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Shallow Groundwater and Cultivated Soil Suitability Assessments with Respect to Heavy Metal Content in the Köprübaşı U Mineralization Area (Manisa, Turkey)

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Abstract Shallow groundwater and cultivated soil samples were collected from the area within Köprübaşı U mineralization and analyzed to determine U and selected heavy metals (Fe, Mn, Cu, As, Pb, Zn, Cr, Co and Ba). After this, the suitability of the shallow groundwater and soil samples were evaluated for irrigation, livestock watering and agricultural use, respectively. One groundwater sample (4) showed Mn-concentration of 112.6, exceeding the FAO (Ayers and Westcot 1985) livestock drinking limit (50 µg/l). Nevertheless, the amount of heavy metals including Fe, Cu, As, Pb, Zn, Cr and Co in groundwater is not high for irrigation and livestock drinking water standards cited by the FAO (Ayers and Westcot 1985). On the other hand, all cultivated soil samples have higher uranium concentrations than the typical concentration of natural uranium in soil (ATSDR 1999). The majority of the cultivated soil samples showed higher concentrations than the values for heavy metals (Fe, Mn, Cu, As, Pb, Zn, Cr, Co, Ba) found in normal soils of the world (Connor and Shacklette 1975). However, according to G.L.C guidelines, these soils are classified as uncontaminated with Mn, Cu, Pb, Zn and Cr, slightly contaminated with Ba and As.

Keywords Shallow groundwater · Cultivated soil · Heavy metal · Köprübaşı

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Uranium is a chemical substance that is also radioactive. Scientists have never detected harmful radiation effects from low levels of natural uranium although some may be possible. However, scientists have seen chemical effects. A few people have developed signs of kidney disease after intake of large amounts of uranium. Animals have also developed kidney disease after they have been treated with large amounts of uranium. So, it is possible that intake of a large amount of uranium might damage your kidneys. People ingest about 1–2 micrograms of natural uranium every day through food, and take in about 1.5 µg for every liter of water they drink. Nevertheless, it is possible that you may eat and drink more uranium if you live in an area with naturally higher amounts of uranium in the soil or water. You can also take in more uranium if you eat food grown in contaminated soil, or drink water that has unusually high levels of uranium (ATSDR 1999). Like uranium, some heavy metals (iron, manganese, copper, arsenic, lead, zinc, chromium, cobalt and barium) are common in our environment and diet. Small quantities of certain heavy metals such as iron, copper, manganese, and zinc, are nutritionally essential for a healthy life but large amounts of any of them may cause acute or chronic poisoning (Heavy Metal Toxicity 2003).

Köprübaşı is a district of Manisa Province in the Aegean region of Turkey (Fig. 1). The first uranium occurrence in the Köprübaşı area was discovered in 1961 by General Directorate of Mineral Research and Exploration (MTA). Later, MTA (1976) reported the occurrence of uranium mineralization in some localities in the Köprübaşı area. There are people living in villages near or adjacent to the Köprübaşı U area. Some areas within the uranium mineralization are currently being used for agricultural purposes by local people. Besides, shallow groundwater located in uranium mineralization area is generally used for drinking water of livestock and irrigation purposes by village

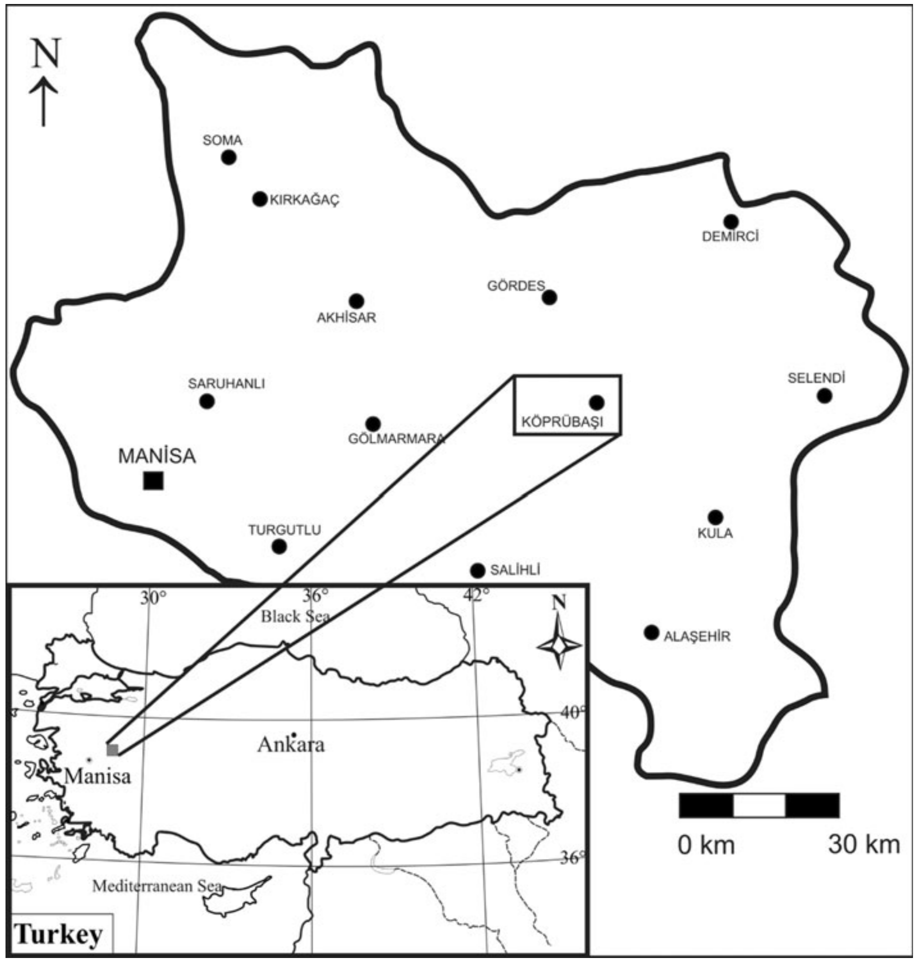

Fig. 1 Location map of the study area

inhabitants. The aim of this study is to determine uranium and selected heavy metal (Fe, Mn, Cu, As, Pb, Zn, Cr, Co, and Ba) content of shallow groundwater and cultivated soil collected in the U mineralization area at Köprübaşı and to evaluate these data in terms of their usability for irrigation, livestock watering and agricultural purposes, respectively.

Materials and Methods

The uranium mineralization is hosted in Neogene fluvial sedimentary rocks of the Köprübaşı area. The sandstones and conglomerates are the most widespread sedimentary rocks within the study area and host the majority of the U ore. The secondary uranium phosphates torbernite, meta-torbernite and meta-autunite were the main ore minerals; jarosite, chlorite-kaolinite and Fe-oxides were also present in the mineral association.The uranium ore grade of the sedimentary rocks varies widely, but is generally low to medium grade (0.01–0.4 U_3O_8%). Moreover, samples from the iron-rich sedimentary rocks have elevated U_3O_8 values up to 1.06% (Kaçmaz 2007).

This study focuses on shallow groundwater and cultivated soil present in the Neogene fluvial sedimentary rocks containing uranium mineralization. Hence, groundwater and soil samples were collected from different locations in Köprübaşı (Manisa) U mineralization area. The sampling locations are shown in Fig. 2. Ground water samples are taken from shallow dug wells (0.5–6 m). All samples were filtered (0.45 µm) and preserved (acidified to pH < 2.0) using ultra pure HNO_3 immediately after filtering. Water samples were sent to an internationally accredited commercial laboratory (ACME Analytical Laboratories Ltd, Vancouver, Canada) for U and heavy metal analyses by enhanced inductively coupled plasma mass spectrometer (ICP-MS).

Surface soil samples were collected from the cultivated area within U mineralization area located at Köprübaşı. These samples were dried in an oven at 70°C for a few hours and were finally powdered and sieved through a 100 mesh sieve. They were also sent to an internationally accredited commercial laboratory for U and heavy metal analyses by ICP-MS.

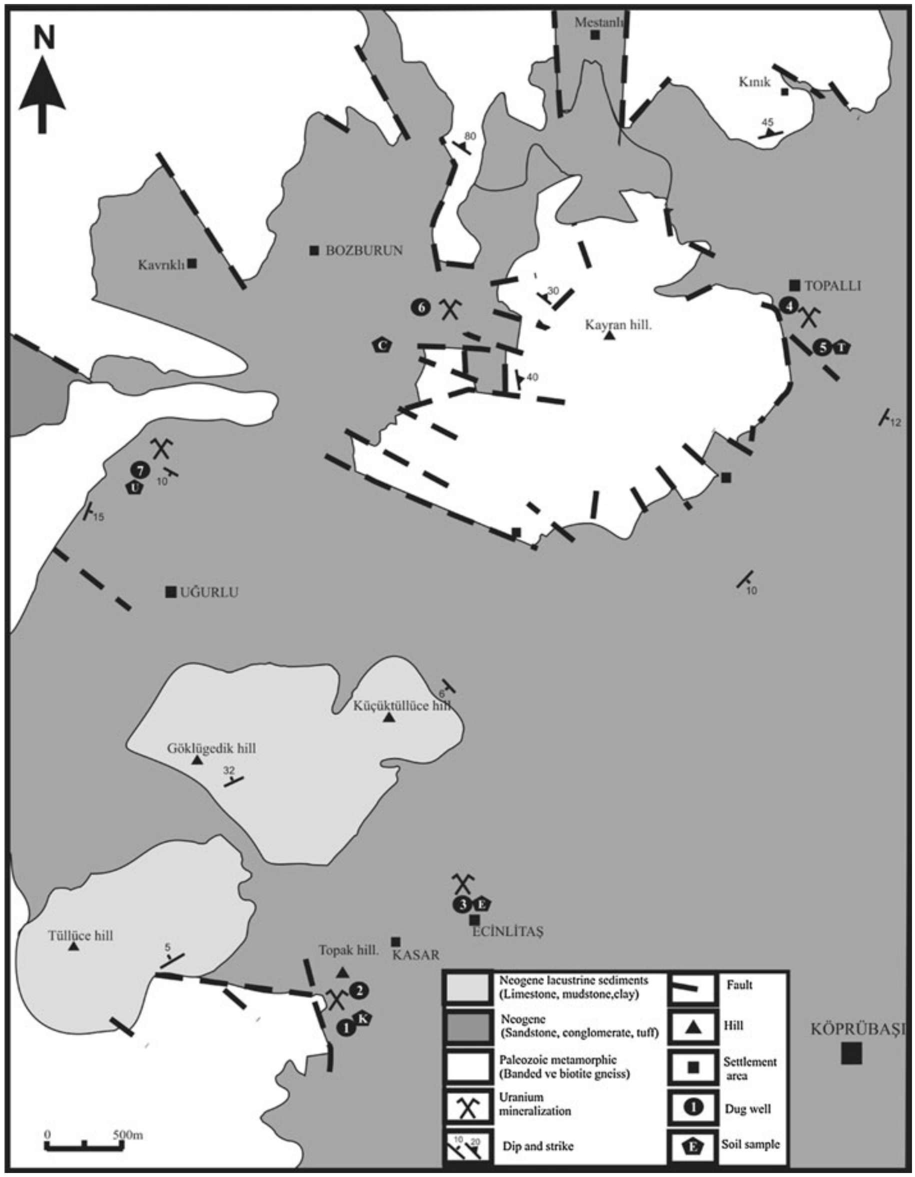

Fig. 2 Geological map of the study area (modified from MTA 1976), showing the sample locations and uranium mineralization

Results and Discussion

Assessment of groundwater contamination is essential to characterize its suitability for any purpose. The heavy metal content of groundwater is one of the most important factors which affected its usability for irrigation and livestock watering. Because, irrigation with heavy metal contaminated water can cause contamination of soil and food crops (Neves and Matias 2008). For example, Hakonson-Hayes et al. (2002) reported that uranium concentration in plants is increased linearly with increasing U concentration in irrigation water, particularly in lettuce and radish. Similarly, Neves and Matias (2008)reported the bioaccumulation of U within the food chain due to elevated U content of irrigation water in the Cunha Baixa (Central Portugal) area. Like plants, livestock can accumulate contaminants in their bodies when they drink heavy metal contaminated water. On the other hand, if heavy metals accumulate in plants and animals, it can induce health problems in human beings who consume them. Therefore, to protect both the livestock and the consumer, there is a quality criterion for water used for livestock watering and irrigation purpose (Ayers and Westcot 1985).

The concentration of uranium and selected heavy metals (Fe, Mn, Cu, As, Pb, Zn, Cr, Co and Ba) for shallow ground waters in Köprübaşı U area is presented in Table 1. The shallow groundwater (0.5–6 m) from aquifer containing uranyl phosphate minerals shows U content in the range between 1.71 and 70.45 μg/l. Concerning uranium; there is no recommended limit for irrigation and drinking water of livestock in the FAO (Ayers and Westcot 1985) standards. Nevertheless, except for one sample (4),

Table 1 Concentration of U and selected elements (U, Fe, Mn, Cu, As, Pb, Zn, Cr, Co and Ba) in shallow groundwater samples

Location Elements (μg/l)	1	2	3	4	5	6	7	Guidelines for levels of toxic substances in livestock drinking water upper limit (μg/l)	Recommended maximum concentration for irrigation (μg/l) in water
U	23.97	16.36	3.52	70.45	3.94	7.45	1.71	NA	NA
Fe	1617	457	479	2837	293	126	636	Not needed	5000
Mn[a]	20.67	5.62	3.63	112.60	3.01	3.37	48.56	50	200
Cu	26.3	13.9	3.3	5.4	2.9	3.0	3.5	500	200
As	16.4	10.2	2.4	82.2	3.8	3.1	1.7	200	100
Pb	3.5	1.4	0.7	3.5	0.4	0.3	0.7	100	5000
Zn	30.4	11.3	12.3	17.6	11.7	15.1	21.8	24000	2000
Cr	3.5	1.3	1	1.4	0.7	0.5	0.8	1000	100
Co	1.07	0.4	0.22	2.74	0.19	0.23	0.53	1000	50
Ba	33.95	21.85	19.95	97.3	46.44	57.64	23.06	NA	NA

Source: Ayers and Westcot 1985, Food and Agriculture Organization of the United Nations Rome, 1985 (FAO)

NA not available

[a] In sufficient data for livestock, value for human drinking water used

uranium concentrations do not exceed the current uranium maximum contaminant level of 30 μg/l set by the United States Environmental Protection Agency (US EPA 2003). Likewise, Kaçmaz and Nakoman (2009) revealed that uranyl phosphate minerals (meta-autunite, meta-torbernite and torbernite) are the sole source of U in shallow groundwater. Furthermore, those authors showed that low U concentration in oxic groundwater samples is related to the limited solubility of U(VI) phosphate minerals under the prevailing conditions (i.e. near neutral pH and low bicarbonate) in the Köprübaşı U area.

Iron, manganese, copper, arsenic, lead, zinc, chromium, cobalt and barium were also detected in groundwater. Compared with the maximum concentration for irrigation guidelines of FAO (Ayers and Westcot 1985), Fe-concentrations did not exceed the guidelines of 5,000 μg/l in all wells. For Mn, one sample (4) showed higher concentrations than the FAO (Ayers and Westcot 1985) livestock drinking limit of 50 μg/l. Other heavy metals including Cu, As, Pb, Zn, Cr, and Co were detected in groundwater in minimal amounts, which are much lower than the allowable concentration for livestock watering and irrigation purposes.

Mineralised areas are characterised by high concentrations of metals in soils due to weathering of naturally ore deposits. Hence, soil pollution by toxic metals in mineralised areas is a widespread and serious problem (Skordas and Kelepertsis 2005). If plants are growing in an area with naturally higher amount of heavy metal in soil, they can get more heavy metal via soil. For instance, Alloway (1990) reported that plants growing in mineralized areas contain up to 100 times more uranium when compared with plants from other areas. Besides, Singh et al. 2001 concluded that higher value of uranium content in plant samples of Balsari village (Kulu district, Himachal Pradesh, India) may also be correlated with higher uranium content in the soil samples of this village. Therefore, the chances of uranium transfer to human organs are expected to be more through the consumption of crops grown in uranium-rich soil (Singh 1997).

The uranium concentration in cultivated soil samples in Köprübaşı varies from 3.1 to 127.09 ppm, while the typical concentration of natural uranium in soil is about 3 ppm (ATSDR 1999). According to the normal soil, the cultivated soils are considered to be enriched in U. The high levels of U in these soils are due to these cultivated areas located in U mineralization area. Nevertheless, there is no stated limit for U in GLC (Great London Council) standards (Kelly 1979). The other heavy metal concentrations of cultivated soil in the Köprübaşı U area are shown in Table 2. In the table it is shown that the heavy metals Fe, Cu, As, Zn, Cr, Co and Ba are generally enriched in Köprübaşı soil in comparison with soil composition for normal world soils (Connor and Shacklette 1975). There is a natural U enrichment of cultivated soil with elevated concentrations of Fe, Cu, As, Zn, Cr, Co and Ba due to the presence of U mineralization. According to GLC standards (Kelly 1979), all the cultivated soil of the study area (Table 2) are characterised as slightly contaminated in Ba (category II). For As, three soil samples (E, T and C) showed higher concentrations than the typical values for uncontaminated soils. So, these soils can be classified as slightly contaminated by arsenic (category II). Low

Table 2 Concentration of U and selected metals (Fe, Mn, Cu, As, Pb, Zn, Cr, Co and Ba) in cultivated soil samples at Köprübaşı U Mineralization Area

Location Elements (ppm)	K	E	T	C	U	Average soil composition[a]	G.L.C. guidelines[b]				
							I	II	III	IV	V
U	10.9	42.7	127.9	3.1	6.2	–	–	–	–	–	–
Fe*	2.52	4.52	1.49	4.80	2.60	2.1					
Mn	232	387	155	387	232	320	500	1,000	2,000	1%	>1%
Cu	21.3	28	8.3	16.5	16.5	15	100	200	500	2,500	>2,500
As	8.1	31.8	33.7	31.8	16.8	7.5	30	50	100	500	>500
Pb	9.2	9.8	22.5	16.8	14.8	17	500	1,000	2,000	10,000	>10,000
Zn	39	51	19	56	42	36	250	500	1,000	5,000	>5,000
Cr	55	82	27	82	55	43	100	200	500	2,500	>2,500
Co	19	26.3	13.8	21.6	18.4	10	–	–	–	–	–
Ba	707	665	657	666	612	300	500	1,000	2,000	2,000–1%	>1%

Typical and allowable levels of U and some heavy metals for soil

* Element values in percent

[a] Connor and Shacklette (1975)

[b] Great London Council suggested range of values in air-dried soils. I: Typical values for uncontaminated soils; II: Slight contamination; III: Contaminated; IV: Heavy contamination; V: Unusually heavy contamination

concentrations of Mn, Cu, Pb, Zn and Cr are observed in all samples of cultivated soil. So, these soils can be classified as uncontaminated by these metals (category 1).

The results of this study indicate that selected heavy metals (Fe, Mn, Cu, As, Pb, Zn, Cr, Co and Ba) in shallow groundwater and cultivated soil do not appear to be at significant levels compared with GLC and FAO standards. On the other hand, there is no stated limit for uranium in these standards. However, it is possible that you may intake more uranium if you consume these plants and animals which accumulated high amounts of uranium. Hence, long-term utilisation of these groundwater and soil is presumed to be unhealthy for the local people. Therefore, to protect the consumer, it is better not to use these shallow groundwater and soil located in uranium mineralization area.

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References

Alloway BJ (1990) Heavy metals in soils. Wiley, New York

ATSDR (1999) Agency for toxic substances and disease registry, Public Health Statement for Uranium http://www.atsdr.cdc.gov/toxprofiles/phs150.html

Ayers RS, Westcot DW (1985) Water quality for agriculture, FAO Irrigation and Drainage Paper No. 29, Rev. 1, UN Food and Agriculture Organization, Rome

Connor JJ, Shacklette HT (1975) Background geochemistry of some soils, plants and vegetables in the conterminous United States, United States Geological Survey and Research Professional Papers, 574-F,164

Hakonson-Hayes AC, Fresquez PR, Whicker FW (2002) Assessing potential risks from exposure to natural uranium in well water. J Environ Radioact 59:29–40

Heavy Metal Toxicity (2003). http://www.lef.org/protocols/prtcl-156.shtml

Kaçmaz H (2007) Manisa-Salihli-Köprübaşı Uranyum zuhurunun incelenmesi, PhD, Dokuz Eylul Universitesi, Fen Bilimleri Enstitüsü, Izmir [in Turkish]

Kaçmaz H, Nakoman ME (2009) Hydrochemical characteristics of shallow groundwater in aquifer containing uranyl phosphate minerals, in the Köprübaşı (Manisa) area, Turkey. Environ Earth Sci 59:449–457

Kelly RT (1979) Guidelines for contaminated soils-suggested range of values (mg per kg) on air dried soils-except for pH. In: Site ınvestigation and materials problems. Proceedings of the conference on reclamation of contaminated land, Eastbourne, U.K. Society of the Chemical Industry, London

Maden Tetkik Arama (MTA) (1976) Köprübaşı Bölgesi Uranyum yataklarına ait rapor, MTA Enstitusü, Radyoaktif Mineraller ve Kömür Dairesi Başkanlığı, Radyoaktif Mineraller Arama Servisi, Ankara [in Turkish]

Neves O, Matias MJ (2004) Focos de poluic¸ão na a′rea mineira da Cunha Baixa (Viseu, Portugal) [Pollution sources in Cunha Baixa uranium mining area (Viseu, Portugal)] Caderno Lab.Xeolo′xico de Laxe, Revista de Xeoloxı′a Galega e do Hercı′nico Peninsular. Coruña 29:187–202

Neves O, Matias MJ (2008) Assessment of groundwater quality and contamination problems ascribed to an abandoned uranium mine (Cunha Baixa region, Central Portugal). Environ Geol 53(8):1799–1810

Singh KP (1997) Uranium uptake by plants. Curr Sci 73:532–538

Singh S, Malhotra R, Kumar J, Singh B, Singh L (2001) Uranium analysis of geological samples, water and plants from Kulu area, Himachal Pradesh, India. Radiat Meas 34:427–431

Skordas K, Kelepertsis A (2005) Soil contamination by toxic metals in the cultivated region of Agia, Thessaly, Greece, identification of sources of contamination. Environ Geol 48:615–624

US EPA (2003). http://www.epa.gov/safewater