Environ Monit Assess (2014) 186:6985–6992
DOI 10.1007/s10661-014-3904-5

Determination of trace heavy metals in harvested rainwater used for drinking in Hebron (south West Bank, Palestine) by ICP-MS

Husam Malassa · Fuad Al-Rimawi · Mahmoud Al-Khatib · Mutaz Al-Qutob

Received: 27 September 2013 / Accepted: 30 June 2014 / Published online: 26 July 2014

Abstract Rainwater samples harvested for drinking from the west part of Hebron (south of West Bank in Palestine), the largest city in the West Bank, were analyzed for the content of different trace heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Bi, and Pb) by inductively coupled plasma mass spectrometry (ICP-MS). This study was conducted to determine the water quality of harvested rainwater used for drinking of south West Bank (case study, Hebron area). A total of 44 water samples were collected in November 2012 from 44 house cisterns used to collect rainwater from the roofs of houses. The samples were analyzed for their pH, temperature, electrical conductivity, total dissolved solids, and different heavy metal contents. The pH of all water samples was within the US Environmental Protection Agency limits (6.5–8.5), while some water samples were found to exceed the allowed WHO limit for total dissolved solids (TDSs) in drinking water. Results showed that concentrations of the heavy metals vary significantly between the 44 samples. Results also showed that the concentration of five heavy metals (Cr, Mn, Ni, Ag, and Pb) is higher than the WHO limits for these heavy metals in drinking water. Overall, our findings revealed that harvested rainwater used for drinking of this part of south West Bank is contaminated with heavy metals that might affect human health.

Keywords Heavy metals · Lead · ICP-MS · Rainwater · Hebron · Palestine

Introduction

Heavy metals are well known to be toxic to human beings when present in high concentrations. Human activities have increased the concentrations of heavy metals in the environment. For example, anthropogenic activities (e.g., industry, agriculture) increase the contents of heavy metals in different environmental matrices, e.g., water, soil, air, fruits, vegetables, fish, etc. (Batayneh 2010; Abderahman and Abu-Rukah 2006; Adekunle et al. 2007; Chen et al. 2007). There are 35 metals that concern us because of occupational or residential exposure; 23 of these are heavy metals: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Ferner 2001). Small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity. Health risks of heavy metals include

H. Malassa · M. Al-Qutob
Department of Earth and Environmental Studies, Faculty of Science and Technology, Al-Quds University, East Jerusalem, Palestine

H. Malassa · M. Al-Qutob (✉)
Aquatic and Aquaculture Research Laboratory, Al-Quds University, East Jerusalem, Palestine
e-mail: qutob@planet.edu

F. Al-Rimawi · M. Al-Khatib
Faculty of Science and Technology, Al-Quds University, P.O. Box 20002, East Jerusalem, Palestine

reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis and diseases of the kidneys, circulatory system, and nervous system. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body via food, water, air, or absorption through the skin in agriculture, industrial, or residential settings (Roberts 1999; Dupler 2001).

Heavy metals are considered as an important pollutant to groundwater, surface water, and harvested rainwater. Harvesting of rainwater is a common practice in the West Bank, especially in south West Bank where there is water scarcity. In these areas of West Bank and during the winter, the rainwater is collected from the roofs of the houses and stored in cisterns. Two types of rainwater catchment systems are used. One system works on a large scale to collect storm water runoff from the ground. This water is then stored in large reservoirs. The other system collects rainwater on a small scale from controlled surfaces, such as a roof. This water is stored in small reservoirs, known as cisterns, constructed underneath or next to house. The average capacity of the existing cisterns is 70 m^3. According to Hebron Municipality, 60 % of the inhabitants of the city have cisterns in their houses. In rural areas, the percentage of inhabitants using cistern collection systems is higher than that in the city. This is because some of the small villages are not connected to water distribution networks, thus experiencing a shortage of water. Also, if connected, rural areas suffer from frequent shortage in water supply (ARIJ 1995).

Many studies have investigated the occurrence of heavy metals in groundwater, surface water, and harvested rainwater. Batayneh (2010) has studied heavy metal content in water springs of the Yarmouk Basin (Jordan), and results of the study showed that Yarmouk Basin in the north of Jordan is contaminated with heavy metals that might affect human health as well as the health of the ecosystem. Alomary (2013) has determined trace metals in drinking water in Irbid (Jordan), and results showed that the level of most elements determined (As, Ba, Cd, Pb, Cr, Cu, Fe, Zn, Mn, Ni, and Se) was within the Jordanian and WHO standards for drinking water. Gutierrez et al. (2008) have studied the occurrence of heavy metals in water of San Petro River in Mexico, and results confirmed that the San Pedro River is contaminated with heavy metals and other contaminants that might affect human health as well as the health of the ecosystem. Kar et al. (2008) have studied the assessment of heavy metal pollution in surface water in Ganga in West Bengal, and results showed that the dominance of various heavy metals in the surface water of the river Ganga followed the sequence: Fe>Mn>Ni>Cr>Pb>Zn>Cu>Cd. Momot and Synzynys (2005) have investigated toxic aluminum and heavy metals in the groundwater of middle Russia, and results showed that some heavy metals (Hg, Cr, As) were detected. Ong and Kamaruzzaman (2009) have studied the presence of heavy metals (Pb and Cu) in bottom sediment from South China Sea Coastal Waters, Malaysia. Voica et al. (2012) have determined different heavy metals in the surface water from Transylvania, Romania, and results showed that toxic heavy metals were detected in water samples in the range of few micrograms per liter. Ismail and Saleh (2012) have analyzed different heavy metals in water samples from Malaysia, and results showed that the concentrations of heavy metals in water samples were below the detection limit. As groundwater and surface water, harvested rainwater is also prone to contamination with heavy metals. According to Mosley (2005) from SOPAC Water Quality Office, heavy metals are contaminants commonly found in rainwater collection systems, where they come from dust, particularly in urban and industrialized areas, and from roof materials (Mosley 2005). A study by Amim and Alazba (2011) has focused on the sources of rainwater contamination in a rainwater harvesting system. Despins et al. (2009) have assessed rainwater quality (pH, turbidity, color, total and fecal coliforms, total organic carbon, total nitrogen, and total metal content) from rainwater harvesting systems in Ontario, Canada. Magyar et al. (2008) have studied lead and other heavy metals which are common contaminants of rainwater tanks in Melbourne where results showed that concentrations of aluminum, cadmium, iron, and zinc were found at levels exceeding acceptable health levels.

It is evident from this literature that studies of the occurrence and determination of heavy metals in water (ground, surface, harvested rain) is an important issue for the human health and for the environment, however, and according to the best of our knowledge, there are no studies in Palestine conducted for the analysis of heavy metals in water, e.g., harvested rainwater. Harvested rainwater was selected as it is used for drinking in the study area (Hebron) since there is water scarcity in this area. The objective of the current study is therefore to study the occurrence of different heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Bi, and Pb) in harvested rainwater collected from south West Bank.

Materials and methods

Study area

Hebron is located in the south of West Bank in Palestine. The climate of the Hebron District ranges from arid to semiarid with an increase in aridity towards the Negev Desert in the south and the Jordan Valley in the east. The monthly average temperature ranges from 7.5 to 10 °C in the winter to 22 °C in the summer. The minimum temperature is −3 °C in January and the maximum is 40 °C in August. Most of the rainfalls are during December through February, although there may be rain from mid-October to the end of April. Figure 1 shows the amount of rainfalls in that region. The amounts of rainfalls per month ranges between 400 mm during the rainfall season and 0 mm during the dry season. Water shortage is a serious problem the Hebron District is facing due to the arid and semiarid climatic conditions (ARIJ 1995).

The location of the sampling side is in the central western areas of the West Bank. These areas are important as recharge zones for the groundwater aquifers of the West Bank (Mizyed 2009). Therefore, any contamination in that region will have direct impacts on the quality of water in the West Bank.

Sampling and analysis

Sampling has been carried out in November 2012 (the beginning of the rain season) where 44 water samples were collected from 44 house cisterns. Figure 2 shows the location of Hebron in the West Bank and cisterns analyzed in this study. The water samples were collected in 1-L high-density polyethylene bottles (pre-cleaned with 10 % nitric acid followed by repeated rinsing with

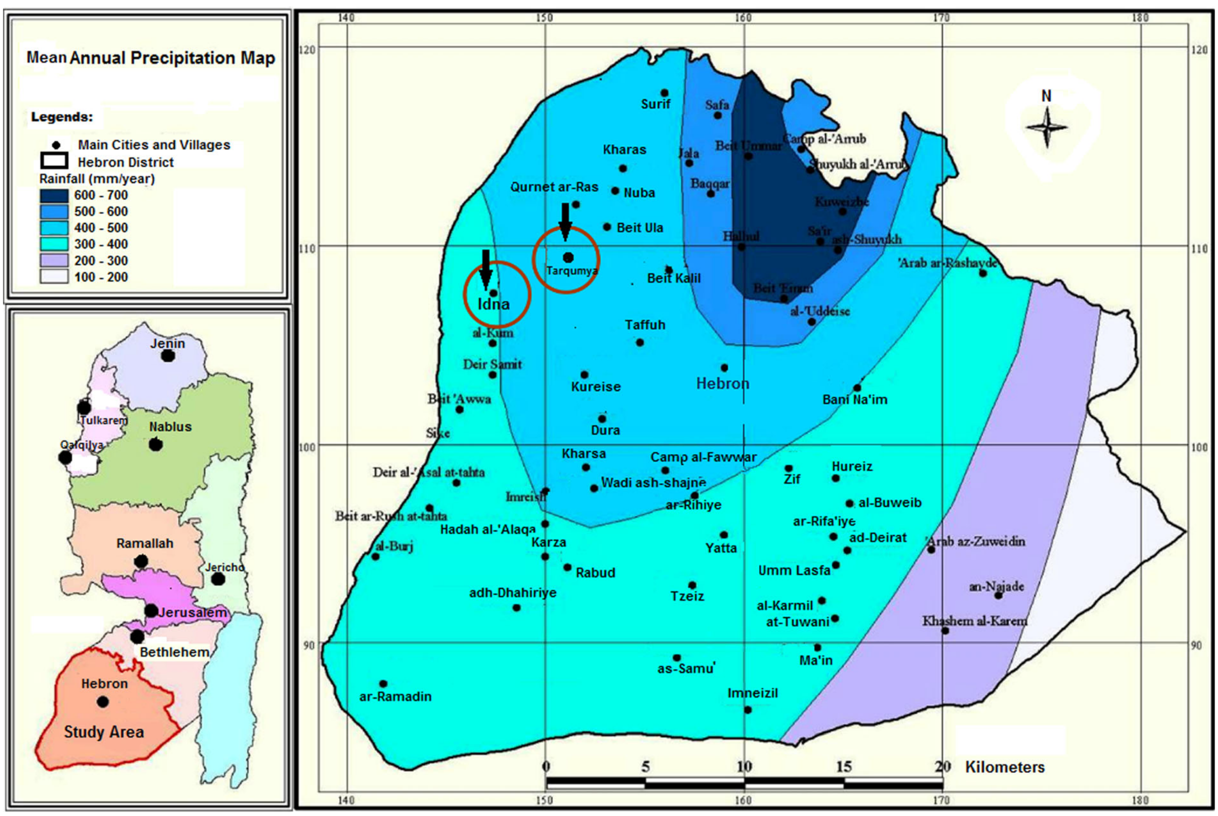

Fig. 1 Study area—mean annual precipitation in Hebron. The *two arrows* indicate the sampling site (source: municipality of Hebron)

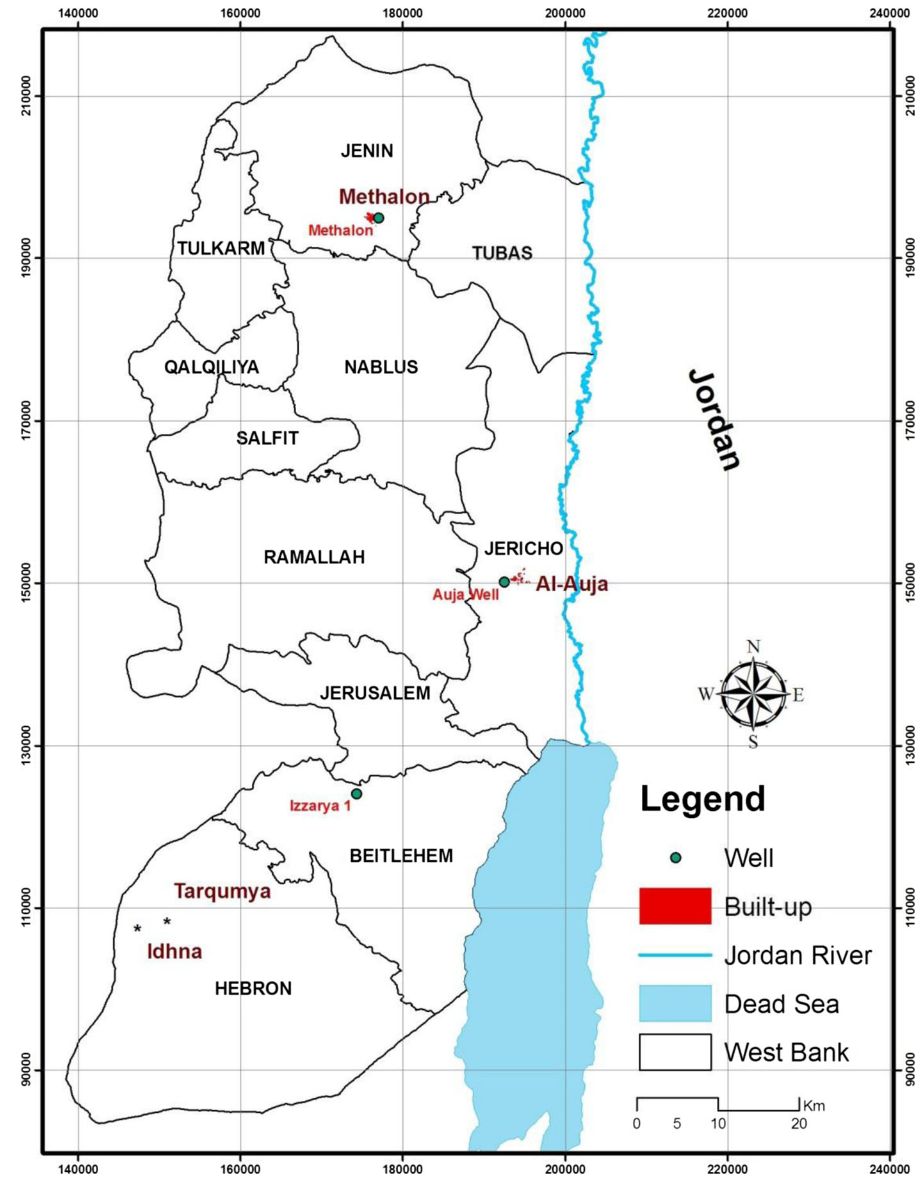

Fig. 2 Map of the West Bank showing Hebron locality in south West Bank and the location of cisterns (marked with *asterisk*) containing harvested rainwater analyzed in this work

bi-distilled water), stabilized with ultrapure nitric acid (0.5 % HNO_3), preserved in a cool place (about 4 °C) and transported to the lab of Al-Quds University for further analysis. Temperature, pH, electrical conductivity, total dissolved solids, and dissolved oxygen were measured in the lab immediately after the arrival of the samples according to standard methods (APHA 1998). The samples were then analyzed for heavy metal content (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Bi, and Pb) by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technologies 7500 Series).

For accurate quantitative determination of heavy metals in water samples, an internal standard method was used using Er as internal standard and a multi-standard calibration method (29 metal standards with a concentration of matrix 5 % HNO_3). Samples were prepared by dilution of 1.0 mL of the water samples to 10.0 mL with 0.3 % ultrapure nitric acid and were analyzed by ICP-MS. Each sample was analyzed three times, and the results are expressed as mean±standard deviation (SD). Relative standard deviation (RSD) of the three results was calculated and found to be less than

5 % for all samples for all heavy metals analyzed in this study, reflecting the precision of the method for the analysis of these heavy metals. Calibration curves for all heavy metals analyzed were constructed by plotting the ratio of the intensity of the analyte heavy metal to that of the internal standard (Er) vs. concentration of the heavy metal (in μg/L), and results showed that the calibration curves are linear with a correlation coefficient (r^2) greater than 0.999 for the heavy metals analyzed with a concentration range of 1–1,000 μg/L.

The instrument

ICP-MS (Agilent 7500) with an onboard peristaltic pump, a nebulizer (MicroMist nebulizer), an ICP argon plasma torch, two pumps for evacuation, a quadrupole mass analyzer, an octapole reaction system (ORS), and an electron multiplier detector was used for analysis of the heavy metals in this study.

The operating conditions of ICP-MS are as follows: nebulizer gas (argon) flow rate, 0.9 L/min; auxiliary gas (argon) flow rate, 0.3 L/min; plasma (argon) gas flow rate, 15 L/min; reaction gas flow (helium) rate, 4 mL/min; lens voltage, 7.25 V; and ICP RF power, 1,100 W.

Statistical analysis

Data were analyzed using Origin 9 software. Statistical differences between the same heavy metal from different water samples (44 samples) were tested using one-way ANOVA. Differences were considered significant at p values ≤0.05.

Results and discussion

This study was conducted to investigate the quality of harvested rainwater which is used for drinking in the west part of Hebron (south of West Bank in Palestine). This region of Hebron has severe water scarcity so they depend mainly on the rainwater harvested and stored in cisterns or wells. The pH of all water samples ranged between 7.1 and 8.2 (with a mean temperature of 18.8 °C) which is neutral to slightly basic and in the allowed limit (6.5–8.5) according to WHO regulations. Electrical conductivity, total dissolved solids, and dissolved oxygen for water samples ranged from 240 to 1,700 μs/cm, 136.7–1,139 mg/L, and 8.3–9.15 mg/L, respectively. The limit for total dissolved solids in drinking water according to WHO is 1,000 mg/L (WHO 2003) where our results showed that 11 samples have exceeded this limit, indicating high amounts of dissolved salts, e.g., heavy metals.

Heavy metal content

Results showed that 11 heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Pb, and Bi) were detected in water samples analyzed (44 sample) in this study. Eight heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Bi, and Pb) were detected in all samples, while Mo, Ag, and Cd were detected in 37, 18, and 38 samples out of 44 samples, respectively. The concentration of Cr, Mn, Co, Ni, Cu, Zn, Mo, Ag, Cd, Pb, and Bi in water samples ranged as follows: 22.6–165.5, 4.56–552.3, 0.34–4.93, 9.15–87.28, 21.93–925.5, 22.19–302.98, 0.0–6.17, 0.0–149.7, 0.0–2.19, 12.94–486.4, and 1.33–96.52, respectively. Table 1 summarizes the concentrations of heavy metals which are detected in the harvested rainwater samples analyzed in this study (minimum, maximum, average, standard deviation, and relative standard deviation).

A one-way ANOVA statistical test was used to test if the concentration of heavy metals is significantly different in the 44 water samples analyzed. Results showed that all heavy metal concentrations are significantly different in the 44 water samples analyzed in this study at 95 % confidence level. This indicates that these 44 water samples are different from each other in terms of heavy metal concentration. This result confirms the locational variations of heavy metals in the 44 water samples analyzed in this study. Figure 3 shows this variation for Pb in the 44 samples.

The allowed WHO limit for Pb in drinking water is 10 μg/L; however, our results showed that all samples analyzed in this study exceeded this limit with a range of 12.94–486.4. It has long been known that lead in drinking water is highly toxic. Exposure to lead is cumulative over time. High concentrations of lead in the body can cause death or permanent damage to the central nervous system, brain, and kidneys. This damage commonly results in behavior and learning problems (such as hyperactivity), memory and concentration problems, high blood pressure, hearing problems, headaches, slowed growth, reproductive problems in men and women, digestive problems, and muscle and joint pain. Infants, children, pregnant women, and fetuses are more vulnerable to lead exposure than others because the lead is

Table 1 Concentrations of heavy metals which are detected in the harvested rainwater samples analyzed in this study (minimum, maximum, average, standard deviation, and relative standard deviation) as well as their WHO limits and the percentage of the samples that exceeded the WHO limit and the percentage of the samples that were found to contain particular heavy metal

Concentration (μg/L)	Heavy metal										
	Cr	Mn	Co	Ni	Cu	Zn	Mo	Ag	Cd	Pb	Bi
Minimum	22.6	4.56	0.34	9.15	21.93	22.19	0.0	0.0	0.0	12.94	1.33
Maximum	165.5	552.3	4.93	87.28	925.5	302.98	6.17	149.7	2.19	486.4	96.52
Average	56.1	112.6	3.16	26.7	143.6	111.8	11.3	39.7	1.17	45.8	32.8
SD	6.1	11.8	1.5	4.1	36.3	29.7	3.6	13.7	0.8	14.3	14.1
RSD (%)	10.9	10.5	47.5	15.4	25.2	26.6	31.9	34.5	68.3	31.2	43.0
% of samples that 100 found to contain that heavy metal	100	100	100	100	100	100	37	18	38	100	100
Limits	50	500	No limits	20	2,000	3,000	70	No limits (usually found in a concentration of 5–50 ppb)	3	10	No limits
% of samples that exceeded the limit	59	4.5	–	34	0	0	0	4.5 (exceeded 50 ppb)	0	100	–

more easily absorbed into the sensitive tissue of actively growing bodies. According to the recently released lead toxicological profile for lead from the Agency for Toxic Substances and Disease Registry (ATSDR), the adverse health effects of lead range from slight increases in blood pressure at 100 μg/L to severe retardation and even death at very high blood lead levels of 1,000 μg/L (WHO 1993).

For Cr, the allowed WHO limit is 50 μg/L; however, 26 water samples out of 44 found to have chromium with concentrations larger than the allowed WHO limit. The highest Cr concentration was found to be 165.5 μg/L. The health hazards associated with exposure to chromium are dependent on its oxidation state; the hexavalent form is toxic. For Mn, the allowed WHO limit in drinking water is 500 μg/L; our results showed

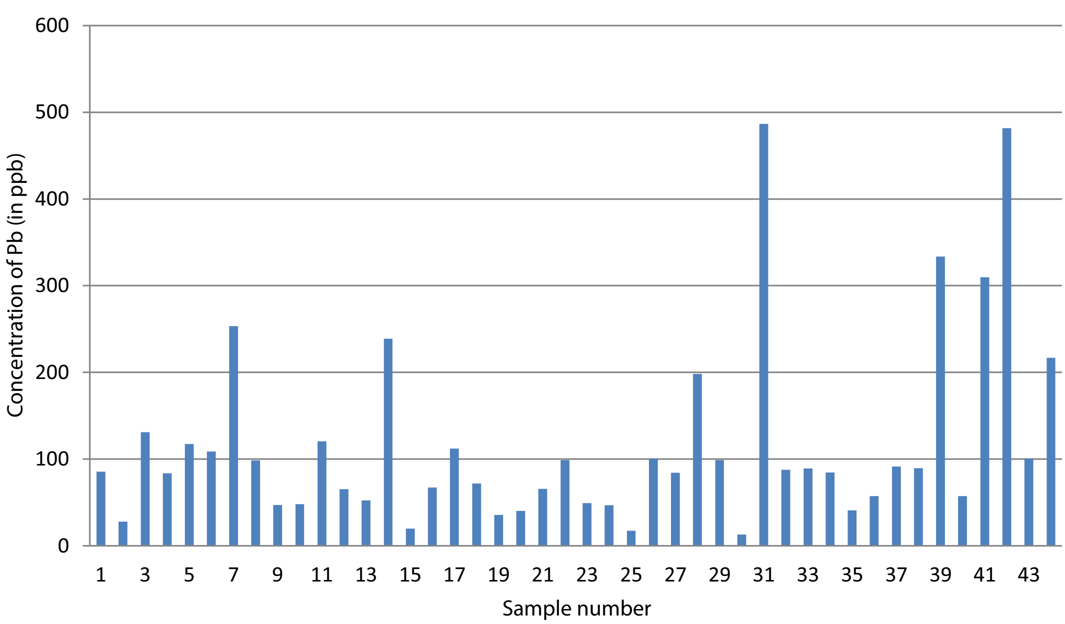

Fig. 3 Concentration of Pb (in μg/L) vs. sample number

that two water samples were found to exceed this limit with concentrations of 538.9 and 552.4 μg/L. Regarding nickel, our results showed that 15 water samples out of 44 have Ni concentration higher than the allowed limit (20 μg/L in drinking water) with the highest concentration of 87.28 μg/L. There is no limit for silver in drinking water according to WHO; however, it is usually found in drinking water in the range 5–50 μg/L, but our results showed that two samples of the analyzed water samples exceeded this upper limit (50 μg/L) with concentrations of 52.0 and 149.7 μg/L.

Co and Bi have no limits in drinking water by WHO; however, both metals were detected in all water samples analyzed in this study. Regarding Cu, Zn, Mo, and Cd, the allowed WHO limits in drinking water is 2,000, 3,000, 70, and 3 μg/L, respectively, and our results showed that these metals were found in the analyzed water samples within these limits.

The sources of these heavy metals in harvested water used for drinking in the west part of Hebron might be attributed to uncontrolled burning (incineration) of solid wastes in illegal waste dumping sites, where it is expected that the ashes and dust of these incinerated wastes containing heavy metals is transported through wind to the house roofs and, consequently, to the harvested rainwater in this region. Other sources of these heavy metals are vehicles' exhausts and leakage from engines, pesticides, and sand, soil, silt, and others. It is noteworthy here to mention that people of this region (west part of Hebron) collect rainwater from their house roofs from the first rain which is expected to be highly contaminated with different micropollutants, e.g., heavy metals. In the study area, the most favored means of waste disposal is through burning. Additionally, poor people of the study area burn specific solid wastes, e.g., batteries, car wheels to get metals recovered from these wastes (iron, copper, silver, etc.) to sell them.

Conclusion

Harvested rainwater from the west part of Hebron in south West Bank contains different heavy metals with five heavy metals (Cr, Mn, Ni, Ag, and Pb) exceeding the WHO limits for heavy metals in drinking water. pH of the water samples is within the WHO limits, while some water samples exceed the limits for total dissolved solids and electrical conductivity. Incineration of solid wastes in the study area may be responsible for the occurrence of heavy metals in harvested rainwater. Uncontrolled consumption of harvested rainwater used for drinking in the west part of Hebron may be dangerous for the human health.

Acknowledgments The authors are grateful for the German research funding organization (Deutsche Forschungsgemeinschaft (DFG)) for their financial support through TRION project.

References

Abderahman, N., & Abu-Rukah, Y. (2006). An assessment study of heavy metal distribution within soil in upper course of Zarqa River basin/Jordan. *Environmental Geology, 49*, 1116–1124.

Adekunle, I., Adetunji, M., Gbadebo, A., & Banjoko, O. (2007). Assessment of groundwater quality in a typical rural settlement in southwest Nigeria. *Public Health International Journal of Environmental Research , 4*, 307–318.

Alomary, A. (2013). Determination of trace metals in drinking water in Irbid City-Northern Jordan. *Environmental Monitoring and Assessment, 185*(2), 1969–1975.

Amin, M. T., & Alazba, A. A. (2011). Probable sources of rainwater contamination in a rainwater harvesting system and remedial options. *Australian Journal of Basic and Applied Sciences, 5*(12), 1054–1064.

APHA (American Public Health Association) (1998). Standard methods for the examination of water and wastewater, 20th Edition. Washington DC. 1294 p.

ARIJ (Applied Research Institute, Jerusalem) (1995). Environmental profile for the West Bank, volume 3: Hebron District.

Batayneh, A. T. (2010). Heavy metals in water springs of the Yarmouk Basin, North Jordan and their potentiality in health risk assessment. *International Journal of the Physical Sciences, 5*(7), 997–1003.

Chen, C., Kao, C., Chen, C., & Dong, C. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere, 66*, 1431–1440.

Despins, C., Farahbakhsh, K., & Leidl, C. (2009). Assessment of rainwater quality from rainwater harvesting systems in Ontario, Canada. *Journal of Water Supply: Research and Technology-AQUA, 58*, 2.

Dupler, D. (2001). Heavy metal poisoning. Gale *Encyclopedia of alternative medicine*. Farmington Hills, Gale group. 2054–2057.

Ferner, D. J. (2001). Toxicity and heavy metals. *eMedicine Journal, 2*(5), 1.

Gutierrez, R., Rubio-Arias, H., Quintana, R., Ortega, J., & Gutierrez, M. (2008). Heavy metals in water of the San Pedro River in Chihuahua, Mexico and its potential health risk. *International Journal of Environmental Research and Public Health, 5*, 91–98.

Ismail, I., & Saleh, I. M. (2012). Analysis of heavy metals in water and fish (tilapia sp.) samples from Tasik Mutiara, Puchong.

The Malaysian Journal of Analytical Sciences, 16(3), 346–352.

Kar, D., Sur, P., Mandal, S., Saha, T., & Kole, R. (2008). Assessment of heavy metal pollution in surface water. *International Journal of Environmental Science and Technology, 5*, 119–124.

Magyar, M. I., Mitchell, V. G., Ladson, A. R., & Diaper, C. (2008). Lead and other heavy metals: common contaminants of rainwater tanks in Melbourne. *Water Down Under, 2008*.

Mizyed, N. (2009). Impacts of climate change on water resources availability and agricultural water demand in the West Bank. *Water Resources Management, 23*, 2015–2029.

Momot, O., & Synzynys, B. (2005). Toxic aluminium and heavy metals in groundwater of middle Russia: health risk assessment. *International Journal of Environmental Research and Public Health, 2*, 214–218.

Mosley, L. (2005). SOPAC water quality officer, water quality of rainwater harvesting systems. *SOPAC Miscellaneous Report, 579*.

Ong, M., & Kamaruzzaman, B. (2009). An assessment of metals (Pb and Cu) contamination in bottom sediment from South China Sea Coastal Waters. *Malaysian American Journal of Applied Sciences, 6*, 1418–1423.

Roberts, H. (1999). Lead poisoning. http://www.setlet.com. Accessed 2 Jan 2013

Voica, C., Kovacs, M. H., Dehelean, A., Ristoiu, D., & Iordache, A. (2012). ICP-MS determinations of heavy metals in surface waters from Transylvania. *Romanian Journal of Physics, 57*(7–8), 1184–1193. Environmental Physics.

WHO (1993). Guidelines for drinking water quality. 2nd edition. Volume 1: recommendations. Geneva: WHO, 49–50.

WHO (2003). Total dissolved solids in drinking water, background document for development of WHO guidelines for drinking water quality (WHO/SDE/WSH/03.04/16).