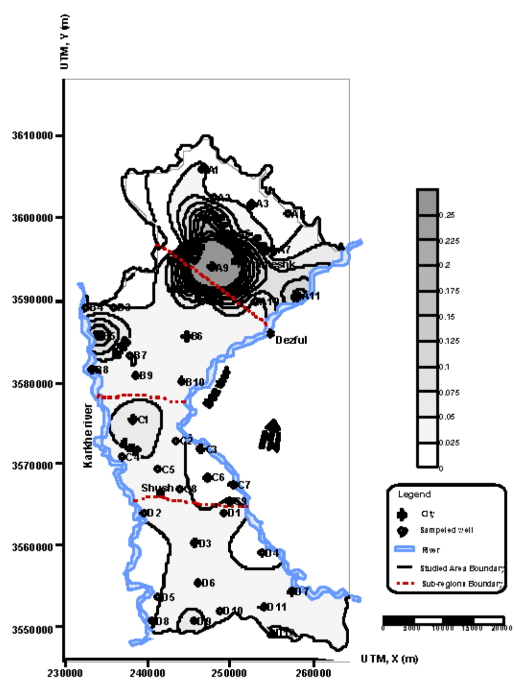

Fig. 2: Distribution of Fe concentration (mg/L) in Shush and Andimeshk aquifer

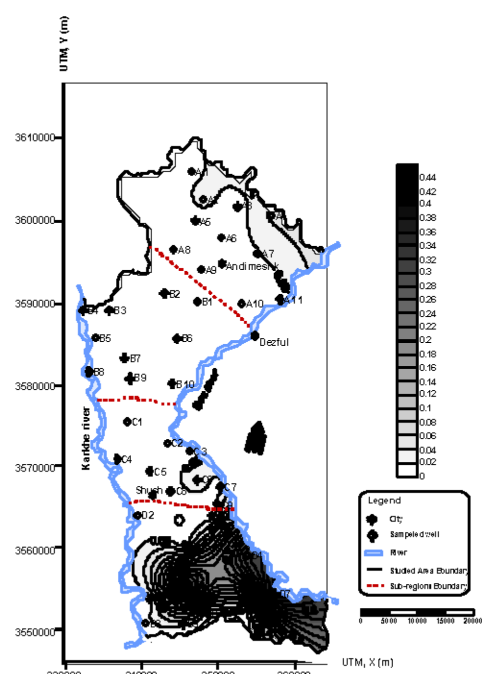

Fig. 3: Distribution of Mn concentration (mg/L) in Shush and Andimeshk aquifer

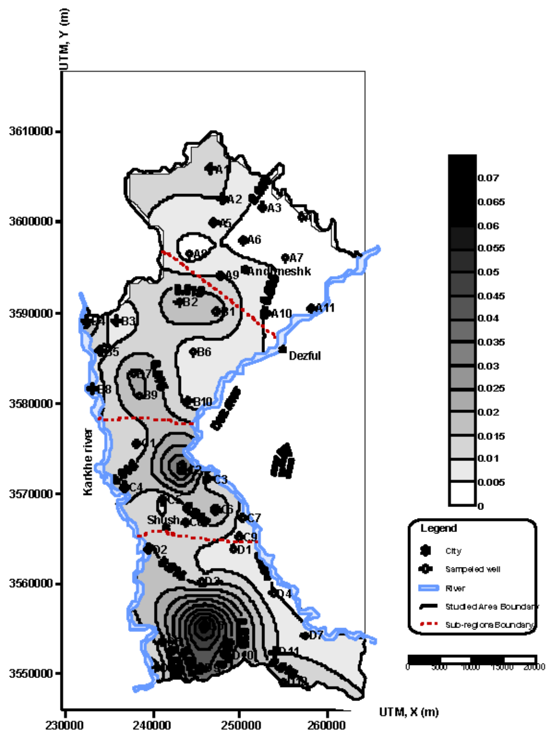

Fig. 4: Distribution of Pb concentration (mg/L) in Shush and Andimeshk aquifer

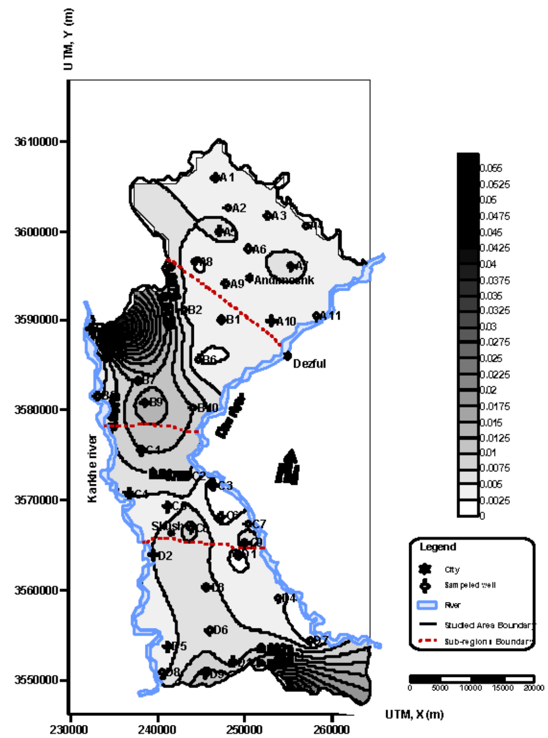

Fig. 5: Distribution of Cr concentration (mg/L) in Shush and Andimeshk aquifer

sampled in Shush and Andimeshk plains. In comparison, sub-regions A, B, C and D show different amounts of each heavy metals contents, which shows in Fig. 1 with compared to WHO guidelines. Regarding to the four sub-regions, the sub-region D had highest average Mn and Pb concentrations in groundwater. According to results the highest Fe and Cr concentrations was observed in sub-regions A and B, respectively. Concentrations of macro and micro elements in groundwater are as follows: Fe, 0.009-0.2 mg L^{-1}, Mn, 0.002-0.42 mg L^{-1}, Pb and it was to 0.07 mg L^{-1} and Cr, <0.001-0.054 mg L^{-1}. The average groundwater Fe, Mn, Pb and Cr concentrations for the studied area showed 0.04, 0.037, 0.014 and 0.0066 mg L^{-1}, respectively. The results indicated that all of the samples, Fe and Cr concentrations have been shown below the WHO guidelines (WHO, 2003), but Mn and Pb contents of 7.1 and 40.5% of all samples was higher than WHO guidelines respectively. Amongst 42 tested water wells, 17 water wells had lead concentration exceed from WHO guideline were as follows:

- 10 cases were used for water supply;
- one case were used for ice production;
- one case were used for aquaculture;
- 5 cases were used for other uses such as poultry, agriculture, household washing and sand washing industry.

The Mn concentration in 3 water wells were presented more than WHO guideline which 2 cases were used for water supply and the last one was to household washing application.

The distribution values of Fe, Mn, Pb and Cr concentrations in groundwater of studied area are presented in Fig. 2-5 which were applied into various maps. These maps provide a basis for making area-wide generalizations concerning the distribution of water-quality parameters and they serve to isolate water-quality problem areas. As illustrated in Fig. 2-5 high Fe, Mn, Pb and Cr concentrations occurred at the sites of 3 water wells (A_5, A_{11} and B_5), (D_4, D_6 and D_7), (C_2, D_6 and D_9) and (B_3, B_9 and D_{12}), respectively.

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 iron and chromium were below of the drinking water WHO guidelines, but manganese and lead content of some samples surpassed the above guidelines. The Mn and Pb concentration of groundwater were more pronounced in southern part than northern part of studied area. Absent of the 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 studied area had higher iron concentration than the other areas that is due to the anaerobic conditions in deeper zones and iron influence by macro element fertilizers, such as ferrous sulfate and ferrous nitrate application in permeable agricultural lands.

Lead may cause a range of health effects, from behavioral problems and learning disability, to seizures and death, with young children, infants and fetuses being most vulnerable. Manganese cause aesthetic, organoleptic and operating problems when it is present in water. This metal consumes chlorine in the disinfection process and promotes biofouling and microbiological induced corrosion in water networks. It is therefore proposed that groundwater with Pb and Mn contents exceed WHO guidelines which used for water supply in present area would be treated or altered with another safe water sources. Application of the best management practices (BMPs) in agricultural regions of the 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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