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Pilot Study of Environmental Monitoring of Konya Region near Abandoned Mercury Mine in Turkey

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Abstract Abandoned mines are an important global concern and continue to pose potential threats to human health including environmental damage/s. There is not any specific regulation for mining wastes in Turkey and this situation puts the mining wastes into the dangerous category. Therefore, this study focuses on the environmental effects of the abandoned mercury mines. To demonstrate environmental mercury contamination, fish samples were collected from two different regions which were contaminated and uncontaminated region. As a biomarker of environmental exposure the levels of Hg in fish samples were measured by Cold Vapor-Atomic Absorption Spectrometry (CVAAS). In fish samples, the levels of Hg were 0.504 ± 0.475 (mg/kg) (Mean $\pm$ SD) in Group 1 and 0.04 ± 0.054 (mg/kg) (Mean $\pm$ SD) in Group 2. Our data suggested that although mercury mine was closed long time ago, mining waste is still a problem and continues to contaminate the environment.

Keywords Mercury · Abandoned mercury mine · Toxicity · Cold vapor atomic absorption spectrometry

Hundreds of pollutants are discharged into the environment every day. Of these, heavy metals are regarded as serious pollutants of the aquatic environment because of their environmental persistence and tendency to be concentrated in aquatic organisms. Contamination of aquatic ecosystems by heavy metals can be confirmed in water, sediment and organisms. Metals transferred through aquatic food webs to fish, humans and other piscivorous animals are of environmental and human health concern (Chen et al. 2000). Most heavy metals released into the environment find their way into the aquatic phase as a result of direct input, atmospheric deposition and erosion due to rain (Altindag and Yigit 2005). Therefore, aquatic animals may be exposed to elevated levels of heavy metals (Kalay and Canli 2000). Mercury is a heavy metal of environmental concern because elevated concentrations can be toxic to living organisms. Therefore, the presence of abandoned mercury mines is a potential hazard to residents and wildlife. Until 1974, Turkey produced more than 12,000 flasks of mercury, which was about 5% of the world output. More than 50 known mercury deposits and occurrences are in the west half of Turkey (Yildiz and Bailey 1978). These mines were gradually abandoned until early 1990s due to the low prices, low demand, and environmental concerns of mercury (Gemici and Oyman 2003; Gemici and Tarcan 2007). However, no environmental recreation studies have been done (Gemici 2004). It is a well known fact that human health is directly affected by the food they consume and environment they live in. Mercury can cause adverse effects on the renal and nervous systems and can cross the placental barrier, with potential toxic effects on the fetus (Tong et al. 2000).

In the present study, the abandoned mercury mine is located to the south of the Central Anatolian was in operation from 1906 to 1974. Mine was operated by Etibank between 1964 and 1975 and approximately 588.639 kg of Hg was produced from the region. The mine was closed in 1976 because of low prices and low demand for mercury. In the present study, it was aimed to demonstrate

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environmental contamination and the pollution level of this aquatic ecosystem via determining the levels of Hg in the fish samples of small dam called Ladik Dam in Kursunlu-Konya near the abandoned mine.

Materials and Methods

All chemicals used were of analytical reagent grade. Concentrated HNO_3, HCl were obtained from Merck, and $SnCl_2 \cdot 2H_2O$ was from Riedel de Hagen. Hg standard solutions were prepared from 1,000 mg/L Hg stock solution (Fisher Scientific). Deionized (DI) water, from Milli-Q Water Purification System (Millipore Corp.), was used throughout the experiments. Nitrogen gas was used as carrier gas. Hg standard solutions were prepared daily by appropriate dilutions of the stock solution in 1.5 M HNO_3. The reducing agent was 10% (w/v) $SnCl_2$ in 1.8 M HCl. Certified reference material (CRM); NRC DOLT-3 dogfish liver was used to validate the method.

Fish samples were collected from two different regions. Group 1 (n = 25); Ladik Dam, Kursunlu region in Konya, Sarayonu which is possible contaminated region. Group 2 (n = 25); region which is supposed to be cleaned and approximately 4.6 km far from the abandoned mercury mine and it was used as a control region. Fish samples were placed in aluminum foil and zip-locked bags prior to cold storage. All fish samples were stored at −80°C freezer until analysis and fish muscles were used for mercury determination. As a biomarker of environmental exposure the levels of Hg were measured by Cold Vapor-Atomic Absorption Spectrometry (CV-AAS). The reason for analyzing the mercury level in muscle tissue is, the amount of mercury in muscle is almost the same through the entire year when compared to other body parts (Cappon and Smith 1981). Amongst the drying procedures for Hg determination in fish samples, oven-drying is the most appropriate method (Ortiz et al. 2002). Thus, muscles were oven-dried at 40°C for 48 h. Dried samples were homogenized and every sample was prepared in triplicate. Mercury measurements were performed using Unicam 939 Atomic Absorption Spectrometer with a deuterium background correction. A mercury hollow cathode lamp was used and the wavelength was set to 253.7 nm. The atomization cell with an optical path length 160 mm with 10 mm (i.d.) and the inlet arm was 50 mm in length and 4.0 mm (i.d.) was made of glass with quartz windows attached to both sides. Peak height was measured throughout the experiments. A batch type reduction vessel was used as the reactor. The carrier gas was used at a flow rate of 500 mL/min to purge Hg vapor to the atomization cell. After each measurement the reduction vessel was rinsed with 5% HNO_3, then with water. Digestion of fish samples was performed in long-necked glass digestion tubes by placing the tubes in the holes of a thermostated heating block, Grant Instruments, Type B (Cambridge).

Approximately 1 g of homogenized sample was weighed and 5 mL HNO_3 was added. After adding HNO_3, solution was kept at room temperature for 15 min. The heating block temperature was increased to 60°C and remained at this temperature for 20 min. Then temperature was increased to 110°C and stayed at this temperature for 30 min. Temperature was increased to 140°C and heated for 2 h. Digested sample cooled down to room temperature and diluted to 10 mL with DI water. Three parallel samples were digested for each sample using the digestion method described above.

A known volume of sample or Hg standard solution was introduced to the reduction vessel. Then, 1.0 mL of 10% (w/v) $SnCl_2$ was added and the reduction vessel was closed immediately. The stirrer was turned on for 70 s, during this time no carrier gas was allowed to pass through the reduction vessel. At the end of stirring time, the carrier gas was switched through the reduction vessel, carrying the Hg vapor to the atomization cell to measure the absorbance. Measurements were performed three times for each parallel and also, external calibration was used. The least squares regression analyses of the calibration curve for mercury is 0.0038[Hg] + 0.0067 ($r^2 = 0.9984$). The linear range of the method was 3.5–100 ng and the limit of detection (LOD) was 0.9 ng. The precision of the method in terms of relative standard deviation (RSD) corresponding to consecutive measurements (n = 11) at 10 ng level was found as 2.1%.

The method was validated using a certified reference material NRC DOLT-3 dogfish liver. The certified reference material (CRM) was digested using the same procedure described above. The concentration of Hg was found as 3.49 ± 0.21 mg/kg (n = 3) while the certified value was reported as 3.37 ± 0.14 mg/kg. The obtained results were in good agreement with certified value at 95% confidence level.

Results and Discussion

The issue of abandoned mines is important because it involves former mining sites that continue to pose a real or potential threat to human safety and health including the environment. Toxic trace elements, such as mercury, are important indicators of human pressure posed on the environment. Several abandoned Hg mines are located in western Turkey. Due to the low prices, low demand and increasing environmental concerns of Hg, the mines were abandoned gradually until early 1990s (Gemici and Oyman 2003). Inorganic mercury released into the environment, it

Table 1 The list of the levels of mercury (mg/kg) in muscle tissue of fish samples in two regions; control region and the possible contaminated regions

Sample no	Control region mean ± SD (mg/kg)	Contaminated region mean ± SD (mg/kg)
1	0.031 ± 0.01	0.29 ± 0.048
2	0.028 ± 0.01	ND
3	0.027 ± 0.01	1.39 ± 0.16
4	0.02 ± 0.01	1.44 ± 0.16
5	0.03 ± 0.01	0.43 ± 0.07
6	0.02 ± 0.01	1.41 ± 0.05
7	0.03 ± 0.01	0.39 ± 0.12
8	0.025 ± 0.01	0.54 ± 0.06
9	0.02 ± 0.01	0.49 ± 0.01
10	0.03 ± 0.01	0.6 ± 0.14
11	0.3 ± 0.01	0.039 ± 0.01
12	0.03 ± 0.01	0.21 ± 0.02
13	0.03 ± 0.01	0.48 ± 0.02
14	0.02 ± 0.01	0.08 ± 0.02
15	0.03 ± 0.01	0.55 ± 0.06
16	0.04 ± 0.01	0.73 ± 0.01
17	0.03 ± 0.01	0.14 ± 0.01
18	0.03 ± 0.01	0.19 ± 0.02
19	0.04 ± 0.01	0.17 ± 0.01
20	0.03 ± 0.01	0.04 ± 0.01
21	0.04 ± 0.01	1.07 ± 0.14
22	0.04 ± 0.01	1.27 ± 0.1
23	0.04 ± 0.01	0.05 ± 0.01
24	0.03 ± 0.01	0.05 ± 0.01
25	0.04 ± 0.01	0.04 ± 0.01

ND not detected

Table 2 The comparison of Hg levels (mg/kg) in muscle tissue of fish samples in two regions; control region and the possible contaminated regions

	n	Mean ± SD	Min–max	*p**
Control region	25	0.040 ± 0.054	0.02–0.3	0.0001
The possible contaminated region	24	0.504 ± 0.475	0.039–1.44	

* Independent *t* test

is converted to organic mercury (methylmercury; MeHg) which is the primary form that accumulates in fish and shellfish. Therefore, fishes are good biomonitoring biologic material to demonstrate environmental effects. To date, although there are many studies investigating the environmental effects of abandoned metal mines in Turkey, to our knowledge, there has been no study in Kursunlu region in Konya-Sarayonu. The objective of this study was to determine if weathering of abandoned mercury mines in Konya-Sarayonu has resulted in any significant effect to surrounding ecosystems, especially fish. Table 1 lists the levels of Hg in fish muscles in two regions; control region and the possible contaminated region. In fish muscles, the levels of Hg were 0.504 ± 0.475 (mg/kg) in Group 1 (mine area) and 0.04 ± 0.054 (mg/kg) in Group 2 (control area). Our results showed that the mean levels of Hg in Group 1 were approximately twelve times higher than Group 2 (Table 2). Similar study to ours was conducted to assess environmental and human exposure of communities near an abandoned mercury mine in Philippines. Total and MeHg levels in fish collected near the three communities near the abandoned mines ranged from 1.65 to 1,152.01 and 1.29–931.6 ng/g, respectively. Their results also showed statistically significant levels of total mercury (1.5 times higher) in fish samples in the case study areas as compared with the control sites ($p < 0.05$, Case area and control area (mean ± SD) (mg/kg) are 0.1587 ± 0.218 and 0.0707 ± 0.072, respectively; Maramba et al. 2006). Our results are consistent with Maramba et al.'s results. Concentrations of total Hg, inorganic Hg and MeHg were measured in stream- sediment, stream-water, and fish collected downstream from abandoned mercury mines in southwestern Alaska to evaluate environmental effects to surrounding ecosystems. Muscle samples of fish collected downstream from mines contain as much as 0.62 mg/kg Hg wet weight (Gray et al. 2000). The Hg contents in fish muscle and distance from the mine were similar to our study and also our data (0.504 mg/kg) were consistent to Gray et al.'s results. Mobility of metals in water, mine wastes, and stream sediments around the abandoned Alaşehir mercury mine, in Turkey, was investigated to evaluate the environmental effects around the area. Hg concentrations of adit water samples and surface waters draining the mine area were between 0.25 and 0.274 µg/L (these levels are below the WHO drinking water standard and above the EPA standard; EPA 1992; Gemici 2008; WHO 1993). In another study, total Hg and MeHg were evaluated in mine wastes, soils, water, and vegetations from the Wuchuan Hg-mining areas, Guizhou, China. Data indicate heavy Hg-contaminations and significant conversion of methyl-Hg was observed (Qiu et al. 2006). Sediment microbial community composition was investigated at four abandoned Hg mine–impacted sites in the California Coast Range: the Abbott, Reed, Sulphur Bank, and Mt. Diablo mines. The Abbott and Sulphur Bank mines had the highest levels of MeHg due to Desulfobacter and Desulfovibrio organisms made up higher percentages of overall microbial biomass at these mines than at the Abbott and Reed mines (Batten and Scow 2003). The impact of mining and metallurgical activities on terrestrial and aquatic environments was evaluated in La Soterrana, an abandoned Hg mine in Asturias, north of Spain. Hg content is 10 times higher than the background level in the area (reach up to

502 mg/kg in soils for total Hg, background level = 4.18 mg/kg; Loredo et al. 2006). Abandoned mines might produce a considerable increase in the bioavailability and bioaccumulation of potentially toxic metals (Pb, Hg, Cd, and Ni) and these elements might represent an environmental risk (Sanchez-Chardi et al. 2007). The geochemical investigations on water and stream sediments were carried out to evaluate the influence from the abandoned Kalecik Hg mine. Hg contents of higher than 100 mg/kg were measured and pollution index values were found the significantly high (varied 69–82; for stream sediment samples; Gemici and Oyman 2003). The impacts of residual Hg almost 20 years after the plant's closure was examined in water, sediment and biota (invertebrates and fish) samples in the vicinity of the processing plant to determine the Hg concentrations. While total Hg and MeHg concentrations were higher in water and sediment samples at sampling sites immediately downstream of the Hg processing plant when compared to the upstream sites, fish MeHg concentrations were just below the US EPA guideline for Hg in fish muscle tissue (300 ng/g; Williams et al. 2011).

In conclusion, the data presented in this study, together with results from similar studies conducted elsewhere indicate that elevated Hg concentrations in freshwater fish collected near the abandoned mines indicate that some biologically available Hg is taken up by the fish. The Hg accumulation in fish might be arise from either through mine source or suspended particulates in stream water. Our study showed that there is still environmental contamination although the mine was closed 36 years ago. We suggest that numerous interorganizational agreements should be implemented to promote cooperation in the characterization of mine site hazards, development of mutually acceptable plans of remediation, and sharing of actual cleanup requirements.

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