Arabian Journal of Chemistry (2015) 8, 240–245

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Assessment of the levels of some heavy metals in water in Alahsa Oasis farms, Saudi Arabia, with analysis by atomic absorption spectrophotometry

Fahad N. Assubaie *

Department of Chemistry, College of Science, King Faisal University, P.O. Box 400, Hofuf 31982, Saudi Arabia

Received 12 May 2011; accepted 20 August 2011
Available online 3 September 2011

KEYWORDS

Heavy metals;
Groundwater;
Irrigation water;
Wastewater

Abstract For the first time, the levels of some heavy metals in water in Alahsa farms, Saudi Arabia were examined. Three types of water were analyzed including groundwater, mixed water and wastewater. The total contents of Mn, Fe, Cu, Zn, Cd and Pb were determined using graphite-furnace atomic absorption spectrophotometry. The results obtained were verified through the analysis of a certified reference material, the results of which are in good agreement with the certified consensus values. As recommended by the Food and Agriculture Organization, the level of heavy metals in groundwater and mixed water have been found to be suitable for irrigation purpose. However, the occurrence of some heavy metals that discharged directly from man-made activities without treatment could result in some environmental problems in the future. On the other hand, the spatial distribution of Mn and Fe has been found to increase from southeast to northwest.

1. Introduction

The accelerated industrialization process in combination with rapid population growth and agricultural activities has brought the risk of increasing the pollution index in natural environments, such as water, soil, air, etc. (Morrison et al., 1990; Dawson and Macklin, 1998; Ekpo and Ibok, 1998; Hassanzadeh et al., 2011; Mandour and Azab, 2011). For its multipurpose usage, persistence in the environment, bioaccumulation and high toxicity, heavy metals are considered as one of the most serious pollutants in the environment. Heavy metals are involved in various industrial processes, agricultural activities, domestic waste and vehicles emission. On the other hand, heavy metals that originated from anthropogenic sources could be found in all components of the environment (Idris et al., 2007; Idris, 2008; Ayni et al., 2011). Due to the increasing anthropogenic contribution by heavy metals, more attention has been devoted to the investigation on those pollutants in the environment (Edmund et al., 2003; Marengo et al., 2006; Al-Hobaib et al., in press). Low efficiency in industrial production processes (e.g. energy power plants, petrochemical and chemical industries, etc.) and the unsuitable handling and management of industrial wastes have been recognized as pollution sources, which are responsible for

* Fax: +966 3 5886 437.
E-mail address: fnassubaie@yahoo.com.
Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2011.08.018
1878-5352 © 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University.

producing considerable load of heavy metals to the environment (Charlesworth and Lees, 1999; Hashisho and El-Fadel, 2004; Kuang et al., 2004; Mireles et al., 2004; Banat et al., 2004; Namaghi et al., 2011).

Nearly, all types of water contain heavy metals, many of which result from the natural weathering of the earth's surface (Newcomb and Rimstidt, 2002). In addition, wastewater used for irrigation land, besides effluent from city sewage and industrial wastewater, could significantly affect water quality. Heavy metals from anthropogenic activities could migrate or infiltrate into aquifers and interact with groundwater (Dawson and Macklin, 1998; Charlesworth and Lees, 1999).

A number of heavy metals in irrigation water cause toxic reaction in plants and, therefore, limit its use for irrigation. Many reports that recommended maximum allowable levels of heavy metals in water used for irrigation for a short and long time are available elsewhere (Todd, 1980; FAO, 1985; Rowe and Abdel-Magid, 1995; Chapman, 1997). Rowe and Abdel-Magid (1995) reported on the toxicity of some heavy metals to plants. For example, lead at high concentration can inhibit plant cell growth. In addition, manganese is toxic to a number of crops at few-tenths to a few mg/L, but usually only in acid soils. On the other hand, iron is not toxic to plants in aerated soils, but can contribute to soil acidification and loss of availability of essential phosphorus and molybdenum. Moreover, copper is toxic to a number of plants at the levels from 0.1 to 1.0 mg/L in nutrient solutions. Furthermore, zinc is toxic to many plants at widely varying concentrations. Zinc toxicity is reduced at pH > 6.0 in fine textured or organic soils. Cadmium is also toxic to beans, beets and turnips at concentrations as low as 0.1 mg/L in nutrient solutions. However, such heavy metals as manganese, zinc and copper in trace levels are important for the physiological functions of living tissue and regulate many biochemical processes.

In Al-Ahssa Oasis, Saudi Arabia, the main source of water or almost the single source is groundwater since rivers are not available and rainfalls are scarce. The groundwater in that area is distributed into three aquifers: (a) Neogen is the upper one with a depth of up to 180 m, (b) Khobar is the middle one with a depth ranging from 180 to 250 m and (c) Umm-Arradma is the bottom one with a depth ranging from 280 to 240 m. Al-Ahssa Oasis is the largest irrigated agricultural area in Saudi Arabia. It includes date palm farms, the product of which is the main popular nutritional food, besides many other farms that produce vegetables and fruits.

The increasing demand of water for agricultural, industrial and domestic purposes in the area under study leads to reuse the wastewater. Wastewater includes emission of industries, domestic sewage and drainage water (the unconsumed part of the irrigation water). Unfortunately, wastewater is directly mixed with groundwater at a ratio of 1–3, respectively, with no treatment. Not least but more, most of industries in that area emit wastes without management.

On the other hand, atomic absorption spectrophotometry (AAS) is widely used as a routine technique for elemental analysis in water samples. In this issue, the extensive worldwide use of AAS is attributed to its popularity, familiarity, ease of use and cost-effectiveness comparing with other elemental techniques such as inductively coupled plasma. Moreover, AAS is a sensitive technique, which can detect elements in up to ng/mL levels especially when graphite furnace mode is used for atomization. Furthermore, AAS enjoys good selectivity, which is due to the use of selective irradiation source.

There is lack of studies on water quality in Alahsa Oasis with the exception of a report on nitrate and nitrite levels in groundwater (Assubaie, 2004). Therefore, it has been proposed in the current study to achieve the following objectives. (i) To determine the levels of some heavy metals, namely Mn, Fe, Cu, Zn, Cd and Pb, in water samples using AAS-GF. Three types of samples including groundwater, mixed water and wastewater in Alahsa Oasis will be examined. (ii) To examine the spatial distribution of the levels of Mn and Fe in the groundwater. (iii) To identify the sources of heavy metals in groundwater and finally. (iv) To assess the irrigation water quality.

2. Methodology

2.1. Study area

Al-Ahssa Oasis, Saudi Arabia, is one of the largest oases in the world. It forms an "L" shape that covers 320 km^2 with about 150 m above the sea level. It is situated between 25°21′ and 25°37′ northern latitude with 49°33′ and 49°46′ eastern longitude. The area is located between the rock desert of As-Summan Plateau in the west and sand dunes covering the plain as far as the east border. The climate belongs to the subtropical arid zone of the northern hemisphere. This area includes two cities Al-Hofuf and Al-Mubaraz, which are densely populated and industrialized, besides more than fifty villages (Fig. 1). The population increased from 741,000 in 1980 (Team of Staff, 1995) to 1,408,000 in 2000. Now they are more than 2 millions (Central Department of Statistics Information, 2011).

Figure 1 Saudi Arabia map showing Al-Hufuf city.

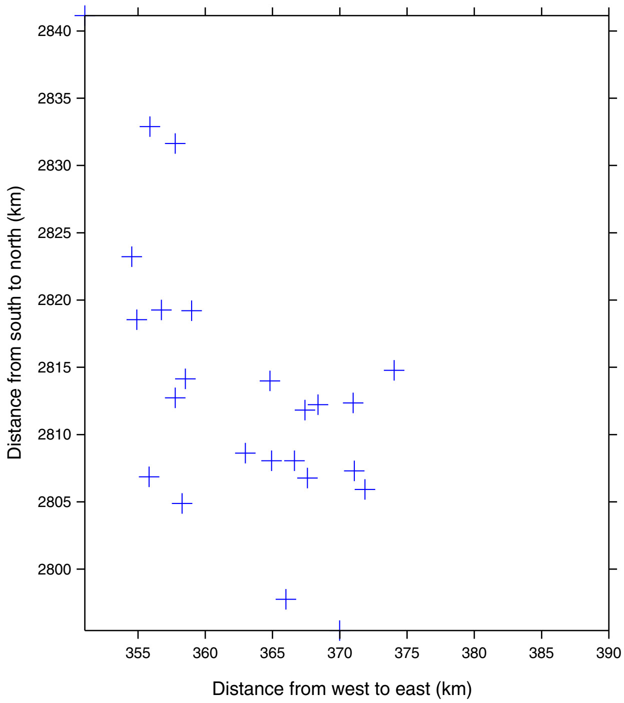

Figure 2 Post plot of 22 groundwater samples collected from Al-Ahssa Oasis from south to north (y-axis) and from east to west (x-axis).

2.2. Sampling

During August and September 2010, a total of thirty water samples including groundwater, mixed water and wastewater were collected from Al-Ahssa Oasis. The hypothesis governing the campaign is to provide good spatial coverage in the studied area (Fig. 2). The latitude and longitude values for all locations are introduced in Table 1. The groundwater samples were collected from the outlets of the wells after flushing water for 10–15 min in order to remove the stagnant water. Samples from the dug wells were collected using water sampler. Mixed water and wastewater samples were collected using grab sampler at a depth of 10 cm below the surface.

Tight-capped high quality polyethylene bottles were used for sample storage. Before use, the bottles were washed by distilled deionized water and rinsed overnight in 10% (v/v) nitric acid. Samples were filtered through the Whatmann® filter papers number 42. To prevent precipitation of metals and biological growth, few drops of concentrated nitric acid were added to samples to obtain pH around 2 (Kramer, 1994; Eaton, 1995). Thereafter, samples were immediately transported to the laboratory in iceboxes and stored at 4 °C up to analysis.

2.3. Materials

AA-6800 atomic absorption spectrophotometer (AAS) coupled with GFA-EX7 graphite furnace atomizer and ASC-6100 auto sampler from Shimadzu (Koyoto, Japan) was utilized for heavy metal analysis. A high-density graphite tube was used for atomization. Normal single hollow cathode lamps were used for irradiation.

Table 1 Locations of samples collected in Alahssa Oasis's Districts.

Sample number	District name	Longitude	Latitude
1	Oyoon	25°35.3′	49°34.5′
2	Oyoon	25°35.3′	49°34.5′
3	Oyoon	25°35.3′	49°34.5′
4	Morah	25°36.2′	49°34.8′
5	Morah	25°36.0′	49°35.0′
6	Morah	25°37.2′	49°35.1′
7	Mitairfi	25°28.3′	49°33.5′
8	Mitairfi	25°28.4′	49°33.9′
9	Mitairfi	25°28.4′	49°34.1′
10	Mubaraz	25°24.2′	49°35.1′
11	Mubaraz	25°24.1′	49°35.2′
12	Mubaraz	25°24.0′	49°35.3′
13	Gara	25°25.0′	49°40.7′
14	Gara	25°24.5′	49°40.6′
15	Gara	25°24.6′	49°40.6′
16	Gara	25°24.6′	49°40.6′
17	Sowaidra	25°22.2′	49°37.3′
18	Sowaidra	25°22.2′	49°37.2′
19	Sowaidra	25°22.1′	49°36.9′
20	Sowaidra	25°21.9′	49°37.2′
21	Seefa	25°22.5′	49°34.5′
22	Seefa	25°22.5′	49°34.4′
23	Seefa	25°22.1′	49°34.4′
24	Qatar Road	25°19.6′	49°38.1′
25	Qatar Road	25°19.7′	49°38.1′
26	Qatar Road	25°18.4′	49°38.6′
27	Qatar Road	25°19.0′	49°38.6′
28	Gowaiba	25°17.8′	49°37.5′
29	Gowaiba	25°17.6′	49°37.5′
30	Gowaiba	26°01.7′	50°21.5′

Reference seawater from the National Research Council, Canada (NRCC, open ocean seawater standard NASS-5) was used to verify the accuracy of results obtained in the current study

Thousand milligrams per litre standard solutions of each of Mn, Fe, Cu, Zn, Cd and Pb, which were prepared from nitrate salts, were supplied from BDH (Poole, England) and used for calibration purpose. Mixed working standard solutions containing all metals were prepared by dilution in appropriate ways using double distilled deionized water. Measurement for each solution was done in triplicate and the average was taken.

3. Results and discussion

The adopted reference material was used to verify the results obtained for Mn, Fe, Cu, Zn, Cd and Pb. The certified and analytical values along with the relative standard deviation values for triplicate measurements, besides the recovery values, are introduced in Table 2. It has been found that the recovery values are in the range of 87.5–104.3%. The analytical values obtained are within the range of certified values. This outcome indicates good quality of results that are obtained in the current study.

The summary statistics of the concentrations of heavy metals in the groundwater, mixed water and wastewater are introduced in Table 3. In general, the concentrations of Mn, Fe, Cu,

Table 2 Results and statistics of the analysis of certified reference material for heavy metals.

Metal	Certified value (mg/L)	Analytical value (mg/L)	Recovery
Mn	0.919 ± 0.057	0.937 ± 0.035	101.9
Fe	0.207 ± 0.035	0.216 ± 0.014	104.3
Cu	0.297 ± 0.046	0.276 ± 0.011	92.9
Zn	0.102 ± 0.039	0.098 ± 0.009	96.1
Cd	0.023 ± 0.003	0.021 ± 0.002	91.3
Pb	0.008 ± 0.005	0.007 ± 0.001	87.5

Zn, Cd and Pb in groundwater are lower than those in mixed water and wastewater.

Some studies that reported the allowable limits of the levels of some heavy metals in irrigation water are available elsewhere (Todd, 1980; FAO, 1985; Rowe and Abdel-Magid, 1995; Chapman, 1997). As recommended by the Food and Agriculture Organization (FAO) guidelines, the maximum allowable limits of heavy metal concentrations in water used for irrigation are depicted in Fig. 3. The maximum concentrations of those metals in groundwater and mixed water are depicted as well. It has been found that the levels of Mn, Fe, Zn and Pb in both groundwater and mixed water are suitable for irrigation use. However, the levels of Cu and Cd in mixed water are to some extent higher than the FAO's allowable limits. High levels of those two metals could be attributed to the contribution from anthropogenic sources. Industrial and/or domestic activities may be the source of contribution by Cu in the environment of the study area. On the other hand, the source of Cd could be from phosphate fertilizer that is usually used in that area. Another study conducted in Australia recommended ranges of some heavy metal concentrations that are fit for irrigation consumption. Those ranges are 0.2–10.0, 0.2–10.0, 0.2–5.0, 2.0–5.0, 0.01–0.05 and 2.0–5.0 mg/L, for Mn, Fe, Cu, Zn, Cd and Pb, respectively. In the current study, it has been also found that the levels of all heavy metals are in the range of the Australian study. It could be concluded that the levels of Mn, Fe, Cu, Zn, Cd and Pb in the groundwater and mixed water in Alahsa Oasis are suitable for irrigation purpose. On the other side, low relative standard deviation

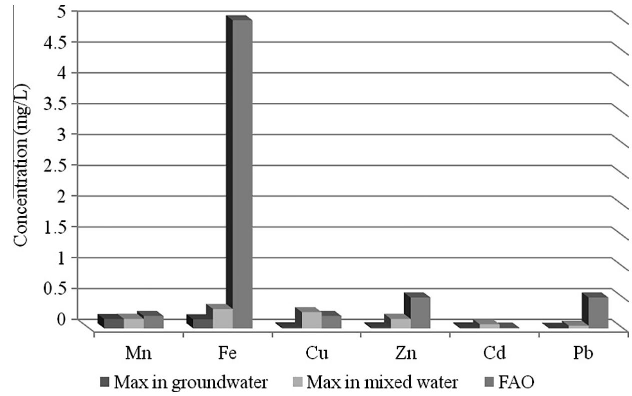

Figure 3 Maximum concentration of heavy metals in groundwater and mixed water in Al-Ahssa Oasis, besides the maximum allowable concentration for irrigation use as recommended by FAO.

(%RSD) of heavy metals in mixed water is an indicator of efficient mixing process. The wide range of the levels and the high level of %RSD of Fe, Cu, Zn, Cd and Pb in wastewater reflect that some sites in the study area could be enriched from man-made effluents.

In more detail, the average values of heavy metal concentrations in each aquifer were calculated. Fe recorded a higher level in the upper aquifer than that in the middle and bottom aquifers while Mn concentrations were distributed evenly in the three aquifers. With the exception of Mn, the levels of heavy metals in wastewater are higher than those in mixed water and groundwater. This may be an indicator of anthropogenic contribution by heavy metals in the environment of the study area (Todd, 1980). Hence, it could be proposed that Khobar and Umm-Arradma aquifers are also free from Mn and Fe contamination. To some extent, a slight increase in the level of Fe in the groundwater of Neogen aquifer was recorded. This may be attributed to a slight enrichment to this upper aquifer by man-made activities. Contamination of groundwater with Fe is most probably due to multipurpose usage of Fe in industrial and domestic activities.

Table 3 Summary statistics of the concentration (mg/L) of some heavy metals in groundwater, mixed water and wastewater in Al-Ahssa Oasis.

Samples type		Mn	Fe	Cu	Zn	Cd	Pb
Groundwater (n = 22)	Min	0.063	0.101	0.011	0.010	0.009	0.005
	Max	0.151	0.145	0.017	0.018	0.013	0.008
	Mean	0.120	0..28	0.014	0.014	0.010	0.007
	%RSD[a]	0.024	0.026	0.00	0.004	0.003	0.003
Mixed water (n = 10)	Min	0.091	0.214	0.217	0.051	0.031	0.031
	Max	0.153	0.315	0.262	0.153	0.066	0.042
	Mean	0.137	0.263	0.200	0.110	0.050	0.030
	%RSD	0.030	0.041	0.018	0.002	0.008	0.006
Wastewater (n = 10)	Min	0.090	0.133	0.192	0.093	0.052	0.034
	Max	0.174	0.481	0.353	0.232	0.091	0.091
	Mean	0.144	0.310	0.270	0.150	0.063	0.054
	%RSD	0.020	0.203	0.181	0.002	0.006	0.006

[a] Relative standard deviation.

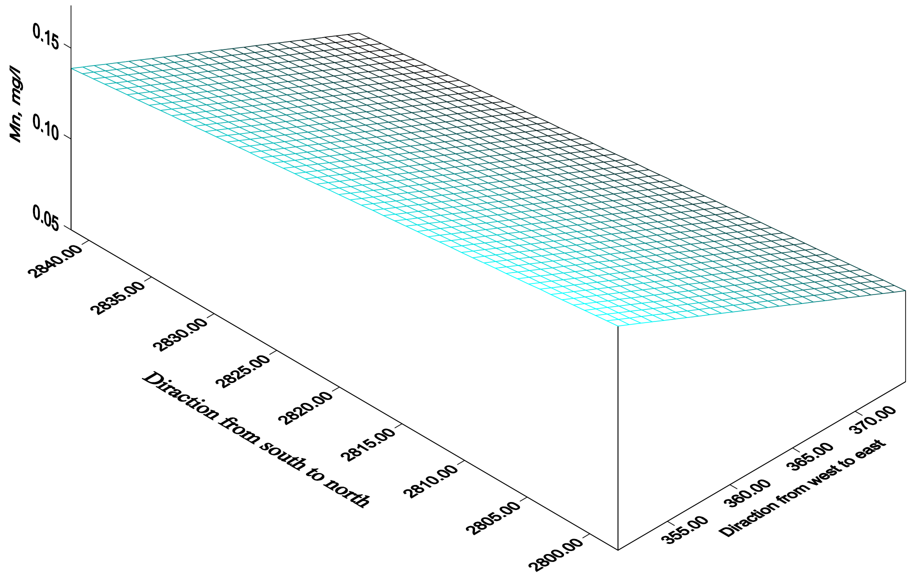

Figure 4 Spatial distribution of Mn content in groundwater of Al-Ahssa Oasis.

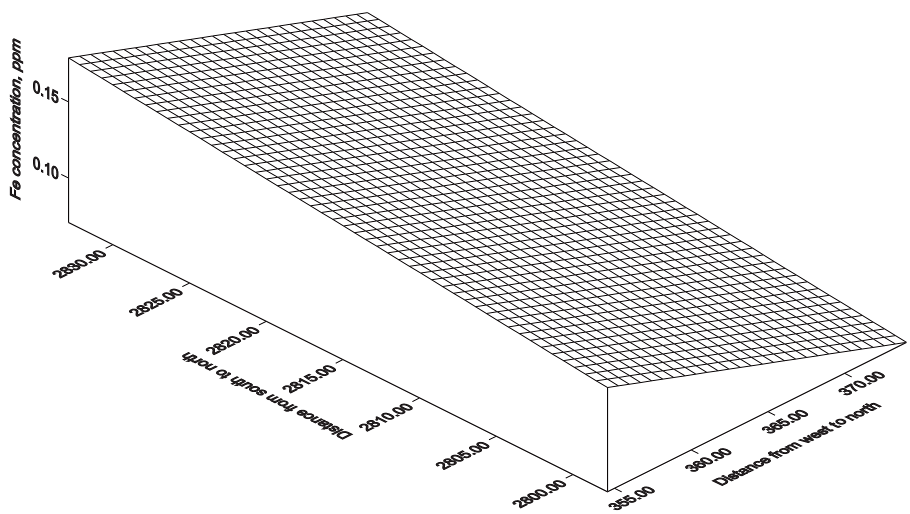

Figure 5 Spatial distribution of Fe content in groundwater of Al-Ahssa Oasis.

On the other side, Figs. 4 and 5 depict the spatial distribution of Mn and Fe in groundwater. The figures exhibit that the content of those metals increases from southeast to northwest. Furthermore, the correlation coefficients between the concentrations of the heavy metals in mixed water and wastewater were calculated and the results are introduced in Table 4. Significant positive correlation was recorded for Mn with Fe, Mn with Cu, Fe with Cu and strong correlation between the contents of Mn, Fe, Cu and Zn in the mixed and waste waters. Insignificant negative correlation was recorded for Pb with other metals except Zn.

Table 4 Correlation coefficients of heavy metals concentration in mixed and waste water in Al-Ahssa Oasis.

	Pb	Cd	Zn	Cu	Fe	Mn
Pb	1.00	–	–	–	–	–
Cd	−0.43	1.00	–	–	–	–
Zn	0.35	−0.16	1.00	–	–	–
Cu	−0.55	0.42	0.80	1.00	–	–
Fe	−0.29	0.35	0.71	0.79	1.00	–
Mn	−0.43	0.53	−0.26	0.72	0.57	1.00

4. Conclusions

The current manuscript reports for the first time the investigation of the levels of some heavy metals in groundwater and mixed water that are used for irrigation purpose in Alahsa Oasis, Saudi Arabia. The levels of heavy metals in waste water from farms in that area were examined as well. From this investigation, the following conclusions can be made.

- The levels of heavy metals under study in water used for irrigation purpose are below the maximum allowable limits recommended by FAO's except for Cu and Cd. Those levels are also within the ranges recommended by a previous Australian study.
- Although the suitability of mixed water in the study area for irrigation purpose, sufficient water treatment is desirable before use.
- The study revealed that the groundwater in Al-Ahssa Oasis was free from significant enrichment by heavy metals from anthropogenic sources.
- The levels of Mn and Fe in groundwater in the area under study increase from east southern to west northern.
- To some extent, higher levels of Fe, Cu, Zn, Cd and Pb were recorded in the wastewater in the area under study.
- Future studies examining the impact of the use of irrigation water quality taking into account of the physical, chemical and microbiological aspects are recommended.

Acknowledgment

The author would like to thank the Department of Chemistry, College of Science, King Faisal University, Saudi Arabia for allowing him to conduct this research.

References

Al-Hobaib, A.S., Al-Jaseem, Q.Kh., Baioumy, H.M., Ahmed, A.H. in press. Arabian J. Geosci.
Assubaie, F.N., 2004. Pak. J. Bio. Sci. 7, 508.
Ayni, F.E., Cherif, S., Jrad, A., Trabelsi-Ayadi, M., 2011. Water Res. Manag. 25, 2251.
Banat, K.M., Howari, F.M., Al-Hamad, A.A., 2004. Environ. Res. 97, 258.
Central Department of Statistics Information. 2011. Kingdom of Saudi Arabia, <http://www.cdsi.gov.sa/>.
Chapman, D. 1997. Water quality assessments, a guide to the use of biota, sediments, and water in environmental monitoring, second ed. UNESCO-WHO UNEP-E and FN SPON.
Charlesworth, S.M., Lees, J.A., 1999. Environ. Geochem. Health 21, 97.
Dawson, E.J., Macklin, M.G., 1998. Environ. Geochem. Health 20, 67.
Eaton, A.D., Clesceri, L.S., Greenberg, A.E., 1995. Standard Methods for the Examination of Water and Wastewater, nineteenth ed. American Public Health Association, Washington.
Edmund, W.M., Shand, P., Hart, P., Ward, R.S., 2003. Sci. Total Environ. 310, 25.
Ekpo, B.O., Ibok, U.J., 1998. Environ. Geochem. Health 20, 113.
FAO. 1985. Water quality for agriculture. Irrigation and drainage paper 33. FAO, Rome.
Hashisho, Z., El-Fadel, M., 2004. Environ. Monit. Assess. 93, 185.
Hassanzadeh, R., Abbasnejad, A., Hamzeh, M.A., 2011. J. Environ. Stud. 36, 101.
Idris, A.M., 2008. Microchem. J. 90, 159.
Idris, A.M., Al-Tayeb, M.A.H., Potgieter-Vermaak, Sanja S., Van Greken, R., Potgieter, J.H., 2007. Microchem. J. 87, 104.
Kramer, K.J.M., 1994. Int. J. Environ. Anal. Chem. 57, 179.
Kuang, C., Neumann, T., Norra, S., Stuben, D., 2004. Environ. Sci. Pollut. Res. 11, 73.
Mandour, R.A., Azab, Y.A., 2011. Int. J. Occup. Environ. Med. 2, 112.
Marengo, E., Gennaro, M.C., Robotti, E., Rossanigo, P., Rinaudo, C., Roz-Gastaldi, M., 2006. Anal. Chim. Acta 560, 172.
Mireles, A., Solys, C., Andrade, E., Lagunas-Solar, M., Pina, C., Flocchini, R.G., 2004. Nucl. Instrum. Methods Phys. Res. B Beam Interact. Mater. Atoms 219, 187.
Morrison, G.M.P., Revitt, D.M., Ellis, J.B., 1990. Water Sci. Technol. 22, 53.
Namaghi, H.H., Karami, G.H., Saadat, S., 2011. Environ. Monit. Assess. 174, 573.
Newcomb, W.D., Rimstidt, J.D., 2002. App. Geochem. 17, 499.
Rowe, D.R., Abdel-Magid, I.M., 1995. Handbook of Wastewater Reclamation and Reuse. CRC Press, Inc., p. 550.
Team of Staff. 1995. General information on the Kingdom of Saudi Arabia, Ministry of Planning, Central Department of Statistics, Saudi Arabia, 20th issue.
Todd, U.K., 1980. Groundeater Hydrology, second ed. John Wiley, New York.