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ORIGINAL PAPER

Impact of sewage and mining activities on distribution of heavy metals in the water-soil-vegetation system

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Abstract Several samples of groundwater and soils and plants have been collected from Sohar (Batina region, NE Oman), which is affected by various activities such as mining, agriculture, and sewage. To characterize quality of groundwater, As and Cu concentrations have been investigated in waters collected from different wells. Comparison of data with local and international standard values revealed that groundwater in Sohar region is characterized by lower concentrations in Cu and As compared with standards. In soils collected from the same area, concentrations of heavy metals have been measured in different fractions in order to investigate the mobility of such elements and risk of vulnerability in this area. A sequential extraction procedure has been applied to surface sediments to determine the partitioning of Zn, Cu, Co, Mn, Fe, Pb, Cr, Cd and Ni among (1) exchangeable and acid-soluble phases, (2) Fe–Mn oxides, (3) organic matter and sulphides and (4) resistant phases. The results showed that the mobile fraction in the sewage area accounts only for 10 % of the total concentration in sediments while in the Cu mining area, the contribution of the mobile fraction may exceed 10 %, especially for Pb, Mn, Cd, Cu and Co. Investigation of concentrations in As and Cu in plants collected from mining and sewage areas revealed an important accumulation of these elements in leaves and may explain enrichment of As in shallow groundwater relative to deep groundwater. This investigation also showed that Cu is more available in sewage area than in mining zone, as opposed to As.

Keywords Batina · Arsenic · Arid · Sediments · Standard · Sohar · Mining

Introduction

Arid areas with high temperatures are characterized by high evapotranspiration rates accompanied with low precipitation, which explains the minimum recharge of aquifers and puts the water resources under depleting conditions. In the Sultanate of Oman, where there are more than 128,000 wells tapping the major aquifers, the total annual rainfall averages 100 mm/year with 0 and 350 mm extremes. As in most of arid countries, groundwater contamination poses a threat in the country. The most important source of degradation of groundwater in Oman is due to mining more than agriculture, oil industry and salt intrusion. Copper mining activities are well developed in Batina area. Several studies have been carried out to investigate the quality of groundwater in Oman (Sharma and AL-Busaidi 2001; Jamrah et al. 2004; Yaghi 2007). Jamrah et al. (2004) established vulnerability map for Barka region (north Batina, Oman) using DRASTIC vulnerability index method in GIS environment by using groundwater quality data such as chemical and biological parameters. These authors concluded that this region is partially highly vulnerable to pollution, especially the central part. In a previous study (Yaghi 2007),

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characterization of groundwater in Batina area revealed a contamination of most of the investigated groundwater with Pb and Cr. Since degradation of quality of groundwater in Oman has been detected, the Ministry of Housing, Electricity and Water, the Ministry of Health, the Ministry of Commerce and Industry and the Ministry of Regional Municipality and Environmental and Water Resources started to give importance to testing and monitoring quality of waters in Oman. These different ministries have conducted several groundwater exploration projects throughout the Sultanate to study the availability and characteristics of groundwater resources in terms of its quantity and quality.

Although the several studies about the quality of water in Oman and in particular in Batina region, no investigation of As concentrations has been carried. Arsenic enters the environment through natural processes (Earth's crust and geothermal fluids) or via human activities such as those related to mining (Eisler 2004; Garelick et al. 2008). Thus, the main objective of the present study was to determine the concentrations of As and Cu in waters collected from wells affected by human activities such as mining, sewage and agriculture, and the mobility of As and Cu from soil to plants in the same zones with the same species of plants.

Investigation of quality of the groundwater during this study was carried out according to local standard considered by Oman and international standard fixed by WHO. Arsenic is a carcinogen that causes many cancers including skin and lung cancers. Some research concludes that even at the lower concentrations, there is still a risk of As contamination, leading to major causes of death. Arsenic contamination of groundwater is found in many countries. The most affected countries by As pollution in waters in the world include Bangladesh, India, China, Taiwan, Japan and Thailand.

Since soils have the capacity of sorbing trace elements, the second objective of this study is therefore to determine the partitioning of heavy metals in surface sediments collected from an area affected by Cu mining and in sediments collected from an area affected by sewage activities (Batina, NE Oman) in order to estimate their environmental mobility and the risk of pollution in this area.. Many different sequential extraction methods have been developed (e.g. Chester and Hughes 1967; Tessier et al. 1979; Karbassi 1998; Gleyzes et al. 2002; Ngole and Ekosse 2012). These methods involved determining the partitioning of trace elements in sediments in order to estimate their mobility and their availability in surface sediments related to environmental pollution risk, especially the anthropogenic contribution to the variation within a system.

In soils, trace elements may be associated with different phases, e.g. exchangeable, carbonate, Fe and Mn oxides, organic matter, sulphides and silicates. Their chemical form in the soil can influence their behaviour, such as their mobility, toxicity and bioavailability. Furthermore, several factors related to soil, such as soil pH, Eh, clay contents, Mn oxide and oxidized Fe, organic matter as well as cation exchange capacity, were involved with distribution of heavy metals and their availability to plants in soils (Mench et al. 1997; de Matos et al. 2000; Martinez and Motto 2000; Sterckeman et al. 2000, Aydinalp and Marinova 2003; Pregitzer and King 2005). The exchangeable and acid-extractable fractions such as carbonates are the mobile fractions that are easily bioavailable. The elements in this fraction may be affected by ion exchange and by changes in pH. The reducible fraction includes Mn and Fe oxides that may become unstable under anoxic conditions while the oxidizable fraction accounts for the fraction bound to organic matter and sulphides. During sequential extraction, the silicate minerals and crystalline Fe/Mn oxides are not easily dissolved and represent the most resistant phases. The elements in these phases are not released under natural conditions.

The trace elements investigated during this study were Cd, Co, Cr, Cu, Ni, Pb and Zn. This investigation included major elements such as Fe and Mn since they are important in trapping of trace elements.

Geology and hydrogeology of the studied area

The geological formations of Batina have undergone substantial tectonic activity involving faulting and thrusting. The geologic setting of basin consists of crystalline bedrock formations, mainly ophiolites, mantled by unconsolidated alluvium deposits. The ophiolites impede groundwater flow and define the base of the hydrogeological system. They formed when the Tethyan oceanic crust abducted against Arabian Plate in the Late Cretaceous between 90 and 105 Ma (Robertson et al. 1990; Hanna 1995). Ophiolites consist in sequences of dunite, harzburgite, gabbros, sheeted dykes and pillow lavas. It makes the main source for the alluvium formed as a result of ophiolites weathering. The limestones are deposited in the Tertiary under shallow marine environment consequent to sea transgression.

The alluviums, formed in the quaternary and unconformably rest on the ophiolites represent the main source of the groundwater in the region and comprise gravelly poorly sorted sedimentary units that directly overlie the ophiolites in the major drainage system. The area is generally arid with varying rainfall. Total annual rainfall averages 100 mm/year with 0 and 350 mm extremes.

Materials and methods

The material of this study is composed of waters, sediments and plants collected from the same area.

Waters

During this study, waters were collected from several wells in different locations penetrating the alluvium-aquifer in Sohar (north of Muscat area) (Fig. 1). These locations include sewage treatment areas, agriculture areas and Cu mining areas. Waters were also collected from 2 wells at downstream of these different areas and are considered a control area.

The different water samples have been collected in 500-ml polypropylene containers. Instantaneous site analysis was carried out for pH, conductivity and temperature. For the laboratory analysis, water samples were vacuum-filtered through a membrane filter with 0.45-µm pore size. Laboratory analyses were conducted within 3 days of sample collection.

Soils

In parallel to waters, sediments were collected from the same locations in Sohar (north of Muscat area) (Fig. 1). These locations include sewage treatment areas and Cu mining areas. Five representative sediment samples were collected from both areas. From each sample, an amount of about 500–1,000 g of sediments was collected from the surface of soils (within 0–10 cm) and packed in polythene bags.

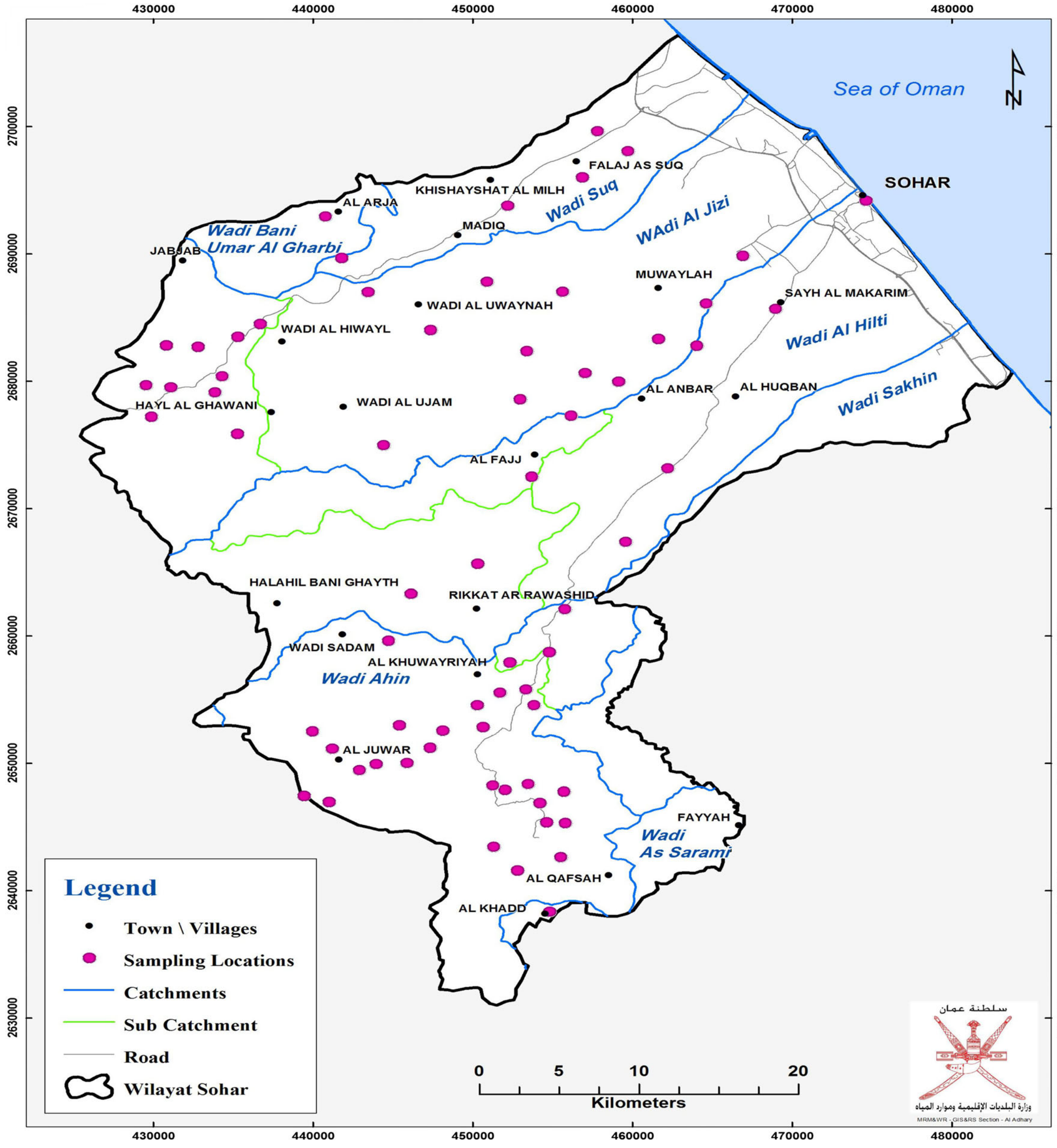


Fig. 1 Batina sampling location

The soil samples were dried in the oven at 60 °C for 24 h and sifted to less than 63 µm and homogenized in an agate mill. Two batches of each soil sample were used: one batch was used for identification of mineral composition using X-ray diffraction whereas from the other batch about 250 g of each sample was used for chemical analysis.

Plants

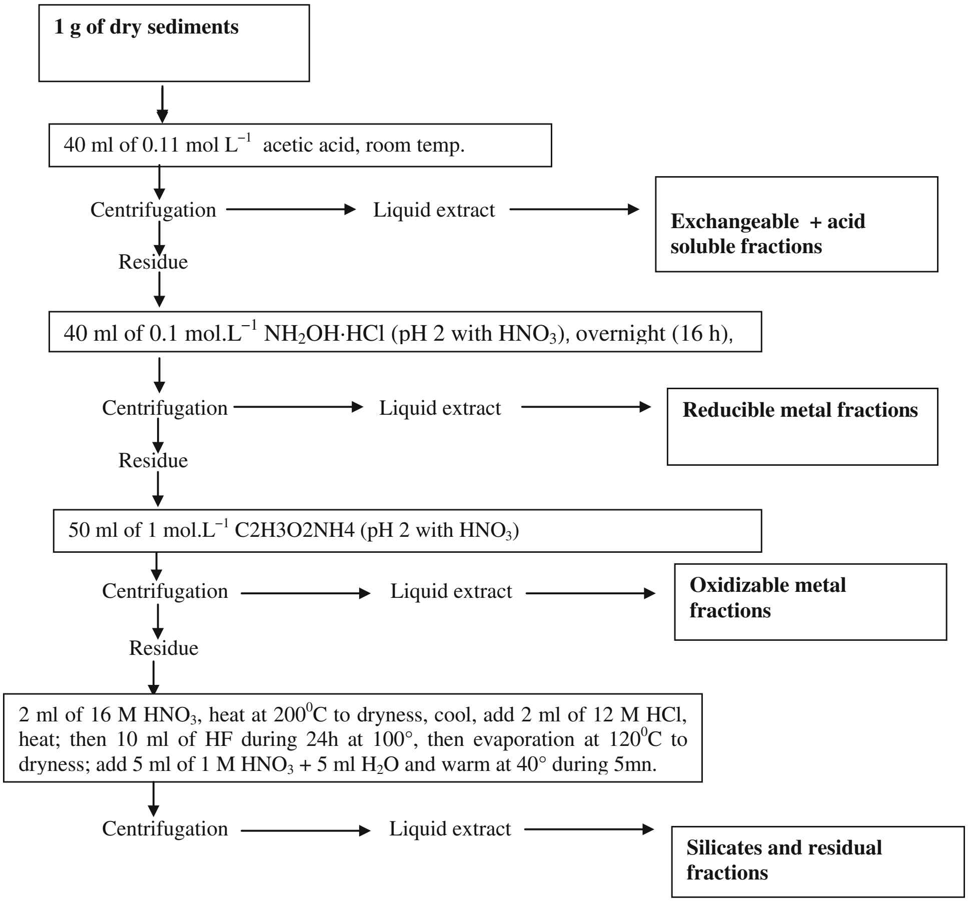
As for soils, plants were collected from Cu mining area and from sewage area. The leaves of about twenty individual plants from each plant sample were removed randomly and grouped in five separate batches. The plants of each batch were processed and analysed separately, so that the chemical data for the plants collected from each area represented an average of five sets of plant individuals in each case. In other words, instead of repeating the analyses for control of the analytical uncertainty, we managed the analytical reproducibility in analysing systematically five batches of each plant at each step and averaged the data within a 2σ error. In summary, plant data in Table 2 represent actually an average measure of 100–125 individual plants split into 5 independent batches.

The collected plants were first washed five times with demineralized water. This washing was followed by a gentle ultrasonic treatment in a bath for about 10 min to remove any solid mineral particles that could have adhered at the surface of the plants. After removing from ultrasonic bath, the plants were washed again with demineralized water.

Sequential extraction experiment

From each investigated site, 5 samples of soil were collected from the upper horizons (about 0–10 cm depth) to determine the partitioning of heavy metals, in the soil. The sequential extraction scheme adopted in this study is shown in Fig. 2 according to BCR's guidelines (the Community Bureau of Reference sequential extraction scheme) and to Álvarez et al. (2002). The different steps were proposed by Tessier et al. (1979), Jennifer and Jicheng (1993) and Ahnstrom and Parker (1999). All the operations were carried out in 50-ml polypropylene centrifuge tubes and Teflon containers. The initial mass of sediment was 1.0 ± 0.0001 g. The extracts were separated from the solid residue by centrifugation at 4,000 rpm for 30 min. After each step, the solution was filtered by suction through a 0.45-µm Millipore filter, and the filtrate collected in a polyester container. Then, the solutions for each step were

Fig. 2 Sequential extraction scheme used in this study



prepared accordingly for ICP-MS measurement. The extraction sequence in 4 steps includes four reagents (weakest to strongest): (1) acetic acid (CH_3COOH) to extract all exchangeable, acid-soluble and water-soluble metals, (2) hydroxylammonium chloride ($NH_2OH\cdot HCl$) to extract all reducible metals, (3) ammonium acetate (CH_3COONH_4) and hydrogen peroxide (H_2O_2) to extract all oxidizable metals and (4) HF which dissolve increasingly more resistant mineral phases (see Fig. 2).

Mobile fraction (exchangeable, acid-soluble and water-soluble metal fraction)

1 g of dry soil (<63 µm fraction) was extracted into 100-ml polypropylene centrifuge tube with 40 ml of acetic acid (0.11 mol/l). The samples were shaken for 16 h (overnight) at room temperature ($\approx$20 °C) on an end-over-end mechanical shaker at 40 rpm. The extract was separated from the solid residue by centrifugation at 4,000 rpm (SIGMA model 3–15). The residue was washed with 20 ml distilled water by shaking for 15 min, centrifuged and the washings discarded.

Reducible metal fraction

The above residue was extracted overnight (16 h) with 40 ml of 0.1 mol/l $NH_2OH\cdot HCl$ (pH 2 with HNO_3). The separation procedure was then performed as described in the previous step.

Oxidizable metal fraction

The above residue was treated by careful addition of 10 ml of 30 % H_2O_2 during 1 h with occasional manual shaking. Digestion was continued by heating the tube at 85 °C in a water bath for 1 h, and then, the tube contents were reduced to 1–2 ml. A second 10-ml aliquot of hydrogen peroxide was added and the tube was again heated at 85 °C for 1 h. Afterwards, the volume was reduced as before. 50 ml of ammonium acetate (1 mol/l, adjusted to pH 2 with nitric acid) was added to the cool, moist residue. The sample was then shaken, centrifuged and the extract separated as described in step one.

Total residual metal

Soil residues from sequential extraction procedure were digested in HF acid for total metal determination.

Availability of heavy metals

Mobility of elements from soil solution to roots has been calculated by normalization of concentrations of different elements investigated in this study in plants collected from different areas to the concentrations of heavy metals in the most mobile and unstable fraction. This unstable fraction includes the exchangeable and acid-soluble fractions in the soil plus the reducible and the oxidizable fractions.

Analytical material

The mineralogical composition of the soil samples was determined by X-ray diffraction.

Digestion of plants was carried out following Semhi et al. (2009). The analytical procedure started with drying the plant batches at 60 °C for 24 h and weighed them afterwards. Then, each weighed plant amount was ashed in a Pt crucible at about 600 °C for 45 min. The ash was transferred into a Teflon beaker and digested in ultrapure concentrated HNO_3 at a temperature of about 70 °C for 24 h and more if needed. The solution was then slowly evaporated to dryness by closing the beakers. Ten drops of $HClO_4$ were added afterwards to ensure dissolution of all remaining organic material, and the aliquot was evaporated again to dryness. The obtained solution was then prepared for analysis by dissolving the dried material with a known volume of 1 $N\cdot HNO_3$.

Plants were analysed for As, Cu, Cd, Co, Cr, Cu, Ni, Pb and Zn. Waters were analysed only for As and Cu while the different fractions extracted during the sequential extraction were analysed for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn.

Arsenic and Cu concentrations in plants and waters were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). Analytical precision ranged between 5 and 10 %.

The concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in plants and the different fractions were determined using the inductively coupled plasma atomic emission spectroscopy (ICP-MS). Analytical precision ranged between 5 and 10 %.

Results and discussion

The average chemical concentrations of the different elements in water, soil and plant samples are provided in Tables 1, 2 and 3 respectively.

Waters

The results of the measured in situ parameters including pH, temperature (T), electrical conductivity (EC) and the chemical composition of groundwater are given in Table 1. The data showed that the pH of waters collected from wells of mining area is about 6.6–8.6. The conductivity also

Table 1 Average chemical composition of groundwater collected from Batina; concentrations are expressed (in ppb)

Waters from:	EC	T(°C)	PH	Depth (m)	Water level (m)	Cu (ppb)	As (ppb)
Cu mining							
1	3,900	31.3	8.6	17.8	16.4	6.57	0.86
2	1,357	33.6	7.32	15	12.5	19.31	1.26
3	8,700	34	7.5	18.7	11.7	5.355	0.43
4	3,900	31.3	8.6	17.8	16.4	0	0.21
5	3,400	30.9	7.92	17.4	15.7	3.39	0.42
6	nd	nd	nd	nd	nd	5.09	1.77
7	nd	nd	nd	nd	nd	32.09	0.66
8	nd	nd	nd	nd	nd	82.00	1.69
9	nd	nd	nd	nd	nd	19.44	3.85
Sewage							
1	1,000	31.1	8.4	17.5	16	nd	0.26
2	5,400	30.4	7.7	16.5	15.4	nd	0.23
3	9,000	31.1	7.6	17.8	16.5	nd	0.32
	nd	nd	nd	nd	nd	nd	0.26
	nd	nd	nd	nd	nd	nd	nd
Agriculture							
1	5,200	30	7.6	7	5.1	nd	0.40
2	6,400	30.3	7.6	8.5	6.2	nd	0.44
	nd	nd	nd	nd	nd	10.53	0.09
	nd	nd	nd	nd	nd	2.71	0.07
Control							
1	670	30	8.38	18.5	15	nd	0.21
2	365	33	9	25	12	0.20	0.64

nd not determined

Table 2 Average chemical composition of sediments collected from Batina in different fractions; concentrations are expressed (in ppm)

Soils from	(In ppm)								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Control	0.05	0.11	0.05	0.05	0.38	13.81	6.14	0.27	1.37
	1.05	63.70	121.23	11.60	5,176.96	946.23	553.46	47.14	108.89
	0.30	0.89	5.95	13.99	0.89	1.79	2.08	5.06	2.08
	0.90	10.02	994.99	13.23	400,962.31	486.07	1,766.04	5.21	86.41
Cu mining									
F1	0.059	0.235	0.176	0.059	0.705	24.965	4.582	0.176	30.486
F2	0.291	2.035	0.872	0.872	10.756	404.942	17.151	0.291	3.779
F3	0.302	0.603	0.603	5.430	1.810	2.112	1.810	4.525	2.413
F4	1.160	10.354	633.727	46.702	65,203.008	753.942	1,204.425	5.113	117.81
Sewage area									
F1	0.040	0.080	0.040	0.040	0.320	9.564	1.240	<nd	0.200
F2	<nd	<nd	<nd	0.098	<nd	<nd	<nd	<nd	<nd
F3	0.133	0.199	0.133	1.195	0.332	0.266	0.531	0.929	0.332
F4	5.195	8.760	985.383	39.929	68,936.084	152.839	1,279.908	4.991	91.367

Nd not determined

measured in the field showed large fluctuation in waters collected from wells in the different sectors. The lowest value is 365 and it was measured in waters collected from wells in the agriculture area. The highest value was measured in waters collected from wells in the sewage plant area.

Concentrations of As in waters collected from wells affected by Cu mining range from 0.21 to 3.85 ppb while Cu

Table 3 Average chemical composition of plants collected from Batina; concentrations are expressed (in ppm) for the concentrations in the whole plant and in ppb for the concentrations of Cu and As in the different parts of the plant

Plants from	(in ppm)								(in ppb)					
	Cd	Co	Cr	Fe	Mn	Ni	Pb	Zn	Cu			As		
									Leaves	Stems	roots	Leaves	Stems	roots
Cu mining area	0.05	0.189	0.805	91.74	7.308	1.384	0.201	33.86	61,473	6,696	9,856	1,196	78	87
Sewage area	0.095	0.13	0.639	61.07	14.75	0.9	0.107	12.23	10,132	nd	5,530	71		40
Agricultural area	nd	nd	nd	nd	nd	nd	nd	nd	4,930	nd	nd	40	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	

Nd not determined

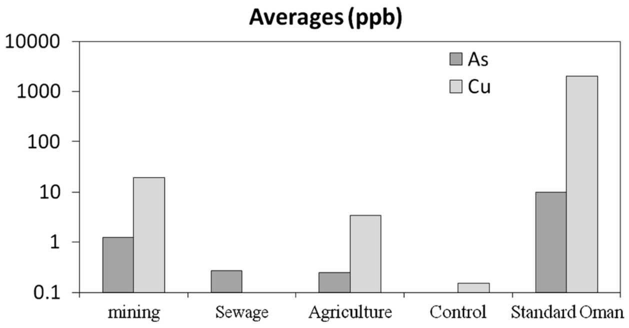


Fig. 3 Average concentration of As and Cu in soils collected from different areas

concentrations range from less than detection limit to 82 ppb (Table 1). Concentrations of As in waters collected from wells affected by sewage range from less than detection limit to 0.32 ppb while Cu concentrations are less than detection limit. The waters collected from wells in areas affected by agriculture are characterized by Cu concentrations ranging from less than detection limit to 10.53 ppb, and As from 0.07 to 0.44 ppb. The concentrations of Cu in waters collected from control areas are from less than detection limit to 0.20 ppb while As concentrations are from 0.21 to 0.64 ppb. Higher As concentrations in Batina region were observed in the Cu mining area and may be associated with Cu mining activities (Fig. 3). Waters in wells from agriculture and from the control areas have higher As concentrations than in sewage areas and may reflect an anthropogenic source although they are below the toxicity characteristics of waters. Nevertheless, the source of As in waters in Batina region is not yet well known and need more investigations.

The standards for maximum concentrations of As in drinking water have been changed from 150 µg/l in 1903 fixed by report of the Royal Commission on As Poisoning in the UK to 50 µg/l in 1942. The FAO has also considered a limit of 50 µg/l for arsenic in groundwater. In 1993, the WHO (1993) guideline value for arsenic in drinking water was reduced from 50 to 10 µg/l. Most western countries adopted this limit in their current drinking water standards (Yamamura 2003). On the other hand, many affected countries still operate a standard of 50 µg/l. Before 2006, the EPA (USEPA 1996, 2000, 2001) recommended a limit of 5 µg/L (Fig. 4).

Since 2001, As standard limit approved and fixed by US Environmental Protection Agency (USEPA) is within 3 to 20 µg/l (USEPA 2001) and fixed to 10 µg/l by WHO (2001). This range is much exceeded in some countries such as Bangladesh where standard for As in drinking water is fixed at 50 µg/l (Gaus et al. 2003; Hoque et al. 2008). According to standard limits established by Oman, concentration of As in drinking waters was fixed at 0.01 ppb. The standard limits established by World Health Organization for Cu is about 2 ppb in groundwater as what was established by Oman for Cu (Fig. 4).

The results of this study are low compared with the standard acceptable levels of drinking water and irrigation. Conductivity could be used to give an idea of the amount of dissolved chemicals in water, and presence of Na, K and Cl. The elevated values of EC in waters of two wells from sewage area and one well from mining area suggested that there is inorganic pollution compared with waters of the other wells. Nevertheless, these high values of EC do not correlate with the high As concentrations and may suggest different sources of pollution in Batina area. The vertical distribution of As revealed its enrichment in shallow wells sampled from Cu mining areas relative to deep wells (Fig. 5). A different tendency is observed for wells sampled from sewage area, where concentration of As in deep wells is higher than in shallow wells. Irregular tendency concerns waters collected from agriculture areas in lack of an important number of samples. The correlation of Cu concentrations with depth is more irregular than As concentrations.

To interpret the enrichment of As in shallow wells of Cu mining area, relationship of concentrations with pH has also been investigated. High concentrations of As in waters of mining area were measured in waters with high pH (Fig. 5). There is no correlation between pH and waters collected from wells of sewage areas. Desorption of As from minerals in shallow waters or precipitation in deep waters may explain the vertical distribution of As in wells of Cu mining areas.

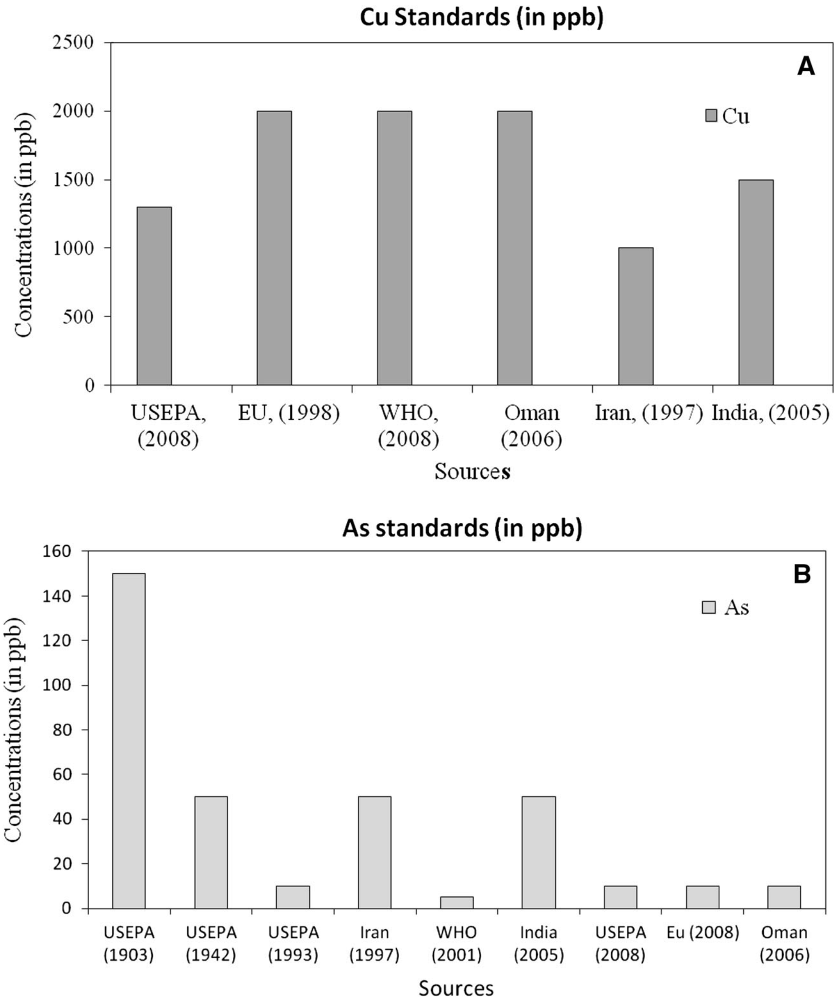


Fig. 4 Standard data of **a** Cu and **b** As

However, since As from minerals (desorption) hypothesis is not enough to explain the whole concentrations in waters, investigation of As in plants has been carried out (see below). A previous study of K/Rb ratios in aqueous systems (Chaudhuri et al. 2007) revealed that high ratios of K/Rb are strongly suggestive that the metal or semi-metal present in the aqueous system must take into consideration the role of all these from plants. Plants can cumulate large amount of nutrients either from soils or from atmospheric inputs (Mandre 1995; Mandre et al. 2000). Transformation and decay of plants may consider a considerable source of elements in surface waters and shallow groundwater.

Soils

The soil of the Batina region consisted in a sandy loamy soil. Its mineral composition determined by XRD consisted in quartz, calcite, dolomite, feldspar and palygorskite with some minor minerals. Measurement of pH revealed alkaline soils (pH about 7.8–8.9).

The average chemical concentration of the different elements in the different fractions separated from the soil is provided in Table 2. The concentrations of various elements in the soil are given as per gram of soil.

Acid-soluble and exchangeable fraction (bioavailable), F_1

Determination of concentration of heavy metals in this fraction may evaluate the mobility and availability of these elements for uptake and risk for the environment. The concentrations of heavy metals in the exchangeable and acid-soluble fraction removed by acetic acid during this study are low compared with the other fractions. However, the affinity order of different metals and Fe and Mn for exchangeable and acid-soluble fraction in soils collected from the area affected by Cu mining is as follows: Mn > Zn > Ni > Fe > Co > Cu > Cr > Pb > Cd (Table 2). In soils collected from area affected by sewage, the descending affinity order for exchangeable and acid-soluble fraction is as follows: Mn > Fe > Ni > Zn > Co > Cr > Pb > Cu > Cd (Fig. 6). Availability of heavy metals in soils of Cu mining area is more important than in soils of sewage area. Significant difference between the two areas concerns Zn and Cr.

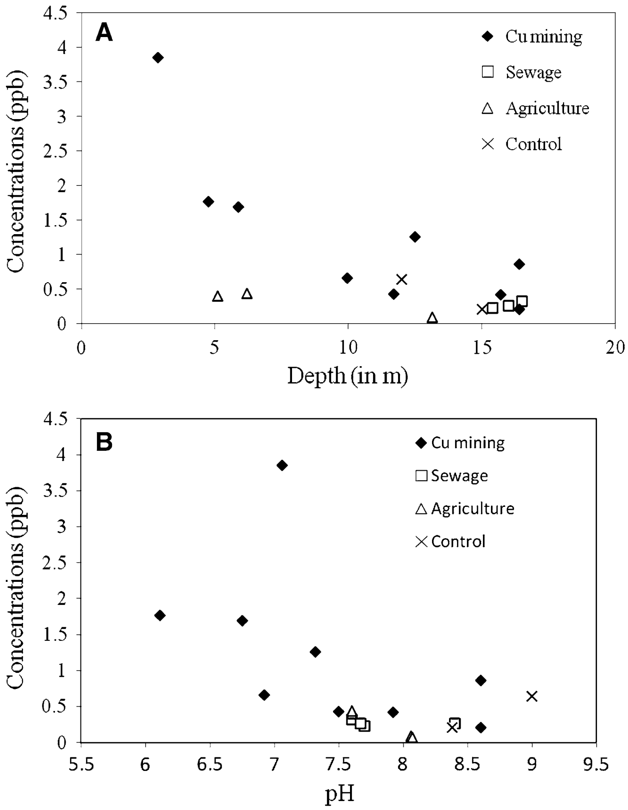


Fig. 5 Variation in As concentrations with **a** depth and **b** pH

Reducible fraction (iron and Mn oxide), F_2

This fraction includes mainly heavy metals carried by Fe–Mn oxides. Determination of concentration of heavy metals and Fe and Mn in this fraction extracted from soils collected from Cu mining area showed the following order: Mn > Fe > Ni > Zn > Co > Cu > Cr > Pb > Cd (Table 2, Fig. 6). In the soils collected from sewage area, the concentrations of heavy metals and Fe and Mn in the reducible fraction are distributed as follows: Fe > Mn > Ni > Zn > Cu > Cr > Pb > Cr > Co > Cd.

Oxidizable fraction (fraction bound to organic matters and sulphides), F_3

This fraction includes heavy metals bound to sulphide and organic matter. These metals are temporarily inaccessible. With time, decomposition of organic matrix under modification of anoxic conditions induces their release to water or to other fractions.

The results of this study showed the affinity order of different metals for oxidizable fraction in soil affected by Cu mining as follows: Cu > Mn > Fe > Zn > Co > Ni > Pb > Cr > Cd; and in soils affected by sewage, the order is as follows: Cu > Pb > Zn > Fe > Ni > Mn > Co > Cr = Cd (Table 2, Fig. 6).

Silicate and residual fraction, F_4

Silicate and residual fraction of metals is the most chemically stable fraction and does not represent a threat for the environment. Either in soils affected by Cu mining or soils affected by sewage, the residual fraction is the most enriched in elements compared with other fractions (Table 2, Fig. 6). The abundance of Fe and Mn and heavy metals in this fraction from soils of Cu mining area is as follows: Fe > Mn > Cr > Ni > Cu > Zn > Pb, while in soils from sewage area, it is as follows: Fe > Ni > Cr > Mn > Zn > Cu > Pb.

These results show that most of heavy metals (more than 90 %) in the sewage area are carried in the residual fraction. Their concentrations in the other fractions are not significant. Their mobility is small and does not represent any risk to the environment. In the opposite, in the soils collected from Cu mining area, although the important fraction is the resistant one, heavy metals are not only carried by this fraction, but they are also distributed significantly in the other fractions. It is the case of Co which has an important concentration in the oxidizable fraction in one soil and an important concentration in reducible fraction in another soil. This study also revealed that a significant amount of Cd is carried by both reducible and oxidizable fractions (about 36% of the total concentration), but less than in the resistant fraction (64 %). The study of Páez-Osuna and Osuna-López (1990) in surface sediments showed that most of Cd was found in association with the oxidizable fraction in contrast to other studies (Helsinger and Friedman 1982; Rapin et al. 1983; Abaychi and Douabul 1986) where most of Cd was found in association with the carbonates and reducible fractions.

As it was reported by (Tessier et al. 1979; Páez-Osuna and Osuna-López 1990), the results of our study showed that the second non-negligible fraction of Cu is associated with organic complexes. The sequential extraction in the soil collected from Cu area revealed that Mn has a significant concentration in reducible and oxidizable fraction. These results are in contrast to those of Páez-Osuna and Osuna-López (1990) who found that Mn is distributed between the exchangeable and the oxidizable phases. Similar results about Pb which is significantly carried by oxidizable fraction have been found by Páez-Osuna and Osuna-López (1990) who reported that more than 10 % of Pb in sediments is associated with organic complexes in contrast to Rapin et al. (1983) and Abaychi and Douabul (1986) who showed that the fraction of Pb associated with Fe/Mn oxides and hydroxides is significant. Our study revealed that Pb is equally carried by oxidizable fraction (organic complexes) and resistant phases. Zn is carried at significant concentrations in acid exchangeable fraction in one soil and in oxidizable fraction in the other soil. In both

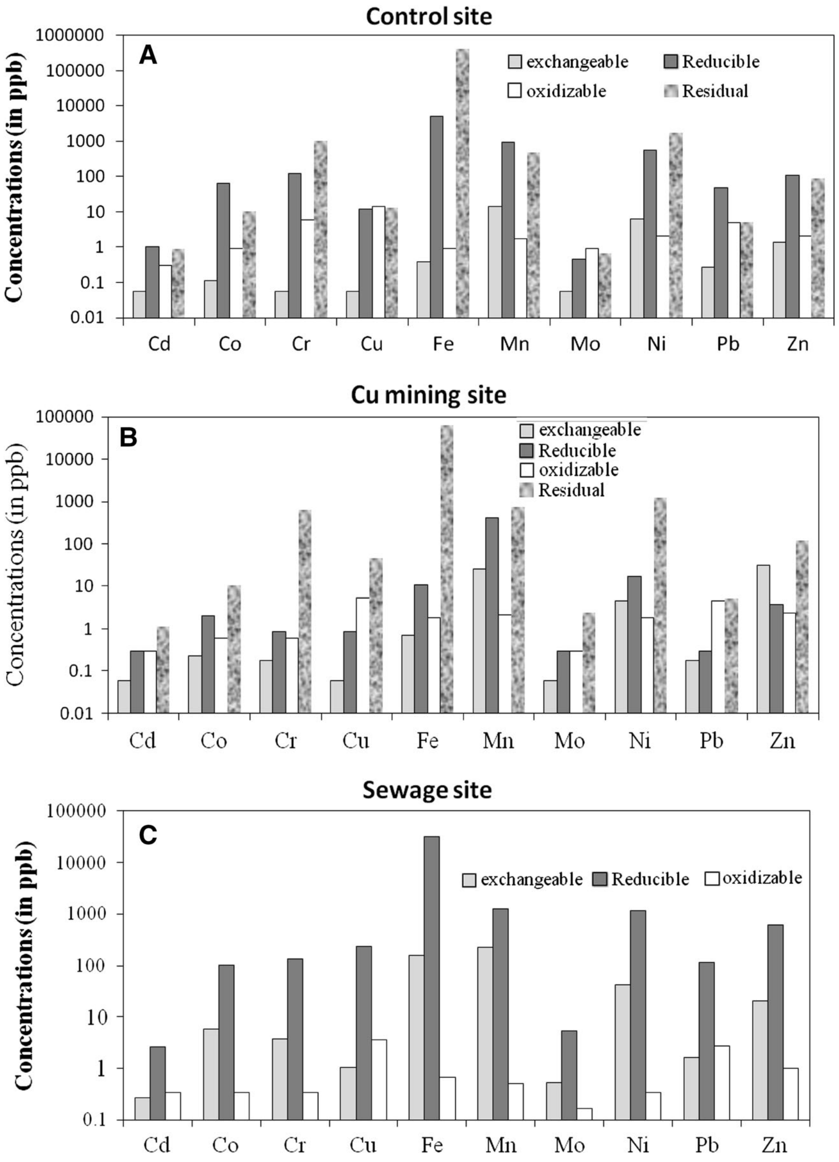


Fig. 6 Average geochemical distribution of elements (in ppm) among the different fractions (F1, F2, F3 and F4) extracted from surface sediments collected in: **a** control area, **b** Cu mining area and **c** sewage area

soils, a significant amount of Zn was found in the residual fraction. Similar results have been found by Zerbe et al. (1999).

In summary, if we calculate the total amount of mobile fraction which includes all fractions except the resistant one, we may evaluate the rate of instability of elements and the risk to environment if anoxic conditions or pH change.

Investigation revealed that in the area affected by sewage, the unstable fractions are negligible (less than 10 % of the total) compared with the resistant fraction, except for Pb whose distribution in the mobile fraction is about 16 %. In this area, elements have a low environmental availability and are poorly affected by human activity.

In soils collected from mining area, the most mobile elements consist in Pb, Mn, Cd, Cu and Co. The preferential association of Cd, Cu and Pb is for oxidizable and organic fraction. The association of Mn and Co is significant in reducible fraction.

These results indicated that these elements may be a threat to the environment in Batina region if anoxic conditions or pH change. In a previous study (Yaghi 2007), characterization of groundwater in Batina area revealed a contamination of most of analysed groundwater in Pb and Cr. This study also revealed higher concentrations of Cu in groundwater collected from wells in Batina region compared to standards.

Plants

The data concern the same species of plants Rhazya *stricta,* but collected from two different areas: (1) areas affected by Cu mining as for groundwater and (2) areas affected by sewage

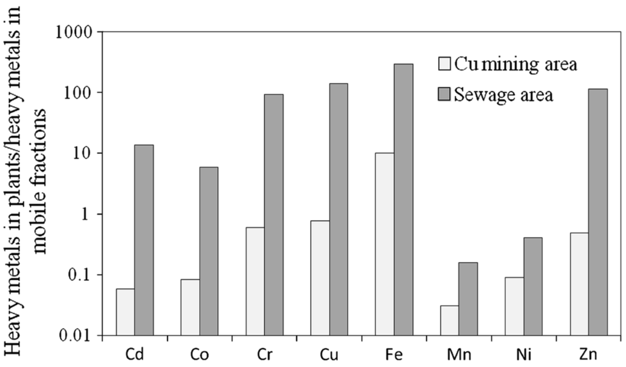


Fig. 7 Concentrations of heavy metals normalized to those in the mobile fraction (F1 + F2 + F3) removed from the soil

activities. The average chemical concentrations of the different elements are given as micrograms (μg) of element per gram (g) of dry plant material (Table 3).

Plants which grew in sewage area are more enriched in elements than plants collected from soils of the copper mining area although the mobile fraction removed from these last soils are more enriched in heavy metals than the mobile fraction removed from soils of sewage area (Table 3). The partitioning of heavy metals showed that availability of elements is more important in soils collected from Cu mining area than in soils from sewage area (Fig. 7).

Availability and uptake of heavy metals by plants do not depend only on their content in the soil, but also on pH of soil, organic matter and amount of clays in the soil (Singh 1994). The same type of soils has been identified in sewage and Cu mining area. The difference in the amount of elements uptake by the same species of plants collected from these two areas may reflect differences in physicochemical properties, especially pH rather than in the amount of organic matter in the soil since sewage soils contain important amount of organic matter (Lindsay and Logan 1998; Zhang et al. 2007) highly than other areas. Organic matter is known to immobilize heavy metals in soils and reduce their uptake by plants which it is in opposite of our results. The organic matter can also complex with heavy metals found in soils (Weng et al. 2002; Silveira et al. 2003; Tukura et al. 2007; Ashworth and Alloway 2008) reducing heavy metal pollution. Several authors have studied the effect of sewage sludge on soil physical, chemical and biological properties (King and Morris 1972, Melo et al. 1994, 2002). The study of Melo et al. (2002) revealed that sewage increased soil organic matter and pH and enzyme activities in soils. Investigation of effect of sewage on soils by Al-Wabel et al. (1998) revealed that the pH values of treated soils by sewage sludge decreased and the concentrations of heavy metals increased in the treated layers of soil compared to the untreated layers. Our results may reflect a change in the pH more pronounced in sewage area than in mining area. Future research will focus more on the physicochemical of the system plant–soil–waters in Batina region.

Conclusion

Comparison with standards showed that there is no risk in groundwater of Sohar area in term of As and Cu levels since all concentrations are below the toxicity characteristics. The weak correlation between Cu and As revealed that As is not only released from the industry of Cu but from other sources. Organic inputs such as plants have to be more investigated.

In industrial and sewage areas of Batina region, the availability of Fe, Mn and trace elements determined by sequential extractions revealed that during each step, the most mobile elements in Cu mining area relative to each other consisted of (1) Mn and Zn more available than the other elements because they are more released by acetic acid, (2) Mn and Cd are susceptible to be released when pH conditions change, (3) Cu and Cd are more kept in oxidizable fraction than in the other elements, (4) more than 90 % of total Fe and Mn are strongly kept in resistant phases and about more than 50 % of total concentrations of Cu, Co, Cd and Zn are carried in this fraction. Lead is equally distributed between resistant fractions (50 %) and the other fractions.

In the sewage area, sequential extractions revealed that Pb is the most mobile element compared with the other elements which are significantly carried in the resistant fraction. The resistant phases in these soils are more enriched in Fe and Ni than in the other elements.

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