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Risk Evaluation of Heavy Metals in Soils Irrigated with Afra Thermal Water Springs, Jordan

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Abstract

The present study investigates the concentrations of six heavy metals (Cu, Ni, Co, Zn and Cr) in Afra thermal springs in Tafila, southern Jordan and their accumulations in soils irrigated by this hot spring water. Thermal water samples were collected during two seasons that is at the end of summer and at the end of the winter season, 2012-2013.

The results show that the concentrations of heavy metals in the soil were relatively low. This was attributed to their low concentrations in the control samples as well as in the thermal water.

The current study investigates water quality in Afra thermal springs in Jordan in terms of heavy metal concentrations. It shows relatively low concentrations and a great variation with seasons. Heavy metal concentrations at the end of winter (in ascending order) were $C_{Cu} > C_{Ni} > C_{Co} > C_{Zn} > C_{Cd}$, whereas at the end of the summer season, they were: $C_{Co} > C_{Ni} > C_{Cu}$. All analyzed metals in the thermal spring water were below the WHO guidelines for drinking water except Ni which showed higher concentrations than those set by the WHO guidelines.

As for soil analysis, the results showed that most of the detected heavy metals were related to pedogenesis rather than to the accumulation from irrigation with thermal water. However, there is an increase in all metals in soils irrigated with thermal springs compared to the control sample, which indicates that there is an accumulation of heavy metals coming from the thermal springs through successive irrigation.

Keywords: Afra Thermal springs, Heavy metal, soil, Jordan.

1. Introduction

Heavy metals are natural constitutes of natural water and their concentrations in the environment depend on the lithology of the aquifer as well as the physiochemical characteristics of the water. The damage resulting from heavy metal accumulation in the soil is difficult to cure as metals cannot be chemically degraded (Salt et al., 1995)

Thermal springs are natural geological phenomena found in all five continents. Geothermal springs are known to be rich in heavy metals which may be attrbiuted to the water rock interaction in the deep aquifers because the chemical composition of the thermal waters reflects the geological formations of the aquifer at depth (Oliver et al., 2008), and the minerals are released through water rock interaction in the deep aquifers.

The chemistry of spring waters reflects the interaction of groundwater with the aquifer host rock as well as any chemical constituents that may be introduced from surface sources. Spring water chemistry is not intrinsically different from groundwater chemistry. The temperature of the hot springs depends on the temperature of the aquifer as well as the speed of water coming to the surface; at a less chance it has to cool down, thus it would be hotter (Durowoju et al., 2016). The solubility of many minerals increases with increasing the temperatures which makes thermal water capable of dissolving minerals over time enriching thermal springs with trace elements (Stauffer et al., 1980). As the hot springs discharge its water at the earth surface, the high concentration of metals will be deposited near the earth surface accumulating in the soil as a result of the changing physiochemical conditions of the water.

Thermal springs have been intensively investigated in the Mediterranean region. In Tunis, an investigation of the deep and shallow geothermal systems in southwestern Tunisia showed that the thermal upward movement of the thermal water from the deep aquifers to the shallow ones is probably due to the abundant fractures in the research area (Ben Brahim, 2013). Also, an isotopic investigation was done by Katsanou et al. 2012 at the Hamamayagi thermal spring in Turkey and showed that the d18O–d2H isotope ratios clearly indicate a meteoric origin for the waters. Another investigation was done by Pasvanoglu et al. (2012) who demonstrated that the thermal-water springs of Banaz area in Tukey have a meteoric origin as the rainwater which percolates downwards along fractures and faults, is heated at depth, and then rises to the surface along fractures and faults which resemble and act as a hydrothermal conduit.

More than ten thermal springs can be found In Jordan, mainly along the eastern flank of the Jordan valley extending from the Yarmouk River in the north to Tafileh province in the south with temperatures ranging from 30°C to 63°C. The main sources of heat for these springs are mainly the hot igneous rocks beneath these springs.

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However, Sawarieh (2008) reported that the source of heat for the thermal water in the lower aquifer is a result of the deep circulation of water within the Paleozoic sandstones receiving heat from normal to slightly elevated geothermal gradient.

The water of some thermal springs to the east of the Dead sea (Main hot spring) originate from three end members mixed with an old groundwater (many thousands of years) at the Dead Sea water under a normal geothermal gradient (Salameh and Rimawi, 1984). A recent investigation of heavy metal concentrations at Main hot springs was found to be higher than the permissible limits set by international organizations (Shakhatreh et al., 2017).

Water quality of cold springs at NW of Afra thermal springs was investigated by Tarawneh et al. (2000). They found that the pollution of the investigated springs comes from surface sources rather than form within the groundwater.

In north Jordan, within Yarmouk basin, Batayneh (2010) found that heavy metal levels in some springs exceeded the Jordanian permissible limits. Schaeffer and Sass, (2014) reported that the shallow aquifer system in Jordan are overexploited in a way that the thermal water system will be affected in quality and quantity increasingly.

Irrigation with thermal water can contaminate the soil with heavy metals. For example, agriculture rice soils irrigated with thermal water during drought seasons in the Gunda plain, northern Taiwan, were reported to be contaminated with Fe, Cu, Mn, Cr, Ni, Zn especially in the deep layers (60-80 cm).

Among the well-known thermal springs in south Jordan is Afra thermal springs which is located at around 30 Km north of Tafila city at altitudes ranging from 304 to 326 m above sea level. The aim of this study is to investigate heavy metal concentrations in Afra thermal water as well as their accumulation in the soils irrigated from a stream fed by the effluent water produced from Afra thermal springs.

2. Study area

Tafila province is characterized by the presence of more than 360 springs of different temperatures. Afra geothermal springs consists of fifteen springs located about 30 km north of Tafila city, on the western limb of Sharah Mountain extending between longitudes (35° 34′), and (35° 38′) and latitudes (30° 52′) and (31° 00′) (Figure 1).

The geothermal system consists of springs with an overall discharging rate of around 500l/sec ranging at a rate of 3.5-80 l/s for each different spring. The temperatures of the springs ranging between 44.5 and 46.3 °C originate from a different aquifer. The thermal water presently flows through open channels to pools, used for swimming and treatment of skin diseases. After being used, the water is discharged to nearby fields where it is used for irrigation purposes. The investigated spring (Afra) originates from the lower cretaceous sandstone underlying gravel beds (Harahsheh, 2002).

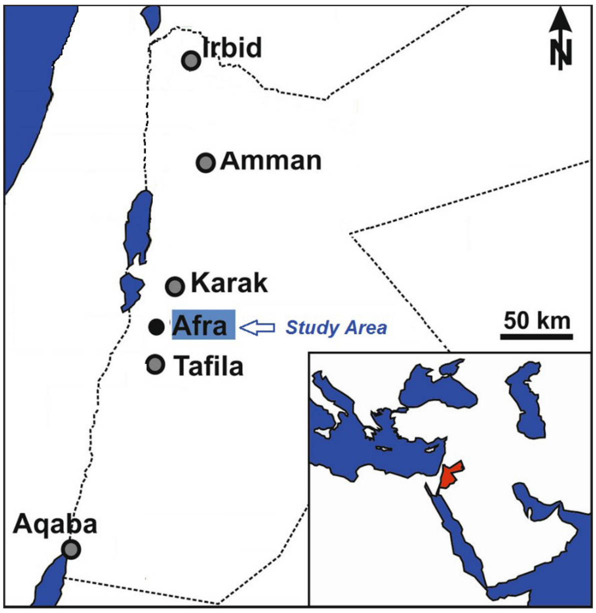

Figure 1. Location map

3. Materials and Methods

The Afra thermal spring water and soils irrigated with streams produced from the thermal springs were investigated in terms of six heavy metals (Zn, Cu, Co, Cr and Ni) for both the soil and water samples.

The water samples were collected at two periods: during March representing the end of the winter season and at the end of summer to show the distribution and potential risks of heavy metals with time.

A 250 ml PVC bottles were used after being washed with 10 % nitric acid. Also the bottles were washed several times with sample water before sampling. Few drops of concentrated nitric acid were added to each bottle to eliminate the precipitation of heavy metals during transportation.

The collected water samples were transferred to the laboratories of “Jordan Abyad Fertilizers and chemicals company and were analyzed within few days after sampling to eliminate any change in their composition.

Soil sampling was carried out only at the end of the winter season from a site located downstream from the Afra thermal water where the source of irrigation water is the effluent water discharge from Afra thermal springs. An additional site was selected where no irrigation is practiced and is considered as a blank sample.

Soil samples from each location were collected from two depths (0-10, and 10-20 cm). All of the samples were in triplicates to ensure reliability of the results. The samples were then transferred to the laboratory at Mutah University for digestion and analysis.

Each sample was oven-dried at 105°C until constant weight was achieved indicating the removal of soil moisture. After drying, each sample was sieved through a 2mm plastic mesh to remove large particles and plant remains from the soil.

For each Soil samples, 1 to 2 grams of the soil was accurately weighed and placed in the test tube, and 10 mL of concentrated nitric acid was added and sonicated for one hour at 90°C (Hewitt et al., 1990). The samples were left to cool, and the contents were filtered through Whatman filter paper No.42. Solutions were made up to a final volume of 25 ml using 1 % nitric acid in polyethylene volumetric flasks.

The digested soil samples were transferred to the laboratories of "Jordan Abyad Fertilizer and Chemical company and were stored at 5ºC until used for the heavy metal analysis which was done also within few days after sampling.

The analysis of Zinc (Zn), Nickel (Ni), Copper (Cu), Chromium (Cr), and cobalt (Co) was determined using Varian atomic absorption spectrophotometer supplied (FAA240). Standard solutions for (Zn, Ni, Cu, Fe, Cr, Co) were prepared by dilution of the stock solution, and calibration curves for all metals were made using their standard solution. Accuracy of the analysis was checked by a periodic analysis of the standard solutions which showed good agreement within less than ±10 %.

4. Results and Discussion

4.1 Thermal Water

Generally, the concentrations of all analyzed metals were found to be low due to neutral pH of the water (pH 6.85-7.14). The dissolution and mobility of metals in natural water are greatly influenced by the (pH) (Hans-EikeGäble, 1997). The slightly alkaline thermal water enhances the precipitation of metals from the aqueous to the solid phase (Jiries et al., 2003)

A statistical summary of the concentrations of six heavy metals (Co, Zn, Cr, Cu, Ni) from the Afra thermal spring waters at the end of summer and winter seasons is presented in Table 1.

The average concentrations of heavy metals for Afra thermal springs at the end of the summer season were as follows: 99, 55, 41 ppb for Co, Ni and Cu, whereas Zn and Cr were below their detection limit. The average concentrations at the end of the winter season were 32, 25, 49, 50, 12, and 543 ppb for Co, Zn, Ni and Cu, respectively. The heavy metals' concentrations in Afra thermal water in ascending order varied with seasons. At the end of winter, the concentrations were Cu > Ni > Co > Zn >Cd, whereas at the end of summer, they were Co > Ni > Cu. The elements Cu and Zn are less reactive in water, but due to the thermal properties of the spring water with temperatures ranging from 36 to 46 ºC, there is more reaction resulting in higher concentrations in winter compared to the summer season (Durowoju et al., 2016). As shown in Table 1, all of the analyzed heavy metals in Afra geothermal spring water fall within the WHO permissible level guidelines for drinking water except for Ni values, which are high in both of the winter and summer seasons.

Table 1. Statistical summary of heavy metals concentrations in ppb for Afra thermal spring during summer and winter season.

	Summer					Winter				
	Co	Zn	Ni	Cu	Cr	Co	Zn	Ni	Cu	Cr
Min	53	ND	40	28	ND	20	18	25	38	11
Max	148	ND	69	54	ND	46	33	70	62	13
Mean	99	ND	55	41	ND	32	25	49	50	12
STD	64	ND	16	15	ND	24	19	20	11	1
WHO Guidelines*	NA	3000	20	2000	50	NA	3000	20	2000	50

*ND: Not Detected, NA: Not available, * after UNEP GEMS (2006)*

Comparing the current results with those from other thermal springs worldwide (Table 2), it was found that the concentration of some heavy metals, such as Co, was much higher than those of other sites such as Limpopo-south Africa. As for Zn and Cr, the results showed higher concentrations than the thermal springs of Tulaz-Turkey and Limpopo-south Africa. The variation can be attributed to the different lithology and different temperatures which make the dissolution of heavy metals vary from one site to another.

Table 2. Heavy metal concentration in ppb of the investigated area compared with other thermal springs worldwide.

	Co	Zn	Ni	Cu	Cr	Reference
Limpopo-South Africa	1.13-3.5	8.65-37.54	4.43-17.33	1.14-6.07	2.85-5.25	Oliver et al. 2008
Main-Jordan	NA	95	58	70	571	Shakhatreh et al 2017
Tulza-Turkey	NA	8-292	NA	1-16	5-329	Baba et al. 2005
This work	32-99	ND-25	49-55	41-50	ND-12	

4.2 Soil

As far as soil is concerned, a statistical summary of heavy metal concentrations at two depths (0-10 cm and 10-20 cm) for soils irrigated with the Afra thermal water is given in Table 3. The average concentrations of the analyzed heavy metals in descending order were Cr > Zn > Co > Ni > Cu. The trend of the increased heavy metal concentrations in the soil was opposite to the trend of heavy metal concentrations of thermal springs at the end of the winter season. Some heavy metals which were found at high concentrations in the soil, such as Zn, were not detectable in the thermal water at the end of summer season; they were found at low concentrations at the end of winter season. This indicates the existence of other additional sources of heavy metals in the soil of the investigated site such as the mineralogical composition of the soil itself as indicated by the high Zn concentration in the control soil as shown in Table 3, whereas there is no remarkable anthropogenic activity in the area.

Table 3. Heavy metal concentration in ppb for soil irrigated by Afra thermal spring water.

Depth		Ni	Cu	Zn	Cr	Co
0-10 cm	Min	160	146	198	200	181
	Max	211	246	450	777	254
	Mean	187	188	327	537	209
	STD	21	42	111	212	27
10-20 cm	Min	135	147	137	168	186
	Max	223	182	385	652	263
	Mean	190	163	257	523	215
	STD	36	17	94	209	31
Control Samples	Min	76	107	108	81	136
	Max	93	131	140	149	173
	Mean	81	117	129	131	143
	STD	9	12	16	35	20

Heavy metals concentrations found in the soil irrigated with Afra geothermal spring were the result of the accumulation from metals in the geothermal spring water and the soil pedogenesis. By comparing the amount of metals found in the soil with that from the control samples (Table 3 and Figure 2), it is noted that there is an increase in all metals in the soils irrigated with thermal springs compared to the control sample. This can be attributed to the accumulation of heavy metals from the waters of the thermal springs through successive irrigation. The trend of the increasing heavy metal concentrations in the soil is not similar to the trend of the thermal water concentrations indicating that pedogenesis is still the main factor controlling heavy metals in the soil as the accumulation of heavy metals through irrigation was not predominant.

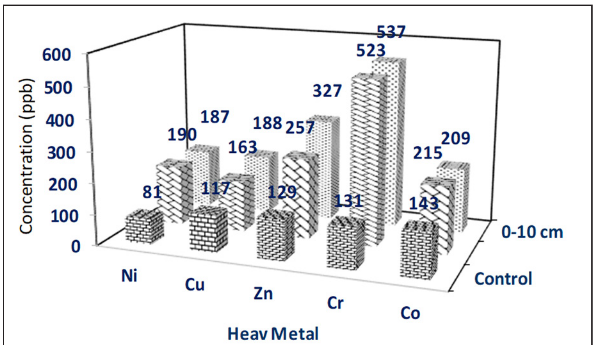

Figure 2. Heavy metal concentration in ppb for soil irrigated with Afra thermal water at two depths (0-10 cm, 10-20 cm and control sample)

The results of the present study show that the concentrations of heavy metals in the soil were relatively low which can be attributed to their low concentrations in the control samples as well as the thermal water.

5. Conclusions

The mean concentrations (C) of the studied metals in Afra thermal springs were in the following order: $C_{Cu} > C_{Ni} > C_{Co} > C_{Zn} > C_{Cd}$. The mean values of metal concentrations were found to be lower at the control site compared with other sites

The data obtained in this study show that the increase in the heavy metal concentrations in soils irrigated by water from the Afra thermal springs was not significant. The concentrations of heavy metals result mostly from pedogenesis rather than from the accumulation through irrigation water.

The mean values of metal concentrations in the soil were found to be lower at the control site compared with the other sites. The results indicate that there was a substantial aerial deposition of the metals on the leaves, which was removed by the washing procedure. The presented results show that irrigation with Afra thermal water does not have any significant impact on heavy metal pollution in the soil.

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