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Assessment of Trace Metals in Groundwater Sources Used for Drinking Purposes in Riyadh Region

Abdulrahman I. Alabdula'aly, Abdullah I. Al Zarah and Mujahid A. Khan

King Abdulaziz City for Science and Technology, P.O.Box 6086, Riyadh 11442, Suadi Arabia

Abstract: Assessment of trace metals in ground water used for drinking purposes in Riyadh region in the kingdom of Saudi Arabia was carried out. Samples were collected from 200 wells supplying drinking water to the inhabitants in the region. All samples were analyzed for 17 trace and macro elements (Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Mo, Ag, Hg,V and Zn) using Inductively Coupled Plasma (ICP) spectrophotometer equipped with an ultrasonic nebulizer. The minimum and maximum trace metals concentrations in different areas for Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Hg, V and Zn ranged between 9.31- 529.33, ND- 11.0, 9.23-864.33, ND- 3.00, ND- 4.00, ND- 30.00, ND- 226.60, ND- 9585.00, ND- 720.00, ND- 38.00, ND- 33.60, ND- 140.00, ND- 126.00, ND- 13.50 and ND- 1422.0 µg/L respectively. Silver (Ag) and Molybdenum (Mo) were also analyzed but were found not detectable (ND) in all samples. The results indicated the presence of iron in all sampled wells. Its concentrations exceeded the maximum contaminant level (MCL) in 46.5% of the samples. Manganese, Al, Se, Ba and Hg exceeded the MCL in 18.0, 2.5, 8.5, 0.5 and 19.5% of the total samples respectively. It is recommended that an adequate and suitable treatment must be applied to the wells having elevated concentrations of the metals and supplying drinking water to the consumers.

Key words: Trace metals • Groundwater • Drinking water sources • Riyadh region

INTRODUCTION

Early concerns over the quality of groundwaters were focused mainly on dissolved mineral salts. However, recently, organics, heavy and trace metals have become a focus of concern for several reasons, including enhanced ability to detect chemicals in the microgram and nano gram per liter concentration levels and an increasing awareness of potentially hazardous risks to public health and the environment. Metals are ubiquitous, persistent and toxic at certain concentrations. Some metals are essential for heath whereas others have no known biological function and have toxic effects. The adverse effects of some metals on the human health are well documented.

Trace elements are contributed to groundwater from a variety of natural and anthropogenic sources. Once liberated to groundwater, element distributions are continually modified by complex geochemical and biological processes [1].

A study of trace metal levels in ten different stations of both surface and ground waters in the Greater Accra region, Ghana was undertaken by Botchway *et al*. [2]. Ninety percent of the sites had Mn levels above the detection limits in both underground and surface waters. Seventy percent of bore holes in Accra plains had Fe levels higher than the WHO recommended limits. Das *et al*. [3] measured arsenic metal in six districts of West Bengal, India. Arsenic metal in the samples was found above the WHO maximum permissible limits of 0.05 mg/L. Abu-Rukh and El-Aloosy [4] studied the various metal ions migration in the El-Akader landfill site in north Jordan and concluded that there is a migration of metal ions to the deep layers. In their study Gharaibeh and Riad [5] indicated the possibility of surface water, ground water and soil pollution in the El-Akder region in Jordan.

The concentrations of Ni, Pb, Cd, Cu and Co in drinking water from wells, direct sources, or storage tanks in 18 sites of Kayesri (Turkey) were determined by Soylak and Elci [6]. All the metals were found within the permissible limits. Groundwater quality data taken in August and December 2000 in the Hanoi city revealed that the groundwaters are contaminated by arsenic (up to 110mg/L) and iron (32 mg/L) [7].

Corresponding Author: Abdulrahman I. Alabdula'aly, King Abdulaziz City for Science and Technology, P.O.Box 6086, Riyadh 11442, Saudi Arabia. E-mail: abdulaly@kacst.edu.sa

Raw and product waters of eight water treatment plants in Riyadh, Buraydah and Unayzah were analyzed for 12 trace metals. All the detected metals were within the permissible limits of WHO [8]. Groundwater samples were collected from 104 monitoring wells from shallow aquifers underneath an industrial city in the Eastern Province of Saudi Arabia by Sadiq and Alam [9]. Concentrations of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V, Zn, Ca, Mg, K, Na, Cl, SO_4, alkalinity, salinity, total dissolved salts and pH were determined in these samples. The groundwater sample from the industrial-dust area contained higher ratios between concentrations of Cl and Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn.

Although most parts of the Riyadh region are supplied with desalinated sea water or treated groundwater, still some areas, mainly in villages are supplied drinking water from wells which use no treatment. This study included wells, both government and private, which are used for domestic supplies. The main objective of this paper is, therefore, to present the results of the occurrence of trace metals in well water used for drinking purposes. The results have been compared with standards prescribed by different regulatory agencies. Also efforts were made to find correlation within the trace elements with well depths.

MATERIALS AND METHODS

Study Area: Ground water samples were collected from wells (n=200) located in the Riyadh region. The sampling was carried out over nine month period. The location of the wells was recorded using Geological Positioning System (GPS). The different locations of the sampled wells are shown in Table 1.

The sampled wells were a mix of government and private property. Many of the sampled wells were the main source of drinking water for the local population.

Collection of Samples: Ground water samples were collected in one-liter plastic bottles, which were previously thoroughly washed with tap water and rinsed with distilled water. These were immediately acidified to pH 2 with HNO_3 in order to keep metals in solution and prevent them from adhering to the walls of the bottles. All samples were transported to the laboratory in iceboxes and refrigerated at 4°C until analyzed.

Sampling protocol was designed in such a way that samples collected in one sampling schedule were analyzed in the shortest possible time.

Table 1: Location of the sampled wells in the Riyadh region

Location of the well site	Number of wells in the site
Riyadh city	104
Villages under Al Kharj area	25
AlFalah	9
Al Salail	8
Al Kharj	6
Al Dawadami	6
Al Ghat	6
Rumah	5
Shaqra	4
Muzahmia	4
Al Guwaia	3
Villages under Muzahmia	3
Ghunaiman	3
Al Majmah	2
Labkha	2
Dhurma	2
Zulfi	2
Hassa	2
Al Hota	1
Tabrak	1
Malaih	1
Al Ratawiah	1
Total	200

Sample Analysis: Samples were analyzed for trace metals (Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Mo, Ag, Hg, V and Zn) using a Perkin Elmer model 1000 Inductively Coupled Plasma.

(ICP) spectrophotometer equipped with an ultrasonic nebulizer model Cetec U 5000 AT. The use of the ultrasonic nebulizer instead of a pneumatic nebulizer provided a 5 to 50 fold improvement in detection limits and a 10 fold enhancement resulting in better reproducibility on trace metal level determinations. Analysis was carried out in triplicate and average values are reported. The ICP was calibrated with relevant Perkin Elmer Pe-Pure spectroscopy grade standards.

Quality Assurance and Quality Control Program: To assess the precision and accuracy of results, replicate analysis of blank, standard and samples was done. The relative standard deviations were determined to find the precision of the analysis. Recovery results were calculated for the determination of accuracy. Experiments were repeated till an accuracy of 95-105% and precision of +/- 5% were obtained. One standard with one set of samples was analyzed routinely.

Statistical Programs Used: Statistical software SPSS was used to calculate the different correlations.

RESULTS AND DISCUSSION

The minimum, maximum and average trace metal concentrations in different parts of the Riyadh region has been presented in Table 2. Silver (Ag) and Molybdenum (Mo) were also analyzed but were not detectable (ND) in all samples.

Aluminum (Al): Only 12 samples (6.0%) had measurable aluminum concentrations and five (5) samples (2.5%) exceeded the drinking water specified limits prescribed by World Health Organization (WHO) (Table 3).

Arsenic (As): The minimum, maximum and average concentrations of As were ND, 11.00 and 0.89 µg/L respectively. The standard deviation within the Riyadh region was 1.26. While 85 well water samples showed measurable concentrations of arsenic, none of the samples exceeded the maximum contaminant limits for drinking water (Table 3).

Barium (Ba): All well water samples had measurable concentrations of barium. However, only one sample (0.5%) exceeded the SASO maximum contaminant limits prescribed for Ba in drinking water (Table 3).

Beryllium (Be): The minimum and maximum Beryllium concentrations varied between ND and 3.00 µg/L. Measurable concentrations of the metal were found in 33 samples (16.5% samples). However, none of the sample exceeded the relevant prescribed limits for drinking water (Table 3).

Table 2: Minimum, maximum and average concentrations of trace metals in the Riyadh region

Metal	Minimum (µg/L)	Maximum (µg/L)	Average (µg/L)	Standard Deviation
Al	9.31	529.33	184.27	165.12
As	ND	11.00	0.89	1.26
Ba	9.23	864.33	51.49	75.20
Be	ND	3.00	0.30	0.58
Cd	ND	4.00	1.00	0.92
Cr	ND	30.00	3.30	4.76
Cu	ND	226.60	6.95	21.31
Fe	ND	9585.00	738.80	1228.00
Mn	ND	720.00	47.78	83.94
Ni	ND	38.00	2.30	3.50
Pb	ND	33.60	7.98	6.80
Se	ND	140.00	32.39	32.97
Mo	ND	ND	--	-
Hg	ND	126.0	1.53	8.91
V	ND	13.50	2.16	2.59
Zn	ND	1422.00	27.95	102.18

Cadmium (Cd): Eighty eight (88) viz. 44% of well water samples had measurable concentrations of Cd metal. However, none of the samples exceeded the relevant maximum contaminant limits prescribed for Cd in drinking water (Table 3).

Chromium (Cr): The minimum and maximum Cr concentrations were found to be ND and 30.00 µg/L respectively. One hundred and twenty-seven well water samples (63.5%) had measurable concentrations of Cr metal. However, none of the sample exceeded the Cr maximum contaminant limits stipulated for drinking water (Table 3).

Table 3: Samples having measurable concentrations of the elements and percentage of samples exceeding the maximum contaminant limits

	Samples having concentrations of the elements			Samples having concentrations of elements exceeding the maximum contaminant levels	
Element	No. of samples	%	MCL µg/L	No. of samples	%
Al	12	6.0	200*	5	2.50
As	85	42.5	50*	0	0.0
Ba	200	100.0	700*	1	0.5
Be	33	16.5	4***	0	0.0
Cd	88	44.0	5*	0	0.0
Cr	127	63.5	50**	0	0.0
Cu	104	52.0	1000*	0	0.0
Fe	195	97.5	300*	93	46.5
Mn	194	97.0	100*	36	18.0
Ni	129	64.5	70**	0	0.0
Pb	88	44.0	50*	0	0.0
Se	25	12.5	10*	17	8.5
Hg	122	61.0	1*	39	19.5
V	128	64.0	--	0	0.0
Zn	196	98.0	5000*	0	0.0

*SASO, ** WHO, ***USEPA

Table 4: Correlation coefficient between the metal concentration and the Well Depths

Metal	Correlation coefficient
Al	0.9
Ba	-0.2
Be	-0.3
Cd	-0.2
Cr	-0.1
Cu	0.0
Fe	0.1
Hg	-0.1
As	0.0
Mn	0.0
Ni	-0.1
Pb	-0.1
Se	-0.3
V	-0.2
Zn	0.0

Copper (Cu): The minimum and maximum copper concentrations were found to be ND and 226.60 µg/L respectively. One hundred and four well water samples (52%) had measurable concentrations of Cu metal, though none of the sample exceeded the Cu maximum contaminant limits stipulated for drinking water (Table 3).

Iron (Fe): The minimum and maximum iron concentrations varied between ND and 9585.00 µg/L. Measurable concentrations of the metal were found in 195 samples (97.5% samples). However, 93 of the samples (46.5%) exceeded the relevant prescribed limits for drinking water (Table 3).

Manganese (Mn): The minimum and maximum manganese concentrations varied between ND and 720.00 µg/L. Measurable concentrations of the manganese metal were found in 194 samples (97.0% samples). However, only 36 of the samples (18.0%) exceeded the relevant prescribed limits for drinking water for that element (Table 3).

Nickel (Ni): One hundred and twenty-nine well water samples (64.5% samples) had measurable concentrations of Ni. However, none of the samples exceeded the Cr maximum contaminant limits stipulated for drinking water (Table 3).

Lead (Pb): The minimum and maximum lead concentrations varied between ND and 33.60 µg/L whereas the average metal concentrations was 7.98 ug/L. Measurable concentrations of the metal were found in 88 samples (44.0% samples). However, none of the samples exceeded the relevant prescribed limits for drinking water for that element (Table 3).

Selenium (Se): The minimum, maximum and average selenium metal concentrations were found to be ND and 140.00 and 32.39 µg/L respectively. Only 25 well water samples (12.5% samples) had measurable concentrations of Ni. Seventeen well water samples (8.5% samples) exceeded the relevant maximum contaminant limits stipulated for Se in drinking water (Table 3).

Mercury (Hg): The minimum and maximum mercury concentrations varied between ND and 126.0 µg/L. Measurable concentrations of Mercury were found in 122 samples (61.0% samples). Thirty nine (39) of the samples (19.5% samples) exceeded the relevant prescribed limits for drinking water for that metal (Table 3).

Vanadium (V): The minimum, maximum and average Vanadium concentrations were found to be ND, 13.50 and 2.16 µg/L respectively. One hundred and twenty eight (128) well water samples (64.0% samples) had measurable concentrations of Vanadium. However none of the samples exceeded the relevant maximum contaminant limits stipulated for V in the drinking water (Table 3).

Zinc (Zn): The minimum and maximum zinc concentrations varied between ND and 1422.00 µg/L. Measurable concentrations of the zinc metal were found in 196 samples (98.0% samples). However, none of the samples exceeded the relevant prescribed limits for drinking water for zinc (Table 3).

Overview: In brief, Fe, Mn, Al, Se, Ba and Hg exceeded the maximum contaminant limits in the groundwater of Riyadh region. Copper, Zn, Pb, Ni, Cd, Cr, As, Be, Mo and V metals did not exceeded the maximum contaminant limits in any of the well water samples in the Riyadh region.

Correlation Between Occurrence of Metals and Well Depths: Correlation between the occurrence of trace metals and the well depths in the Riyadh region has been presented in Table 4. The software SPSS was used to calculate the correlation factors. Both positive and negative correlations were observed. A strong positive correlation (0.9) was observed between Al concentrations and the well depth whereas a weak positive correlation (0.1) was found for iron. For most of the other metals a weak negative correlation was observed which means that the metal concentrations decreased as the well depth increased.

CONCLUSIONS AND RECOMMENDATIONS

- Water samples were collected from 200 wells covering the whole Riyadh region.
- The minimum and maximum trace metals concentrations in different areas for Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Hg, V and Zn ranged between 9.31- 529.33, ND- 11.0, 9.23-864.33, ND- 3.00, ND- 4.00, ND- 30.00, ND- 226.60, ND- 9585.00, ND- 720.00, ND- 38.00, ND- 33.60, ND- 140.00, ND- 126.00, ND- 13.50 and ND- 1422.0 µg/L respectively. Silver (Ag) and Molybdenum (Mo) were also analyzed but were found not detectable (ND) in all samples.
- Trace metals like Al,, Ba, Fe, Hg, Mn and Se exceeded the maximum limits for drinking water in several sampled wells in the Riyadh region.
- A strong positive correlation was observed for the occurrence of Al (0.9) with the well depth. Weak negative correlations were, however, observed for most of the other metals.
- It is recommended to adopt some kind of inexpensive treatment to reduce the levels of trace metals in areas supplying water directly to consumers without any type of treatment.

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