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Assessment of the Physicochemical Parameters and Heavy Metals Toxicity: Application to Groundwater Quality in Unconsolidated Shallow Aquifer System

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ABSTRACT

Impact of heavy metals on the environment is a series issue worldwide. The objective of this study is to determine the groundwater quality variations of the unconsolidated shallow aquifer system in the Midyan Basin of northwestern Saudi Arabia. A total of 72 groundwater samples have been collected in January 2012 and analyzed for physicochemical parameters (total alkalinity, total solids, suspended solids and chemical oxygen demand). The level of heavy metals (lead, cadmium, chromium and zinc) and metalloid (arsenic) have also been assessed among the entire collected samples. The concentration of physicochemical parameters, heavy metals and metalloid do not exceed a maximum permissible level as per the World Health Organization standards. The observed total alkalinity, total solids, suspended solids and chemical oxygen demand concentrations have a mean value of 175.49, 2432.3, 662.7 and 1.178 mg L⁻¹ for the studied water samples, respectively. The results for heavy metals lead, cadmium, chromium and zinc concentrations in this study show location based variability, ranging between 0.00015 and 0.0038 mg L⁻¹, 0.0004 and 0.0009 mg L⁻¹, 0.0008 and 0.0114 mg L⁻¹ and 0.00035 and 0.1597 mg L⁻¹ with a mean of 0.00112, 0.00059, 0.002133 and 0.00779 mg L⁻¹, respectively. The range of metalloid arsenic concentration in the studied groundwater is 0.0008-0.0051 mg L⁻¹ with a mean of 0.00185 mg L⁻¹. The Hydrogen ion concentration values of the groundwater samples indicates an alkaline nature with an average value of 7.80, where the maximum value of 8.29 and a minimum value of 7.38 have been recorded. Calculated average daily dose and noncarcinogenic risk indicate that the range in all the studied boreholes is below the Reference Dose. In addition, the noncarcinogenic risk values are less than 1, indicating that they are within the tolerable range. Chemical contents in the studied groundwater are mainly contributed by the surrounding rocks, agriculture and other anthropogenic sources. In addition, surface and subsurface flow direction, wells locations and surface geological structures (including faults and fractures) appeared to be significantly causing the elevated chemical contents. The results also show that boreholes located in the southeast are more vulnerable to metals contamination.

Key words: Heavy metals-physicochemical parameters, groundwater quality, human health

INTRODUCTION

The concern for water resources containing contaminants, such as heavy metals and toxic metalloids, that pose a threat to health, has increased worldwide. The presence of heavy metals in

water is caused by two factors. The first one is generated by weathering of soils and rocks (White *et al.*, 2005; Bozkurtoglu *et al.*, 2006; Yazdi and Behzad, 2009; Batayneh, 2010; Mahjoobi *et al.*, 2010) with their products being transported by air (Moreno *et al.*, 2006; Duruibe *et al.*, 2007; Giuliano *et al.*, 2007; Zorer *et al.*, 2009) and water (Das and Krishnaswami, 2007; Elmaci *et al.*, 2007; Kar *et al.*, 2008). The second one is caused by anthropogenic activities that disturb the natural distribution of heavy metals in the groundwater aquifers, which could potentially be hazardous to the local environment and human health. Some of the metals may stay in water as free or complex ions or adsorbed onto solids, some may incorporate within insoluble organic or inorganic matter. Keeping in view their toxic effects, monitoring and assessment of such metals are of significant importance for managing environmental health (Batayneh, 2012).

Environmental pollution by heavy metals is very prominent in around the mining areas, but with increasing distance from mining sites they record a gradual decrease. Other sources of anthropogenic metals of terrestrial origin is from industrial and urban development as well as other human practices (Abderahman and Abu-Rukah, 2006; Buccolieri *et al.*, 2006; Ip *et al.*, 2007; Ong and Kamaruzzaman, 2009; Batayneh, 2012). As one of the principle polluter, mining activities can emphatically affect the water resources of that area by supplying heavy metals either as dissolved species or as an integral part of the suspended system. They may then become a part sediments layer or seep into the groundwater, particularly in the wells and springs. The extent of contamination in such a situation depends on the distance of the water well and spring to the mining site. As a combined result of these factors, metal concentration in the natural environment changes in space and time. In fact, during the past few decades, industrial and urban activities have contributed to increasing intake of metals contamination into semi-arid environment that directly influenced the urban ecosystems, causing toxic, mutagenic or carcinogenic effects to the human health as per the substances properties (Low *et al.*, 2000; Bulut and Baysal, 2006; Pekey, 2006).

The environmental impact of heavy on the groundwater of Midyan Basin (northwestern Saudi Arabia) have not been previously assessed or investigated. Such an investigation is required if the groundwater quality in this basin is to be understood determined both quantitatively and qualitatively. The main objective of this study is: (1) to assess the extent and degree of metals concentration and their origin and (2) to determine if the concentration is significantly high, so that they can be considered toxic in terms of aquatic environment.

MATERIALS AND METHODS

Description of the study area: The Midyan Basin, which covers an area of about 15000 km² with a population of about 5000, is located in the western part of Tabouk province, northwestern Saudi Arabia (latitude 28°00' to 28°40' N and longitude 34°40' to 35°20' E). This basin is bounded to the north, east and northeast by the Proterozoic rocks, to the west by sedimentary and Proterozoic rocks and to the south by the Red Sea (Fig. 1). The area under study is located in an extremely arid zone with annual average precipitation of 20 mm. Rainfall generally occurs during the winter months; however, some of the years pass without any rainfall, while others receive heavy rainfall of short duration. The climate of the region is very hot in summer with temperatures in the excess of 47°C (Batayneh *et al.*, 2012).

As a preliminary work, Clark (1986) has produced a regional geological map (1:250,000 scale) for the Midyan Basin. Following this, Wyn Hughes *et al.* (1999) have reported that the plain of

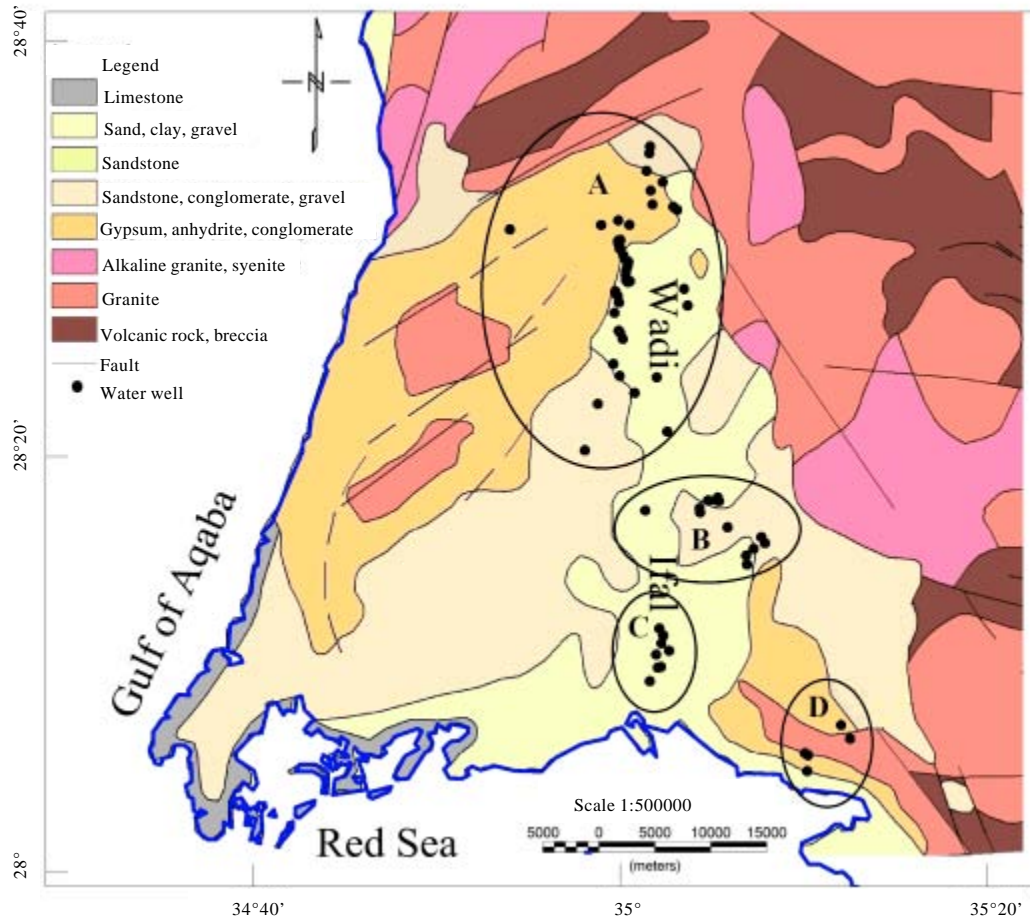


Fig. 1: Geological map of the Midyan region, northwestern Saudi Arabia (modified after Wyn Hughes *et al.*, 1999). Boreholes locations are shown as black circles. The encircled areas represent the clustering A, B, C and D

Wadi Ifal occupies most of the basin (Fig. 1). Recently, the most updated chronostratigraphic succession for the Midyan Basin (Fig. 2) has been reported by Wyn Hughes and Johnson (2005). The oldest sedimentary rocks in the basin are the Late Cretaceous Adaffa Formation from Suqah Group (fluvial in origin), which unconformably overlies the Proterozoic basement. The Suqah Group is then unconformably overlain by the Early Miocene Burqan Formation from Tayran Group (deep marine), which in turn is overlain by marine mudstones, carbonates and evaporites of the middle Miocene Maqna Group. The poorly exposed middle Miocene Mansiyah and middle to upper Miocene Ghawwas formations are made of marine evaporites and shallow to marginal marine sediments, respectively.

The youngest rocks in the basin are the alluvial sands and gravels of the Early Pliocene Lisan Formation, which was deposited during the opening of the Gulf of Aqaba, representing a shallow alluvial aquifer system in the basin (Bokhari, 1981; Jado *et al.*, 1990; Batayneh *et al.*, 2012). The recharge to this aquifer is taking place either from elevated areas in the north, east and west, or from local surface water infiltrations. The drainage system in the basin is generally radial in nature concentrating to the center of the basin.

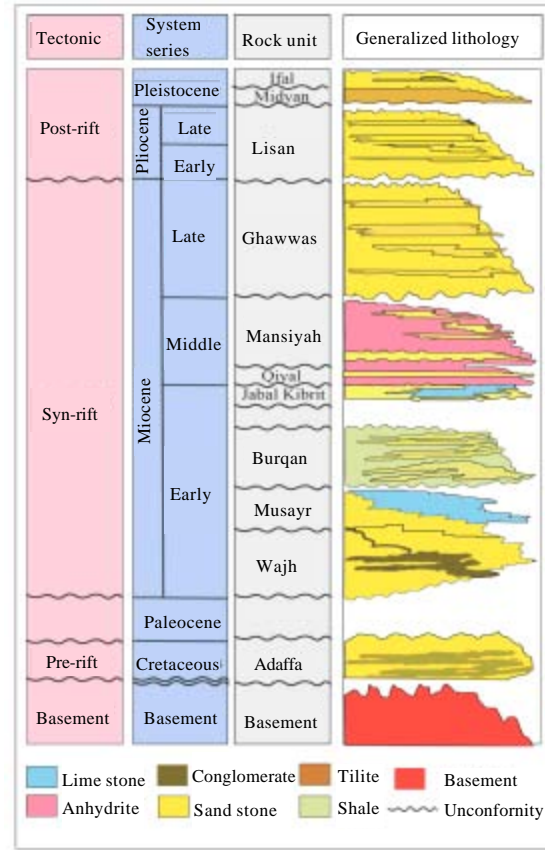


Fig. 2: Generalized chrono-lithostratigraphic succession of the Midyan region (modified after Wyn Hughes and Johnson (2005))

Data collection: Water samples for chemical analyses were collected in January 2012. A total of 72 samples of groundwater were collected from 72 boreholes in the Midyan Basin, northwestern Saudi Arabia. Samples were collected in polyethylene bottles of one-liter capacity. Prior to their filling with sampled water, these bottles were rinsed to minimize the chance of any contamination. The samples preservation and the used analytical techniques were in accordance with the standard methods from APHA (1998). Hydrogen ion concentration (pH) was determined at the sampling sites with the help of a pH-meter (Hanna Instruments, Michigan, USA).

Laboratory analysis: Physicochemical characteristics like Total Alkalinity (TA), Total Solids (TS), Suspended Solids (SS) and Chemical Oxygen Demand (COD) were determined. The TA was measured as mg CaCO₃ L⁻¹ based on the volume of acid consumed by the groundwater samples. The parameters related to solids (TS and SS) were determined by gravimetric method (APHA, 1998). COD was determined through potassium dichromate by open reflux method. The metals of concern in the investigation are lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr) and zinc (Zn). Statistical analyses of physicochemical parameters, heavy metals and metalloid are presented in Table 1. For quality control, all groundwater samples were analyzed in triplicate for mean values

Table 1: Statistical analyses of heavy metals elements, metalloid and physicochemical parameters

| Parameter (mg L ⁻¹) | Min. | Max. | Average | Median | GM | SD |
|---------------------------------|---------|--------|----------|---------|---------|----------|
| Pb | 0.00015 | 0.0038 | 0.001120 | 0.00090 | 0.00084 | 0.000790 |
| Cd | 0.00040 | 0.0009 | 0.000590 | 0.00060 | 0.00057 | 0.000130 |
| As | 0.00080 | 0.0051 | 0.001850 | 0.00175 | 0.00172 | 0.000750 |
| Cr | 0.00080 | 0.0114 | 0.002133 | 0.00190 | 0.00187 | 0.001453 |
| Zn | 0.00035 | 0.1597 | 0.007790 | 0.00035 | 0.00113 | 0.024480 |
| TA | 30 | 300 | 175.49 | 180 | 165.03 | 50.85 |
| TS | 967 | 8523 | 2432.4 | 1853 | 2102.8 | 1484.4 |
| SS | 422 | 1496 | 662.7 | 601 | 638.1 | 201.0 |
| COD | 0.4 | 4.8 | 1.178 | 1.2 | 1.045 | 0.657 |
| pH | 7.38 | 8.29 | 7.80 | 7.81 | 7.80 | 0.224 |

GM: Geometric mean, TA: Total alkalinity, TS: Total solids, SS: Suspended solids, COD: Chemical oxygen demand, n = 72

Table 2: Concentration, blank, sample-to-blank ratio, detection limits and wavelengths for the studied metals

| Element | Concentration* (mg L ⁻¹) | Blank* (mg L ⁻¹) | Sample-to-blank ratio | Detection limit (mg L ⁻¹) | Wave length (nm) |
|---------|--------------------------------------|------------------------------|-----------------------|---------------------------------------|------------------|
| Pb | 0.001120 | 0.00030 | 4.0 | 0.00030 | 220.353 |
| Cd | 0.000590 | 0.00005 | 12.0 | 0.00003 | 228.802 |
| As | 0.001850 | 0.00060 | 3.1 | 0.00060 | 189.042 |
| Cr | 0.002133 | 0.00008 | 27.0 | 0.00006 | 283.563 |
| Zn | 0.007790 | 0.00030 | 26.0 | 0.00030 | 213.857 |

*Average values are taken, n = 72

calculation. Blank samples (acids blank) were also prepared among one or two batches during samples digestion. Acid blank samples were analyzed along with the groundwater samples and the average contribution of the added acids and reagents were estimated (Table 2). All the obtained results were then corrected by subtracting the average blank concentration observed for certain elements from the concentration observed for the same element in each sample. Sample-to-blank ratio for most of the measured elements is greater than 3. This means that blank subtraction does not have significant affects on the observed concentrations. The absorption wavelengths and detection limits of metals are given in Table 2. The accuracy and precision of the analytical data were checked by periodic analysis of Standard Reference Materials (SRMs) obtained from the National Institute of Standards and Technology (NIST). Three SRMs were used: SRM-1646a (Estuarine Sediments), SRM-1633b (Trace elements in Coal Fly Ash) and SRM-2702 (Inorganics in Marine Sediments). Approximately 0.5 g of the SRM was transferred into a Teflon beaker for digestion using the same procedure adopted for the groundwater samples and analyzed. The results obtained from SRM analysis are in good agreement with the certified concentration values within 10% for all the measured elements.

Statistical analysis: With increasing number of chemical and physical variables in groundwater, a wide range of statistical techniques are now in use. Statistical analysis procedures, as powerful tools, can provide knowledge and assist the interpretation of environmental data (Sena *et al.*, 2002). The Excel program was used to analyze the results statistically and to assess an adequate distinction between different cases. Average concentrations, Standard Deviations (SD), Geometric Means (GM), medians, minimum (Min) and maximum (Max) concentration and T-test of water samples analyzed are presented. The probability values of $p < 0.05$ and $p > 0.05$ have been used as statistically significant and statistically not significant, respectively.

Risk assessment: Calculations of risk were depend on the concentration level detected and their distance from anthropogenic activities. Calculations were made for both adult and children. According to the US Environmental Protection Agency (US EPA, 2002) technique, the following points have been taken into consideration: (1) the water consumption every day for the whole human lifetime, (2) the water quality is specified for the same period, (3) the average amount of water used every day for drinking is 2.0 liters for adult and 1.0 liter for children and (4) the mean body weight is 50 kg for adult and 20 kg for children. Thus, the dose of a chemical substance taken by a person with drinking water every day is given by:

$$ADDd = \frac{DW \times C}{BW} \quad (1)$$

where, ADDd is the dose taken with drinking water, BW is the body weight (kg), C is the substance content in water (mg L^{-1}) and DW is the mean volume of water drank every day (liters).

The Hazard Quotient (HQ) was calculated by Eq. 2 to estimate noncarcinogenic risk (US EPA, 2010):

$$HQ = \frac{ADDd}{RfD} \quad (2)$$

where, ADDd is the exposure dose obtained from Eq. 1 and RfD is the reference dose of the contaminant.

The RfD represents a dose below which toxicity does not affect the humans (including sensitive subgroups) during a lifetime. The recommended RfD values are $0.0003 \text{ mg Pb kg day}^{-1}$, $0.0005 \text{ mg Cd kg day}^{-1}$, $0.0003 \text{ mg As kg day}^{-1}$, $0.003 \text{ mg Cr kg day}^{-1}$ and $0.05 \text{ mg Zn kg day}^{-1}$ for lead, cadmium, arsenic, chromium and zinc (Zn), respectively (Dourson and Stara, 1983; Dourson *et al.*, 1992).

To assess the overall noncarcinogenic risk posed by all metals in one groundwater sample, the HQ of each chemical was summed and expressed as Hazard Index (HI) by Eq. 3 (US EPA, 2010):

$$HI = \sum_{i=1}^n HQ_i \quad (3)$$

RESULTS AND DISCUSSION

Physicochemical parameters: Statistical analyses on the concentration of four evaluated physicochemical parameters (TA, TS, SS and COD) are presented in Table 1. As listed in this table, standard deviations are high for most of the measured parameters, which may be due to large variability in samples locations, industrial and human activities, physical and chemical nature of the sampling site, changes in the air mass transport patterns and variations in the source strengths (Batayneh, 2012).

Analytical maps for the physicochemical parameters distribution (not shown here) reveals the trend of concentrations observed at different locations. The observed TA has a mean value of 175.49 mg L^{-1} and standard deviation of 50.85 mg L^{-1} ; ranging between 30 to 300 mg L^{-1}

(Table 1). The TA distribution map shows relatively higher values in the wells located down-slope of the main wadi "Ifal". The trend observed for the solids (TS and SS) also shows higher values were recorded in the down-gradient area of wadi Ifal, which poses more environmental risks than other areas. In the study area, the TS and SS have mean values of 2432.3 and 662.7 mg L⁻¹ and have standard deviation of 1484.4 and 201.0 mg L⁻¹, respectively (Table 1). These results imply that the southern and southeastern parts of the study area (downstream of wadi Ifal) are possibly undergoing biodegradation as indicated by increasing input of solids, while the northern, northeastern and northwestern parts have already been degraded by leaching in the upstream areas. This view is further supported by COD results from the study area. The COD values have range between 0.4 and 4.8 mg L⁻¹, making an average value of 1.178 mg L⁻¹ and standard deviation of 0.657 mg L⁻¹ (Table 1). A maximum value of COD has been recorded in the southeastern part (downstream of wadi Ifal), which strongly upholds the view that the upstream of wadi Ifal (the northern parts) is much degraded and thus having lesser organic matters.

Trace metals and metalloid: The lead (Pb) element occurs naturally in Earth in the form of four isotopes: Pb-204, -206, -207 and -208. It is chemically a post-transition metal with two main oxidation states, i.e., +2 and +4. The former is considered more stable compared to later state, where the later is counted as an oxidizer with lead (IV) ions exist only in highly acidic solutions. Water in the presence of oxygen attacks Pb to start an accelerated reaction. The presence of carbonates or sulfates leads to formation of insoluble Pb salts, which prevent this metal from corrosion. It is usually found as ore in association with zinc, silver and copper and is extracted together with these metals. The main mineral is category is galena (PbS), which contains 86.6% Pb by weight. Other common members are cerussite (PbCO₃) and anglesite (PbSO₄) (Keisch *et al.*, 1967; Keisch, 1968a, b). The results for Pb concentration in this study show location based variability, ranging between 0.00015 and 0.0038 mg L⁻¹ for the studied water samples (Table 1). In the case of Midyan Basin, the Pb concentration is lower than the maximum allowable concentration level of 0.01 mg L⁻¹ recommended by World Health Organization (WHO, 2008) for drinking water. The highest concentration of Pb has been detected in borehole No. 30.

Chemically cadmium (Cd) is not always considered as a transition metal rather it shows oxidation state of +2 in most of its compounds and low melting point compared to transition metals. The average concentration of cadmium in the Earth's crust is between 0.1 and 0.5 ppm (Wedepohl, 1995; Fthenakis, 2004). Cd occurs as a minor component in most zinc related ores and, therefore, is a byproduct of zinc them. It is produced mainly as a byproduct of sulfide ores (zinc) from mining, smelting and refining and to a lesser degree from lead and copper. Small amounts of cadmium are produced from secondary sources as well mainly from dust generated by iron and steel recycling (Fthenakis, 2004). Rocks mined for phosphate fertilizers contain varying amounts of cadmium, leading to a concentration of up to 300 mg kg⁻¹ in them, which provide high cadmium contents to agricultural soils (Jiao *et al.*, 2004; Grant and Sheppard, 2008). Coal can also contain significant amounts of cadmium, which ends up mostly in the flue dust (Bettinelli *et al.*, 1988). Cd concentration in the studied water samples ranged between 0.0004 and 0.0009 mg L⁻¹ (Table 1). These results, thus, indicate that the Cd concentrations in the studied groundwater are lower than

the maximum allowable level of 0.003 mg L⁻¹ recommended by WHO (2008) for drinking water. Similar Pb concentration, the highest amount of Cd has been detected in the water of borehole No. 30.

Chromium (Cr) element is widely distributed in the Earth's crust, which can exist in oxidation states of +2 to +6. Soils and rocks may contain small amounts of chromium, but always in the trivalent state. The average concentration of chromium in rainwater is in the range of 0.0002 to 0.001 mg L⁻¹. In general, the chromium contents in surface water reflect the extent of industrial activities in that area (Shiller and Boyle, 1987). The range of chromium concentration in the studied groundwater samples is 0.0008-0.0114 mg L⁻¹ (Table 1) and the highest value is detected in borehole No. 5. This range of chromium concentration places the studied water samples within the safe limit for drinking, which is much lower than maximum allowable level of 0.05 mg L⁻¹ recommended by WHO (2008).

Zinc (Zn) occurs in small amounts in almost all igneous rocks. The principal zinc ores are sulfides, such as sphalerite and wurtzite (Nriagu, 1980; Elinder, 1986). The zinc contents in natural soils have been estimated to be 1-300 mg kg⁻¹ (Nriagu, 1980). In surface waters the concentration of zinc is usually below 0.010 mg L⁻¹ and in groundwaters it is between 0.010 and 0.040 mg L⁻¹ (Nriagu, 1980; Elinder, 1986). In Midyan Basin, the range of zinc concentration in the studied groundwater samples is 0.00035 to 0.1597 mg L⁻¹ (Table 1), where the highest value has been detected in borehole No. 36. As shown in Table 1, concentrations of zinc in the studied samples are much lower than the maximum allowable level of 4.0 mg L⁻¹ for drinking water (WHO, 2008).

Metalloid arsenic (As) occurs naturally in one stable isotope (As-75) and when heated in air it oxidizes to arsenic trioxide. Arsenic has been less commonly observed in the pentavalent state. However, the most common oxidation states for arsenic are: -3 in the arsenides (such as alloy-like intermetallic compounds), +3 in the arsenites, arsenates and most organoarsenic compounds (Gokcen, 1989; Matschullat, 2000). The range of arsenic (As) concentration in the studied groundwater is 0.0008-0.0051 mg L⁻¹ (Table 1), where the highest value is detected in the borehole No. 30. This range is lower than the maximum allowable level of (0.01 mg L⁻¹) recommended by the WHO (2008).

Statistical analysis of the physicochemical and trace elements: The results of chemical analysis for the evaluated metals in this study show variability on the basis of sampling locations. Accordingly, the groundwater samples have been classified into four clusters (denoted by A, B, C and D, Fig. 1), which can be mainly attributed to inhabitants' settlements and anthropogenic activities in the study area. In order to assess whether the means of physicochemical parameters and trace metals at four locations (A, B, C and D) are statistically different, student's T-test analysis has been used to compare the mean concentrations of each parameter through clusters (Table 3 and 4). Student's t-test is used to determine whether water quality parameters of a particular site is contaminated or not and then compare it with that of other monitoring sites (Keppel and Wickens, 2004). In this study, the calculated T-test difference between cluster A and B (Table 3) has been found statistically significant for the means of TA, TS, SS, pH, Cd and As parameters ($p < 0.05$) at the 95% confidence interval. This type of behavior indicates that the source of solids (TS and SS), Cd and As chemicals at these two locations are different, while statistically insignificant differences have been observed for the other parameters such as COD, Pb, Cr and Zn, ($p > 0.05$) at 95%

Table 3: Comparison of the physicochemical parameters and heavy metal and metalloid levels between the clusters A-B, A-C and A-D using students t-test

| Parameter | Cluster A and B | | | Cluster A and C | | | Cluster A and D | | |
|-----------|-----------------|---------|----------------------|-----------------|---------|----------------------|-----------------|---------|----------------------|
| | df | t-value | p-value | df | t-value | p-value | df | t-value | p-value |
| TA | 57 | 3.07 | 0.0033* | 52 | 1.520 | 0.1400 ^{ns} | 49 | 3.240 | 0.0020* |
| TS | 57 | 7.87 | 0.0001* | 52 | 12.570 | 0.0001* | 49 | 4.520 | 0.0001* |
| SS | 57 | 8.08 | 0.0001* | 52 | 9.430 | 0.0001* | 49 | 4.600 | 0.0001* |
| COD | 57 | 0.87 | 0.3900 ^{ns} | 52 | 0.102 | 0.9200 ^{ns} | 49 | 3.280 | 0.0019* |
| pH | 57 | 2.45 | 0.0170* | 52 | 0.630 | 0.5300 ^{ns} | 49 | 1.960 | 0.0600 ^{ns} |
| Pb | 57 | 0.26 | 0.8000* | 52 | 3.630 | 0.0007* | 49 | 0.530 | 0.6000 ^{ns} |
| Cd | 57 | 3.07 | 0.0030* | 52 | 4.980 | 0.0001* | 49 | 4.220 | 0.0001* |
| As | 57 | 2.44 | 0.0180* | 52 | 6.360 | 0.0001* | 49 | 4.710 | 0.0001* |
| Cr | 57 | 0.69 | 0.4900 ^{ns} | 52 | 0.580 | 0.5600 ^{ns} | 49 | 0.071 | 0.9400 ^{ns} |
| Zn | 57 | 0.35 | 0.7300 ^{ns} | 52 | 0.650 | 0.5200 ^{ns} | 49 | 0.360 | 0.7200 ^{ns} |

df: Degree of freedom, TA: Total alkalinity, TS: Total solids, SS: Suspended solids, COD: Chemical oxygen demand, *Statistically significant at $p < 0.05$, ns: Not significant

Table 4: Comparison of the physicochemical parameters and heavy metal and metalloid levels between the clusters B-C, B-D and C-D using students t-test

| Parameter | Cluster B and C | | | Cluster B and D | | | Cluster C and D | | |
|-----------|-----------------|---------|---------------------|-----------------|---------|---------------------|-----------------|---------|---------------------|
| | df | t-value | p-value | df | t-value | p-value | df | t-value | p-value |
| TA | 19 | 1.450 | 0.160 ^{ns} | 16 | 1.53 | 0.150 ^{ns} | 11 | 2.67 | 0.022* |
| TS | 19 | 2.340 | 0.030* | 16 | 0.27 | 0.790 ^{ns} | 11 | 0.87 | 0.410 ^{ns} |
| SS | 19 | 1.330 | 0.200 ^{ns} | 16 | 0.26 | 0.800 ^{ns} | 11 | 0.43 | 0.670 ^{ns} |
| COD | 19 | 0.470 | 0.640 ^{ns} | 16 | 2.23 | 0.040* | 11 | 1.35 | 0.200 ^{ns} |
| pH | 19 | 2.450 | 0.020* | 16 | 0.37 | 0.720 ^{ns} | 11 | 2.22 | 0.048* |
| Pb | 19 | 3.140 | 0.005* | 16 | 0.75 | 0.460 ^{ns} | 11 | 1.49 | 0.160 ^{ns} |
| Cd | 19 | 2.710 | 0.014* | 16 | 2.94 | 0.009* | 11 | 0.05 | 0.960 ^{ns} |
| As | 19 | 3.870 | 0.001* | 16 | 5.86 | 0.0001* | 11 | 0.79 | 0.490 ^{ns} |
| Cr | 19 | 0.058 | 0.950 ^{ns} | 16 | 0.99 | 0.340 ^{ns} | 11 | 0.89 | 0.390 ^{ns} |
| Zn | 19 | 0.240 | 0.810 ^{ns} | 16 | 0.47 | 0.650 ^{ns} | 11 | 1.25 | 0.240 ^{ns} |

df: Degree of freedom, TA: Total alkalinity, TS: Total solids, SS: Suspended solids, COD: Chemical oxygen demand, *Statistically significant at $p < 0.05$, ns: Not significant

confidence interval. On the other hand, cluster A and C (Table 3) show significant difference in the TS, SS, Pb, Cd and As parameters, indicating different sources for these parameters at two locations but show insignificant difference for TA, COD, pH, Cr and Zn parameters. In addition, comparison of cluster A and D (Table 3) show statistically different means for TA, TS, SS, COD, Cd and As parameters, indicating different sources for these chemicals at the two sites. However, at these two locations insignificant differences have been observed for pH, Pb, Cr and Zn chemicals.

Furthermore, a difference between cluster B and C (Table 4) has been statistically found significant for the means of TS, pH, Pb, Cd and As parameters ($p < 0.05$) at 95% confidence interval, indicating Pb, Cd and As are of different natural and/or anthropogenic sources at these two locations. However, statistically insignificant differences have been observed for other parameters ($p > 0.05$) at 95% confidence interval. These results also indicate that the mean values of COD, Cd and As parameters at locations B and D are statistically different at 95% confidence interval (Table 4), demonstrating different natural and anthropogenic sources for these parameters at these

Table 5: Comparison with geometric means of other studies for metal concentrations (mg L⁻¹)

| Element | This study | Yarmouk basin (Jordan) ^a | Asa (Nigeria) ^b | Middle Rnssia ^c | Wadi Hanifah (Saudi Arabia) ^d | Chihuahua (Mexico) ^e |
|---------|------------|-------------------------------------|----------------------------|----------------------------|--|---------------------------------|
| Pb | 0.00084 | 0.00220 | 0.11 | 0.0100 | 0.00095 | - |
| Cd | 0.00057 | 0.00048 | - | 0.0240 | 0.00087 | 0.003 |
| As | 0.00172 | - | - | 0.0300 | - | 0.070 |
| Cr | 0.00187 | 0.00230 | 0.01 | 0.0490 | 0.0064 | 0.070 |
| Zn | 0.00113 | 0.00915 | 0.42 | 0.0040 | - | - |

^aBatayneh (2010, 2012); ^bEletta (2007); ^cMomot and Synzynys (2005); ^dAbdel-Baki *et al.* (2011); ^eGutierrez *et al.* (2008)

two locations. Statistically insignificant differences for other parameters (TA, TS, SS, pH, Pb, Cr and Zn) have been observed at these locations. Table 4 also shows insignificant difference for most chemical parameters between C and D locations.

Comparison with literature data: In most environmental studies, comparison of the obtained data with those in the literature is one of the essential steps in order to know the extent of groundwater contamination by heavy metals. The study area is classified as urban, which is directly influenced by local anthropogenic emissions. Therefore, in order to roughly estimate the extent of pollution in the area under study, the results should be compared with the literature data in which the pollution level is known. Comparison of the observed data with those available from resembling areas help find the reason behind any unusual result, which could be due to any particular analytical problem. Calculated Geometric Means (GM) values for the analyzed element in the studied groundwater samples (Table 1) are compared with those found by other researchers around the world (Table 5).

Table 5 reveals that geometric mean concentrations of lead (Pb) in the studied groundwater samples is about 2 times lower than the level reported from Yarmouk Basin in Jordan (Batayneh, 2010, 2012), 140 times lower than the level reported from Asa in Nigeria (Eletta, 2007), 12 times lower than the level reported Middle Russia (Momot and Synzynys, 2005) and almost the same level with that reported from Wadi Hanifah in Saudi Arabia (Abdel-Baki *et al.*, 2011). For cadmium (Cd) metal, the geometric concentration in the studied groundwater samples is about 5 and 42 times lower than the level reported from Chihuahua in Mexico (Gutierrez *et al.*, 2008) and Middle Russia (Momot and Synzynys, 2005), respectively and almost the same level as reported from Yarmouk Basin (Jordan) and Wadi Hanifah (Saudi Arabia). In addition, the respective levels of arsenic (As) metal reported from Chihuahua (Mexico) and Middle Russia are about 41 and 17 times higher than the level observed in this study (Table 5). On the other hand, the level of chromium (Cr) metal in this study is about 37 times lower than that reported from Chihuahua (Mexico), 5 times lower than that reported from Asa (Nigeria), 26 times lower than that reported from Middle Russia, 3 times lower than the level reported from Wadi Hanifah (Saudi Arabia) and almost the same level as reported from Yamouk Basin (Jordan). The level of zinc (Zn) in this study (Table 5) is about 9 times lower than that reported from Yarmouk Basin (Jordan), 372 times lower than that reported from Asa (Nigeria) and about 4 times lower than that reported from Middle Russia.

Risk assessment: On the basis of heavy metal and metalloid concentrations detected in the studied groundwater samples (Table 1), boreholes 5, 30 and 36 have been found the worst among the 72 boreholes. Thus, these 3 wells are used for risk assessment.

The estimated ADDd, HQ and HI values from evaluated trace elements and metalloid at each borehole are given in Table 6. For lead, cadmium and arsenic elements in the both of age stages,

Table 6: Average daily dose (ADDd), hazard quotient (HQ) and hazard index (HI) values from metals exposure

| Water source | Substance | C (mg L ⁻¹) | Adult | | | | | Children | | | | |
|-----------------|-----------|-------------------------|------------------|-----------------|--------|-------|------------------|-----------------|--------|-------|--|--|
| | | | ADDd (mg/kg/day) | RfD (mg/kg/day) | HQ | HI | ADDd (mg/kg/day) | RfD (mg/kg/day) | HQ | HI | | |
| Borehole No. 5 | Lead | 0.00200 | 0.000080 | 0.0003 | 0.2670 | 0.606 | 0.0001 | 0.0003 | 0.3333 | 0.757 | | |
| | Cadmium | 0.00050 | 0.000020 | 0.0005 | 0.0400 | | 0.000025 | 0.0005 | 0.0500 | | | |
| | Arsenic | 0.00110 | 0.000044 | 0.0003 | 0.1470 | | 0.000055 | 0.0003 | 0.1833 | | | |
| | Chromium | 0.01140 | 0.000456 | 0.0030 | 0.1520 | | 0.00057 | 0.0030 | 0.1900 | | | |
| | Zinc | 0.00035 | 0.000014 | 0.0500 | 0.0003 | | 0.0000175 | 0.0500 | 0.0004 | | | |
| Borehole No. 30 | Lead | 0.00380 | 0.000152 | 0.0003 | 0.5070 | 1.270 | 0.00019 | 0.0003 | 0.6333 | 1.590 | | |
| | Cadmium | 0.00090 | 0.000036 | 0.0005 | 0.0720 | | 0.000045 | 0.0005 | 0.0900 | | | |
| | Arsenic | 0.00510 | 0.000204 | 0.0003 | 0.6800 | | 0.000255 | 0.0003 | 0.8500 | | | |
| | Chromium | 0.00100 | 0.000040 | 0.0030 | 0.0130 | | 0.00005 | 0.0030 | 0.0167 | | | |
| | Zinc | 0.00035 | 0.000014 | 0.0500 | 0.0003 | | 0.0000175 | 0.0500 | 0.0004 | | | |
| Borehole No. 36 | Lead | 0.00110 | 0.000044 | 0.0003 | 0.1470 | 0.483 | 0.000055 | 0.0003 | 0.1833 | 0.602 | | |
| | Cadmium | 0.00060 | 0.000024 | 0.0005 | 0.0480 | | 0.00003 | 0.0005 | 0.0600 | | | |
| | Arsenic | 0.00180 | 0.000072 | 0.0003 | 0.2400 | | 0.00009 | 0.0003 | 0.3000 | | | |
| | Chromium | 0.00260 | 0.000104 | 0.0030 | 0.0350 | | 0.00013 | 0.0030 | 0.0433 | | | |
| | Zinc | 0.01580 | 0.000632 | 0.0500 | 0.0130 | | 0.00079 | 0.0500 | 0.0158 | | | |

the highest ADDd values are observed in borehole 30. In addition, the highest ADDd value for chromium metal is observed in borehole 5 and for zinc in borehole 36 in the both of age stages (Table 6). The noncarcinogenic HQ calculated for the trace metals and metalloid in the three wells, places them well below the threshold value of concern in terms of adverse health effects. Furthermore, the total noncarcinogenic HI calculated for the both age stages (adult and children) in the borehole 5 is 0.606 and 0.757, in borehole 30 is 1.27 and 1.59 and in borehole 36 is 0.483 and 0.602 (Table 6), which indicates that no adverse health effects are expected to occur for boreholes 5 and 36. As seen from the above, the range of exposures to trace metals in the two wells (5 and 36) is below the allowable level, suggesting that the water posed negligible health risk on local residents.

CONCLUSIONS

This study has been conducted to monitor trace elements levels in the groundwater wells of the Midyan Basin, northwestern Saudi Arabia. The concentrations of heavy metals, metalloid and physicochemical parameters in the studied water do not exceeded the maximum permissible level. The obtained results farther suggest that the contribution of chemicals in these waters are mainly attributed to an inputs from rocks, agriculture and human activities. Surface and groundwater flow directions, borehole locations and land structures (fractures) appeared to be significant factors contributing to the elevated chemical contents. The results also showed that boreholes located in the south and southeastern areas of the basin are more vulnerable to metals contamination. For the residents consuming groundwater, the calculated Average Daily Dose intake through drinking water (ADDd) and the noncarcinogenic risk (HQ) associated with exposure to trace metals indicate that the range of exposures to evaluated metals in all the studied boreholes is below the Reference Dose (RfD) of these metals. In addition, the HQ values are less than 1, indicating that they are within the tolerable range and essentially having no chance of affecting human health by noncarcinogenic.

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REFERENCES

- APHA, 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edn., American Public Health Association, Washington, DC., USA., ISBN: 0875532357, Pages: 1270.
- Abdel-Baki, A.S., M.A. Dkhil and S. Al-Quraishy, 2011. Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of Wadi Hanifah, Saudi Arabia. *Afr. J. Biotechnol.*, 10: 2541-2547.
- Abderahman, N. and Y. Abu-Rukah, 2006. An assessment study of heavy metal distribution within soil in upper course of Zarqa River basin/Jordan. *Environ. Geol.*, 49: 1116-1124.
- Batayneh, A., 2010. Heavy metals in water springs of the Yarmouk Basin, North Jordan and their potentiality in health risk assessment. *Int. J. Phys. Sci.*, 5: 997-1003.

- Batayneh, A., 2012. Toxic (aluminum, beryllium, boron, chromium and zinc) in groundwater: Health risk assessment. *Int. J. Environ. Sci. Technol.*, 9: 153-162.
- Batayneh, A., A. Laboun, S. Qaisy, H. Ghrefat and T. Zumlot *et al.*, 2012. Assessing groundwater quality of the shallow alluvial aquifer system in the Midyan Basin, northwestern Saudi Arabia. *Arab Gulf J. Sci. Res.* 30: 7-13.
- Bettinelli, M., U. Baroni and N. Pastorelli, 1988. Determination of arsenic, cadmium, lead, antimony, selenium and thallium in coal fly ash using the stabilised temperature platform furnace and Zeeman-effect background correction. *J. Anal. Atomic Spectrom.*, 3: 1005-1011.
- Bokhari, M., 1981. Explanatory notes to the reconnaissance geologic map of the Maqna Quadrangle, Sheet 28/34 D, Kingdom of Saudi Arabia. Saudi Arabian Directorate General of Mineral Resources. Open File Report DGMR-OF-01-16, pp: 32.
- Bozkurtoglu, E., M. Vardar, F. Suner and C. Zambak, 2006. A new numerical approach to weathering and alteration in rock using a pilot area in the Tuzla geothermal area, Turkey. *Eng. Geol.*, 87: 33-47.
- Buccolieri, A., G. Buccolieri, N. Cardellicchio, A. Dell'Atti, A. Di Leo and A. Maci, 2006. Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy). *Mar. Chem.*, 99: 227-235.
- Bulut, Y. and Z. Baysal, 2006. Removal of Pb (II) from wastewater using wheat bran. *J. Environ. Manage.*, 78: 107-113.
- Clark, M., 1986. Explanatory notes to the geologic map of the Al Bad Quadrangle, sheet 28A, Kingdom of Saudi Arabia. Saudi Arabian Deputy Ministry for Mineral Resources. Geoscience Map Series GM-81A, C, scale 1:250,000, with text, pp: 46.
- Das, A. and S. Krishnaswami, 2007. Elemental geochemistry of river sediments from the Deccan Traps, India: Implications to sources of elements and their mobility during basalt-water interaction. *Chem. Geol.*, 242: 232-254.
- Dourson, M.L. and J.F. Stara, 1983. Regulatory history and experimental support of uncertainty (safety) factors. *Regulatory Toxicol. Pharmacol.*, 3: 224-238.
- Dourson, M.L., L.A. Knauf and J.C. Swartout, 1992. On reference dose (RfD) and its underlying toxicity data base. *Toxicol. Ind. Health*, 8: 171-189.
- Duruibe, J.O., M.O.C. Ogwuegbu and J.N. Ekwurugwu, 2007. Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.*, 2: 112-118.
- Eletta, O.A.A., 2007. Determination of some trace metal levels in Asa river using AAS and XRF techniques. *Int. J. Phys. Sci.*, 2: 056-060.
- Elinder, C., 1986. *Handbook on the Toxicology of Metals*. 2nd Edn., Elsevier Science Publishing, Amsterdam.
- Elmaci, A., A. Teksoy, F.O. Topac, N. Ozengin, S. Kurtoglu and H.S. Baskaya, 2007. Assessment of heavy metals in Lake Uluabat, Turkey. *Afr. J. Biotechnol.*, 6: 2236-2244.
- Fthenakis, V., 2004. Life cycle impact analysis of cadmium in CdTe PV production. *Renewable Sustainable Energy Rev.*, 8: 303-334.
- Giuliano, V., F. Pagnanelli, L. Bornoroni, L. Toro and C. Abbruzzese, 2007. Toxic elements at a disused mine district: Particle size distribution and total concentration in stream sediments and mine tailing. *J. Hazard. Mat.*, 148: 409-418.
- Gokcen, N., 1989. The As (arsenic) system. *Bull. Alloy Phase Diagrams*, 10: 11-22.
- Grant, C. and S. Sheppard, 2008. Fertilizer impacts on cadmium availability in agricultural soils and crops. *Hum. Ecol. Risk Assess. Int. J.*, 14: 210-228.

- Gutierrez, R., H. Rubio-Arias, R. Quintana, J. Ortega and M. Gutierrez, 2008. Heavy metals in water of the San Pedro river in Chihuahua, Mexico and its potential health risk. *Int. J. Environ. Res. Public Health*, 5: 91-98.
- Ip, C.C.M., X.D. Li, G. Zhang, O.W.H. Wai and Y.S. Li, 2007. Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *J. Environ. Pollut.*, 147: 311-323.
- Jado, A.R., H. Hotzl and B. Roscher, 1990. Development of sedimentation along the Saudi Arabian Red Sea coast. *J. King Abdulaziz Univ.*, 3: 47-62.
- Jiao, Y., C. Grant and L. Bailey, 2004. Effects of phosphorus and zinc fertilizer on cadmium uptake and distribution in flax and durum wheat. *J. Sci. Food Agric.*, 84: 777-785.
- Kar, D., P. Sur, S.K. Mandal, T. Saha and R.K. Kole, 2008. Assessment of heavy metal pollution in surface water. *Int. J. Environ. Sci. Technol.*, 5: 115-124.
- Keisch, B., R. Feller, A. Levine and R. Edwards, 1967. Dating and authenticating works of art by measurement of natural alpha emitters. *Science*, 155: 1238-1242.
- Keisch, B., 1968a. Dating works of art through their natural radioactivity: Improvements and applications. *Science*, 160: 413-415.
- Keisch, B., 1968b. Discriminating radioactivity measurements of lead: New tool for authentication. *Curator: Museum J.*, 11: 41-52.
- Keppel, G. and T. Wickens, 2004. *Design and Analysis: A researcher's Handbook*. 4th Edn., Pearson College Div., USA.
- Low, K.S., C.K. Lee and S.C. Liew, 2000. Sorption of cadmium and lead from aqueous solutions by spent grain. *Process Biochem.*, 36: 59-64.
- Mahjoobi, A., M. Albaji and K. Torfi, 2010. Determination of heavy metal levels of kondok soils-haftgel. *Res. J. Environ. Sci.*, 4: 294-299.
- Matschullat, J., 2000. Arsenic in the geosphere-A review. *Sci. Total Environ.*, 249: 297-312.
- Momot, O. and B. Synzynys, 2005. Toxic aluminum and heavy metals in groundwater of middle Russia: Health risk assessment. *Int. J. Environ. Res. Public Health*, 2: 214-218.
- Moreno, T., X. Querol, S. Castillo, A. Alastuey and E. Cuevas *et al.*, 2006. Geochemical variations in aeolian mineral particles from the Sahara-Sahel dust corridor. *Chemosphere*, 65: 261-270.
- Nriagu, O., 1980. *Zinc in the Environment. Part 1, Ecological Cycling*. John Wiley, New York.
- Ong, M.C. and B.Y. Kamaruzzaman, 2009. An assessment of metals (Pb and Cu) contamination in bottom sediment from south china sea coastal waters, Malaysia. *Am. J. Applied Sci.*, 6: 1418-1423.
- Pekey, H., 2006. The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Mar. Pollut. Bull.*, 52: 1197-1208.
- Sena, M.M., R.T.S. Frighetto, P.J. Valarini, H. Tokeshi and R.J. Poppi, 2002. Discrimination of management effects on soil parameters by using principal component analysis: A multivariate analysis case study. *Soil Till. Res.*, 67: 171-181.
- Shiller, A.M. and E. Boyle, 1987. Variability of dissolved trace metals in the Mississippi river. *Geochim. Cosmochim. Acta*, 51: 3273-3277.
- US EPA, 2002. *National Recommended Water Quality Criteria*. United States of Environmental Protection Agency, Washington, DC., USA.
- US EPA, 2010. *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual*. U.S. Environmental Protection Agency, Washington, DC., USA.

- WHO, 2008. Guidelines for Drinking-water Quality. 3rd Edn., Incorporating the First and Second Addenda, Recommendations, Geneva.
- Wedepohl, K.H., 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta*, 59: 1217-1332.
- White, A.F., M.S. Schulz, D.V. Vivit, A.E. Blum, D.A. Stonestrom and J.W. Harden, 2005. Chemical weathering rates of a soil chronosequence on granitic alluvium: III. Hydrochemical evolution and contemporary solute fluxes and rates. *Geochim. Cosmoch. Acta*, 69: 1975-1996.
- Wyn Hughes, G. and R. Johnson, 2005. Lithostratigraphy of the Red Sea region. *Geo-Arabia*, 10: 49-126.
- Wyn Hughes, G., D. Perincek, A. Abu-Bshait and A. Jarad, 1999. Aspects of Midyan geology, Saudi Arabian Red Sea. *Saudi Aramco J. Tech.*, 1999/2000: 12-42.
- Yazdi, M. and N. Behzad, 2009. Heavy metals contamination and distribution in the parks city of Islam Shahr, SW Tehran, Iran. *Open Environ. Poll. Toxicol. J.*, 1: 49-53.
- Zorer, O.S., H. Ceylan and M. Dogru, 2009. Determination of heavy metals and comparison to gross radioactivity concentration in soil and sediment samples of the Bendimahi river basin (Van, Turkey). *Water Air Soil Poll.*, 196: 75-87.