

Assessment of the Pollutants in Farming Soils and Waters Around Untreated Abandoned Türkönü Mercury Mine (Turkey)

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Abstract There are several abandoned Hg mines located in western Turkey. Hg production in these mines was eventually halted in the early 1990s because of low prices and environmental concerns (Gemici, 2004). However, acid mine drainage waste causes potential environmental problems near the Hg mines. In Türkönü Hg mine (Fig. 1) nearly 7,000 flasks of mercury had been produced in recent years. In 1965 a private company began to investigate the deposit and by 1968 had installed a 100-tpd rotary furnace. Since, the ore supply has been inadequate and the furnace plant used to process ore hauled from other deposits. Mercury production was terminated in 1975, owing to low prices, and in 1976 the furnace plant was used to process antimony ore (Yıldız and Bailey, 1978). Areas near the mine are currently being used for agricultural purposes. Soils are directly influenced by contaminants, leaching from the mine wastes, which are transported by surface waters in the rainy season. The aim of this study is to evaluate the geochemical dispersal within soil and water, of Hg derived from the abandoned Türkönü mine relating to past mining activities.

Materials and Methods

Three water samples were collected from the mine area. Sample 1 is an adit water. Samples 2 and 3 are surface water samples collected from puddles located on waste rocks. Two specimens were taken from each sampling location

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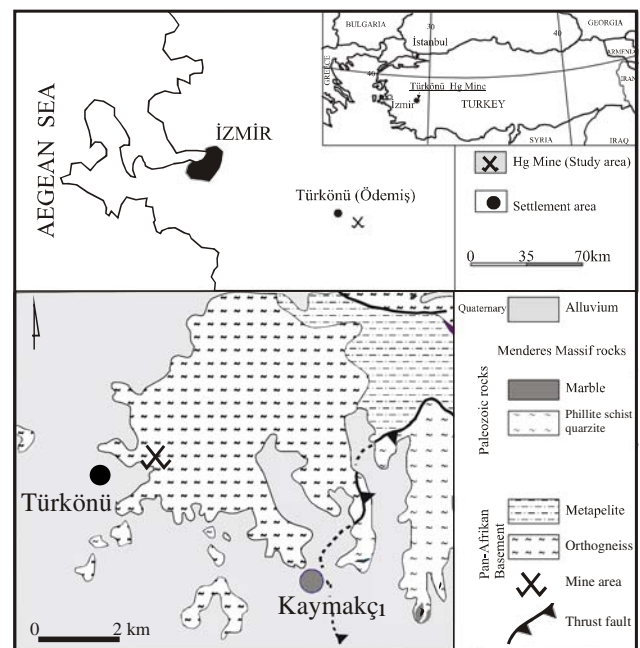


Fig. 1 Location of the study area and geological maps (modified from Dora et al., 2002)

and stored in polyethylene bottles. One of the bottles was acidified with HNO_3 to decrease the pH value to 2 and the other was left unacidified for anion analyses. Electrical conductivity, pH and temperature were measured in the field. All samples were subjected to multi-elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) in Acme [Acme Analytical Laboratories Ltd. 852 East Hastings St. Vancouver, British Columbia V6A 1R6, CANADA (www.acmelab.com)]. For mercury analyses 50 cc of sample was put in a glass bottle and sent to Actlabs (Activation Laboratories Ltd. 1428 Sandhill Drive

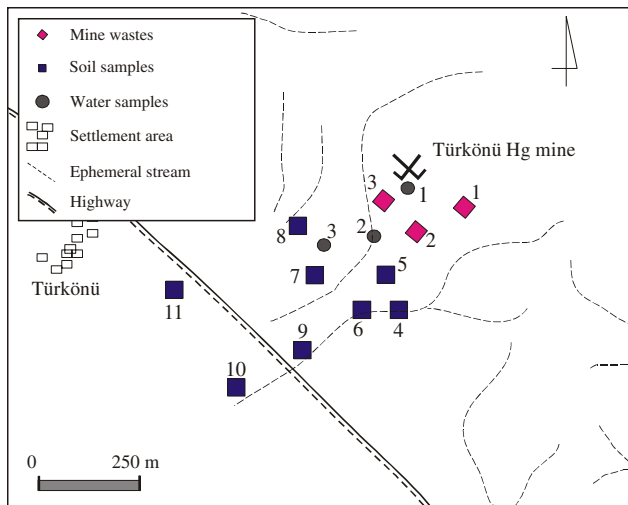


Fig. 2 Distribution of water, mine waste and soil samples taken at and around Türkönü Hg mine

Ancaster, Ontario Canada L9G 4V5) to be analyzed by cold vapor with atomic absorption spectroscopy (AAS). Samples from the mine waste (samples 1, 2 and 3) and soils (samples 4, 5, 6, 7, 8, 9, 10 and 11) were collected in order to determine the dispersion of heavy metals and other pollutants within farming soils close to the mine. Three kilograms of soil were collected at each sampling site with a plastic scoop (Fig. 2). Following Herr and Gray (1995), samples were sieved to –10 mesh (2 mm sieve) in the field.

The sediment samples were air-dried and sieved to –80 mesh (0.18 mm). Samples were analyzed by ICP-MS in Acme. Mercury was determined after aqua-regia digestion using cold vapor AAS.

Results and Discussion

Metamorphic rocks of Menderes Massif, which are high- to low-grade metamorphic types (gneiss, mica schists, phyllites, quartz schists, marbles) form the basement around the Türkönü Hg mine area (Fig. 1). Hg mine is located in orthogneiss rock. Ore occurs where cinnabar accompanied by some pyrite is disseminated in a clayey zone along a fault that strikes east and then steeply north. The ore zone is about 500 m long, ranges in width from one to five metres, and has been mined on several levels (Yıldız and Bailey, 1978).

The results of the chemical analyses of water samples from the study area are presented in Table 1. The Ca, Na and SO₄ ions are dominant in the water samples and their EC values are range between 171–1175 μS/cm. There is a remarkable metal enrichment especially in waters collected from puddles on the mine wastes (samples 2 and 3).

Arsenic levels reached the very high concentration of 53 mg/l for sample 3. This value is 5,300 times the WHO 1993 standard (10 μg/l). Hg value is 9.5 μg/l, which exceeds the WHO 1993 standard (1 μg/l). Like the As and Hg values, Cd, Cr, Pb, Sb, Zn, Cu, Ni and Fe values are much higher in sample 3 than in the other samples. Sb and Fe concentrations exceeded the drinking water standards.

Metal contents increase in the water from the puddles on the mine wastes depending on water-rock interactions. Sample 1, which was taken from the gallery, has no acid drainage water character. The pH value is 6.93 indicating neutral groundwater type. The total dissolved solids (TDS) and EC values of this water are low (Table 1). Although there is no significant increase in the metal content, As and Fe concentrations are a little in excess of drinking water standards. Other ion concentrations are below the standards. Contamination caused by an old gallery in the area was not observed. The surface waters leaching from the waste site in the rainy season, especially As, Sb and Hg type contaminants, are transported to the farming region in the southern part of the mine area. Mine wastes are a danger to the environment. Metal enrichment of the standing waters located on the mine waste explains this situation.

Mine wastes and soil samples were collected from the study area to evaluate the distribution of metals within the environment (Table 2).

The waste rocks have abnormally high values, especially for Hg where concentrations for samples 1 and 2 are above 100 mg/kg. The other waste rock sample has an Hg concentration of 77.4 mg/kg. Arsenic values are remarkable high for the mine waste samples with concentrations reaching to 65.2 mg/kg. Waste rocks are one of the main sources of the contaminants. Cu and Zn are also important contaminants with high values in waste rocks: Cu and Zn values are between 5–310 mg/kg and 99–2714 mg/kg, respectively. In mining wastes contents of other metals are 6.4–113 mg/kg for Pb; 0.5–19.8 mg/kg for Ni; 0.9–52 mg/kg for Sb; 2.7–24.3 mg/kg for Cr and 12.8–20.5 mg/kg for Co. Effects of mining activities on farming soils were assessed using including indices of geoaccumulation (I_{geo}), enrichment factor (EF) and pollution index (PI). I_{geo} enables the assessment of contamination by comparing current and preindustrial concentrations. I_{geo} was originally used with bottom sediments by Müller 1969. It is computed by the following equation; $I_{geo} = \log_2 C_n/1.5B_n$

C_n represents the measured concentration of the element n and B_n the geochemical background value of the element in fossil argillaceous sediment (average shale) (Loska et al., 2004). However, a modified geoaccumulation index was used in the study as defined by Loska et al. (2004). The concentrations of the elements in the Earth's crust (Shachlette and Boerngen, 1984) were used as B_n value.

Table 1 Chemical analyses of water samples

| | | 1 | 2 | 3 | Turkish drinking water standards (TS 1997) | |
|------|-------|-------|-------|----------|--|-------|
| | | | | | *GL | **MAC |
| EC | μS/cm | 522 | 171 | 1175 | 400 | 2,000 |
| PH | 6 | 93 | 8.75 | 9.4 | 6.5–9.2 | |
| T | (°C) | (°C) | 9 | 10 | 10 | |
| Eh | mV | –10 | –112 | –150 | | |
| Na | mg/L | 29.6 | 8.5 | 231.4 | 20 | 175 |
| K | mg/L | 10.5 | 13.7 | 28.3 | | |
| Ca | mg/l | 49.1 | 11.5 | 20.8 | 100 | 200 |
| Mg | mg/L | 12.1 | 2.9 | 3.9 | 30 | 50 |
| SO4 | mg/L | 72 | 39 | 228 | 25 | 250 |
| Cl | mg/L | 117 | 60 | 115 | 25 | 600 |
| HCO3 | mg/L | 134.2 | 34.2 | 207.4 | | |
| Al | mg/L | 0.45 | 0.89 | 2.62 | 0.05 | 0.2 |
| As | mg/L | 77 | 329.2 | 53,293.5 | 0 | 50 |
| Cd | mg/L | <.05 | <.05 | 0.06 | 0 | 5 |
| Co | mg/L | 0.85 | 0.56 | 1.35 | | |
| Cr | mg/L | 0.7 | 1.1 | 2.1 | 0 | 50 |
| Cu | mg/L | 5.8 | 3.7 | 15.5 | 100 | 3,000 |
| Fe | mg/L | 1.01 | 0.86 | 1.86 | 0.05 | 0.2 |
| Hg | mg/L | <.1 | 0.6 | 9.5 | 1 | |
| Li | mg/L | 11 | 8.3 | 4.9 | | |
| Mn | mg/L | 0.029 | 0.014 | 0.027 | 0.02 | 0.5 |
| Ni | mg/L | 2.1 | 2.8 | 4.4 | 0 | 50 |
| Pb | mg/L | 0.9 | 1.6 | 1.9 | 0 | 50 |
| Sb | mg/L | 0.58 | 168.9 | 418.6 | 0 | 10 |
| Zn | mg/L | 8 | 5 | 12.7 | 100 | 5,000 |

*Goal level, **maximum admissible concentration

The constant 1.5 was used because of the lithogenic effect (Salomos and Förstner, 1984). The following descriptive classification is given for the index of accumulation by Muller (1969):

- < 0 = practically uncontaminated
- 0–1 = uncontaminated to moderately contaminated
- 1–2 = moderately contaminated
- 2–3 = moderately to heavily contaminated
- 3–4 = heavily contaminated
- 4–5 = heavily to extremely contaminated
- >5 = extremely contaminated.

The indices of geoaccumulation are presented in Table 3. The Igeo results show that mine wastes are rich in As and Hg, being classified as extremely contaminated with As and Hg metals according to Igeo index. Cu, Pb and Zn have variable Igeo values indicating moderate contamination. Negative Igeo values show farming soils are uncontaminated with Cu, Pb, Zn, Ni, Cr and for some samples Co. The Igeo results for As vary between –0.3 to 1,

indicating moderate contamination on average. The most prevalent contaminant in the field is Hg, for which the Igeo value ranged from 6.5 to 8.3 for farming soils. The average Igeo for Hg denoted extreme contamination.

The EF was calculated using the following formula by Buat-Menard and Chesselet (1979). $EF = (C_n/C_{ref})_{sample} / (B_n/B_{ref})_{background}$

where C_n (sample) is the content of the examined element, C_{ref} (sample) is the content of the reference element, B_n is the background value of the examined element and B_{ref} is the background value of the reference element. Al was used as the reference element as 83000 mg/kg, which is the crustal abundance value (Turekion and Wedepohl, 1961). Five contamination categories are proposed for EF by Sutherland (2000): <2= minimal enrichment; 2–5=moderate enrichment; 5–20=significant enrichment; 20–40=very highly enriched; >40=extremely enriched. The EF values for Ni, Cr, Zn and Pb (Table 4) are low and classified as moderately polluted for mine wastes (samples 1, 2 and 3). Co, Cu and As are classified as moderately to

Table 2 Chemical analyses of mine wastes and soils from the Türkönü Hg mine

| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|----|-------|------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cu | mg/kg | 9.9 | 2714.7 | 14.7 | 9.8 | 13.5 | 12.7 | 13.8 | 10.4 | 10.0 | 16.9 | 11.2 |
| Pb | mg/kg | 6.4 | 111.3 | 6.7 | 5.7 | 9.8 | 10.1 | 7.0 | 5.2 | 8.6 | 6.3 | 10.0 |
| Zn | mg/kg | 5.0 | 316.0 | 29.0 | 20.0 | 23.0 | 25.0 | 20.0 | 19.0 | 21.0 | 55.0 | 31.0 |
| Ni | mg/kg | 0.5 | 19.8 | 12.5 | 6.8 | 7.3 | 7.6 | 7.5 | 7.0 | 6.1 | 15.3 | 7.1 |
| Co | mg/kg | 20.5 | <.1 | 12.8 | 12.4 | 14.6 | 16.1 | 13.9 | 13.0 | 11.4 | 20.6 | 18.6 |
| Mn | mg/kg | <1 | <1 | 133.0 | 129.0 | 194.0 | 162.0 | 122.0 | 130.0 | 124.0 | 186.0 | 148.0 |
| Fe | % | 0.9 | 1.5 | 2.0 | 1.0 | 1.0 | 1.1 | 1.3 | 1.2 | 1.0 | 1.9 | 1.1 |
| As | mg/kg | 10.8 | 65.2 | 14.8 | 8.9 | 6.9 | 10.9 | 10.1 | 9.0 | 15.4 | 10.9 | 21.9 |
| Cd | mg/kg | <.1 | <.1 | <.1 | <.1 | 0.1 | <.1 | 0.1 | <.1 | <.1 | 0.1 | <.1 |
| Sb | mg/kg | 52.1 | 20.3 | 0.9 | 6.9 | 1.6 | 8.1 | 0.5 | 3.0 | 8.1 | 8.5 | 8.2 |
| Cr | mg/kg | 2.7 | 24.3 | 18.0 | 10.5 | 10.2 | 9.3 | 11.8 | 11.4 | 8.8 | 22.3 | 10.1 |
| Al | % | 0.3 | 5.9 | 1.2 | 0.6 | 0.6 | 0.7 | 0.7 | 0.8 | 0.6 | 1.0 | 0.9 |
| Hg | mg/kg | >100 | >100 | 77.4 | 19.5 | 22.1 | 12.1 | 41.6 | 22.0 | 26.0 | 15.9 | 25.8 |

Table 3 The geoaccumulation index values (*I_{geo}*) for the soils

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|----|------|------|------|------|------|------|------|------|------|------|------|
| Cu | -1.2 | 2.7 | -1.2 | -3.3 | -3.3 | -0.8 | -0.5 | -0.7 | -3.0 | -4.5 | -0.6 |
| Pb | -2.0 | -1.8 | -1.8 | -2.3 | -2.1 | -2.1 | -1.3 | -3.2 | -8.2 | -2.0 | -1.7 |
| Zn | -0.9 | -0.1 | -0.8 | -3.3 | -2.4 | -0.6 | -0.3 | 0.0 | -4.9 | -4.5 | -0.4 |
| Ni | 0.8 | 8.5 | 2.1 | -1.0 | 1.0 | 4.4 | 4.7 | 8.5 | 2.8 | 0.3 | 4.6 |
| Co | 0.4 | 5.5 | 0.4 | -0.5 | 1.0 | 2.4 | 2.3 | 4.7 | 0.8 | -0.6 | 2.1 |
| Mn | -0.9 | -5.2 | -1.4 | -9.7 | -8.7 | -0.9 | -0.4 | -1.6 | -9.7 | -9.7 | -0.9 |
| As | 1.2 | 6.8 | 0.4 | 4.6 | 2.8 | 3.4 | 4.1 | 6.5 | 6.0 | 3.5 | 3.6 |
| Cr | -1.4 | 4.3 | -1.6 | 1.0 | 1.8 | 0.2 | 0.8 | 6.3 | 0.7 | 0.6 | 0.7 |
| Hg | 3.7 | 6.2 | 1.5 | 9.2 | 7.1 | 4.8 | 6.4 | 8.0 | 9.5 | 9.5 | 6.0 |

Table 4 Enrichment factors (EF) for the heavy metals for the soil samples

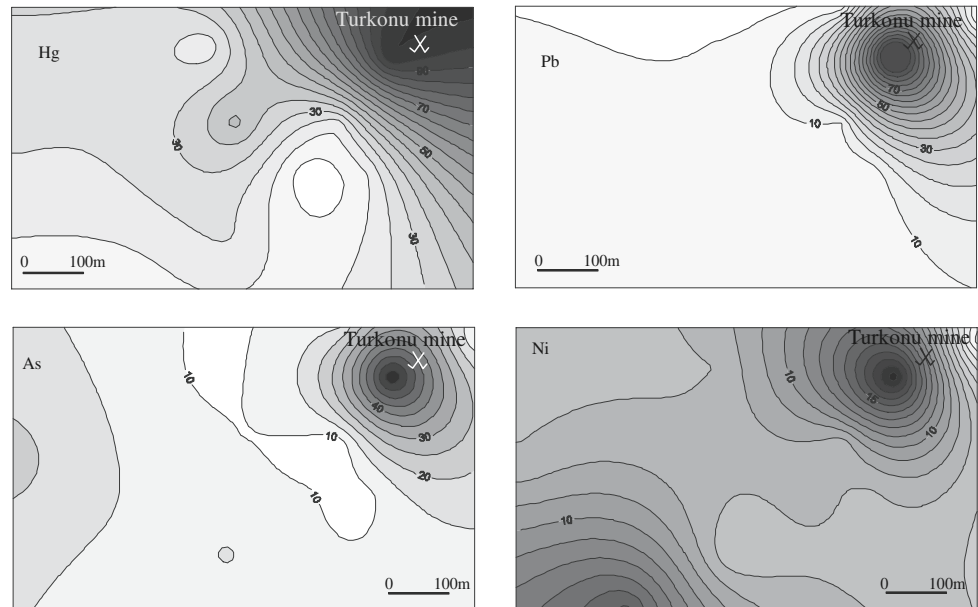
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|----|------|---------|-------|--------|-------|-------|-------|--------|--------|-------|-------|
| Cu | 8.2 | 207.6 | 17.9 | 12.9 | 14.0 | 13.0 | 17.2 | 4.2 | 12.7 | 1.6 | 16.3 |
| Pb | 4.7 | 9.2 | 12.1 | 25.8 | 33.0 | 5.3 | 9.7 | 0.7 | 0.4 | 8.4 | 7.6 |
| Zn | 9.9 | 29.7 | 23.1 | 12.5 | 26.1 | 14.8 | 19.3 | 6.9 | 3.5 | 1.5 | 18.3 |
| Ni | 32.7 | 10921.1 | 182.0 | 63.8 | 284.4 | 466.3 | 622.0 | 2348.6 | 721.9 | 43.4 | 595.1 |
| Co | 25.3 | 1435.2 | 53.2 | 88.5 | 272.6 | 114.3 | 118.1 | 179.3 | 180.9 | 22.0 | 108.2 |
| Mn | 9.9 | 0.9 | 15.7 | 0.2 | 0.3 | 12.1 | 18.2 | 2.3 | 0.1 | 0.0 | 13.2 |
| As | 44.7 | 3355.7 | 54.6 | 2956.9 | 991.4 | 241.7 | 405.0 | 619.2 | 6422.9 | 389.4 | 299.3 |
| Cr | 7.0 | 611.3 | 13.6 | 250.1 | 481.1 | 25.3 | 40.6 | 509.9 | 170.2 | 51.2 | 39.2 |
| Hg | 250 | 2317 | 115 | 71753 | 19522 | 636 | 2052 | 1693 | 77715 | 25905 | 1589 |

Table 5 Pollution index (PI) values for the soil samples

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| PI | 6.8 | 9.7 | 4.5 | 1.3 | 1.4 | 1.0 | 2.4 | 1.4 | 1.8 | 1.2 | 1.8 |

significantly polluted based on the EF their values. EF value for Hg is remarkably high and indicates extreme pollution. Soil samples show similar classifications as for the above mentioned metals. Values for Hg vary between 1,426 and 5,386 denoting extremely pollution in farming

Fig. 3 Distribution of some selected metals (in ppm) in farming soils



soils. EF value for other metals indicates moderate to significant pollution in farming soils in the lower parts of the mine area.

PI is computed by averaging the ratios of the total concentrations of the heavy metals to the tolerable levels (Nishida et al., 1982).

$$PI = (As/20 + Cd/3 + Cu/100 + Hg/2 + Pb/100 + Sb/5 + Zn/300 + Ni/50 + Cr/100)/9$$

PI values above 1.0 indicate metal concentrations greater than the permissible levels: elemental enrichment can be by anthropogenic inputs or natural geological resources (Nimick and Moore, 1991). PI values for mining wastes are between 4.5 and 9.7 which are much higher than the permissible level. Close to the mine area PI values of farming soils increase to around 2.4. PI values gradually decrease in the lower parts of the mine area to 1.2. PI values for farming soils are relatively lower however their values are found higher than the permissible level of 1.0.

Figure 3 shows the distributions of Hg, As, Ni, and Pb metals in farming soils around the mine area. Concentrations of the metals are high around the mine and decrease towards the lower parts of the area. Distribution of the metals clearly shows that mine wastes are the main source of contamination in the soils. Mine wastes transported from mining area with surface waters are potentially hazardous to the environment adjacent to the abandoned Hg mine and are in need of remediation.

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