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The Determination of Heavy Metal Contents and Some Chemical Properties in Soils around an Old Mercury Mine in Turkey

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Abstract. In this study area are under major environmental pollution problem. The abandoned mine area which is the subject of this study had been operated for approximately 40 years before it was put out of operation and is closed at present. However, the waste soil excavated from the mine was collected in the open .The preliminary survey studies revealed the existence of pollution both in the waste soil and waters existing in the area surrounding the dump site. In this study, the interaction between the chemical properties with heavy metal contents of the soils of this mercury mine areas were investigated. Multivariate correlation coefficient analysis were used to analyze the data .Total 34 soil samples were sampled from the mercury mine areas and analyzed using ICP-MS for heavy metals. Also these soil samples were analyzed other soil chemical properties. The results indicate that the total contents of Fe, As and Hg in soils are between 2.28-7.71%, 21-382 mg/kg and 0.60->100 mg/kg, respectively. The results of the analysis showed that soils had pH of 6.70-7.59, lime content of 0.91-21.85% and had sandy loam textures. The present study would provide us information to manage the sources of these elements in the study area.

Keywords: Mercury mine, heavy metals, contamination, soil pollution, soil chemical property.

1. Introduction

The heavy metal soil contamination from mining and smelting creates a wide spectrum of hazards. Adverse environmental impacts from contaminated mining sites include risk to human health, phytotoxicity, contamination of water and soil, and ecotoxicity [1]. It is well-known that metal ore processing is associated with contamination of the environment with a cocktail of contaminants rather than one metal. Metal mining, smelting, and processing throughout the world have contaminated soils with heavy metals in excess of natural soil background concentrations. These processes introduce metal contaminants into the environment through gaseous and particulate emissions, waste liquids, and solid wastes [2]. Researchers are not enough about soil and environmental pollution which is caused from mining studies in industrialized countries.These studies have been increased since 2000s at developing countries. According to studies: At surface soil samples collected from a Pb and Zn mining area in India were obtained that heavy metal concentrations were very high especially as Pb,Zn, Mn, Cu, As, and Tl elements[3].The same researchers were found an another study that the area surrounding a historical Pb–Zn mining and smelting area in Zawar- India detected significant contamination of the terrestrial environment by heavy metals. The median concentrations of metals in surface soils were: Pb 420.21 μg/g, Zn 870.25 μg/g, Mn 696.70 μg/g, and Cd 2.09 μg/g. Zn concentrations were significantly correlated with Cd ($r = 0.867$), indicating that levels of Cd are dependent on Zn. However, pH, electrical conductivity and total organic matter were not correlated significantly with Cd, Pb, Zn, and Mn [3].A historical Pb–Zn mining area in the town of Bytom in Upper Silesia, Poland were found that median topsoil concentrations (0 ±10 cm) for Pb, Cd, Zn and As were 430 mg g^{-1}, 13 mg g^{-1}, 1245 mg g^{-1} and 35 mg g^{-1}, respectively [4]. Also the area surrounding a Pb-Zn smelting and mining centre in Bukowno-Poland was detected significant contamination by heavy metals. The median concentrations for

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field and garden topsoils (C-10 cm depth) were: Pb 545 µg/g, Zn 2.175 µg/g, Cd 14.8 µg/g and As 81 µg/g [5].

The 500-year history of mercury mine area of Idrija-Slovenian (1490 – 1995), over 12 million tons of ore in were excavated and a total of 153.309 tons of commercial mercury was extracted, which represents over 13% of the entire world production to date [6]. Over this period approximately 38.000 tons of mercury were lost to the environment, mostly in the form of mercury vapour, deposited as smelting residues into the river Idrijca and its banks, or used as construction material [6].At Pšenk site of the same area, detailed soil sampling was performed on 210 x 180 m large area to establish the extension of mercury pollution and to investigate mercury transformations and transport characteristics through the 400 year-long period. The organic matter-rich surface soil layer (SOM) and soil samples were collected from 73 sampling points. 3 soil profiles were sampled to determine vertical distribution of Hg in soil [7].The determined Hg contents in soil samples of the investigated area vary from 5.5 to almost 9,000 mg/kg with the median of 200 mg/kg. In SOM Hg contents are ranging from 1.4 to 4.200 mg/kg with the median of 20 mg/kg [7]-[9].In 2004/2005 Geological survey of Slovenia conducted a research project concerning Tersıc et al.(2012) studied at the abandoned mine and ore roasting facilities in Podljubelj[10]. They were collected 26 topsoil samples (0–5 cm) and 23 subsoil samples (20–30 cm) within a research grid in the narrow area of the mine and smelter. The determined Hg in soil is ranging between 0.17 and 719 mg/kg. In topsoil Hg concentrations vary from minimum 0.35 to maximum 244 mg/kg with the median of 3.67 mg/kg.

According to these studies in different countries, our country has an important place in mineral resources for the geographical position. There is some mining areas is located in the old mining areas that are not longer in managing, some heavy metal pollution in the vicinity of the old mining areas often encountered. Where we are living in the region, some mining operation closed in Konya-Sarayönü old mercury mine on the surrounding land areas are also exposed to heavy metal pollution. Sarayönü district of Konya-Turkey in the bed of a large number of mercury, stibnite, and locally in addition to Cu and Pb-Zn resources have also been reported [11].The region around town that is former mining area containg mineral deposits of mercury, the corrosion of metals in this soil to be deposited in an open place, rust and the surrounding soil and water samples taken from agricultural areas and local people come out of the high fat content of heavy metal oral interviews (although without scientific data); region directly affecting the health of people living in the community of cases of cancer-related death has been extremely active in the preparation of this project. The first screening studies in this area, especially the land of Pb, Ni, Co, As, Ba, Hg and Cd contents were found to be much higher than the acceptable standard of values. Also natural vegetation samples were taken from plants common in these areas and analyzed. Root, stem, leaf and flower samples of this plant, the heavy metal measurements showed that still high level of As, Hg, Pb, Cr, Ni, and Zn were found in our project.

For this purpose, pre-scanning studies by taking into consideration on the soil, to be held in this study, heavy metal pollution in soils was researched in the former mercury mining area.

2. Material and Method

Soil samples were taken from the area of approximately 4 km^2 around the dump site located near an old mercury mine site in Konya province of Turkey (Fig. 1). This area; a study by Wiesner (1967) have been reported that above 300 square kilometers area encompasses the mining area approximately at 30 km north-west of the Konya city and some sections of Ilgın L 28-c1, L 28-c2, L 28-c3, L 28-c4, L 28-d2 (scale 1:25,000). The field examined in this study is located in Ilgın L28-C2. Total 34 soil samples were randomly taken from a depth of 0-20 cm from during 2012 year.

After these soil samples were subjected to necessary pre-treatments such as drying and sieving through 2 mm. They were analyzed for physical and chemical methods. For this purpose, pH and electrical conductivity were determined at a soil: water ratio being 1: 2.5[12]; particle size was analyzed by the Bouyoucous hydrometer method [13] and calcium carbonate by Scheibler calcimeter method [14]. Total soluble salt content was calculated from the value of electrical conductivity. The elemental analysis of the soils was carried out by taking extracts in a mixture consisting of 4 acids (HNO_3-$HClO_4$-HF and HCl) (Group 1EX) and the reading process was performed using ICP-ES and ICP-MS device. These procedures were carried out by Canada Acme Analytical Laboratories. The data obtained through the measurements were statistically analyzed using Minitab software [15].

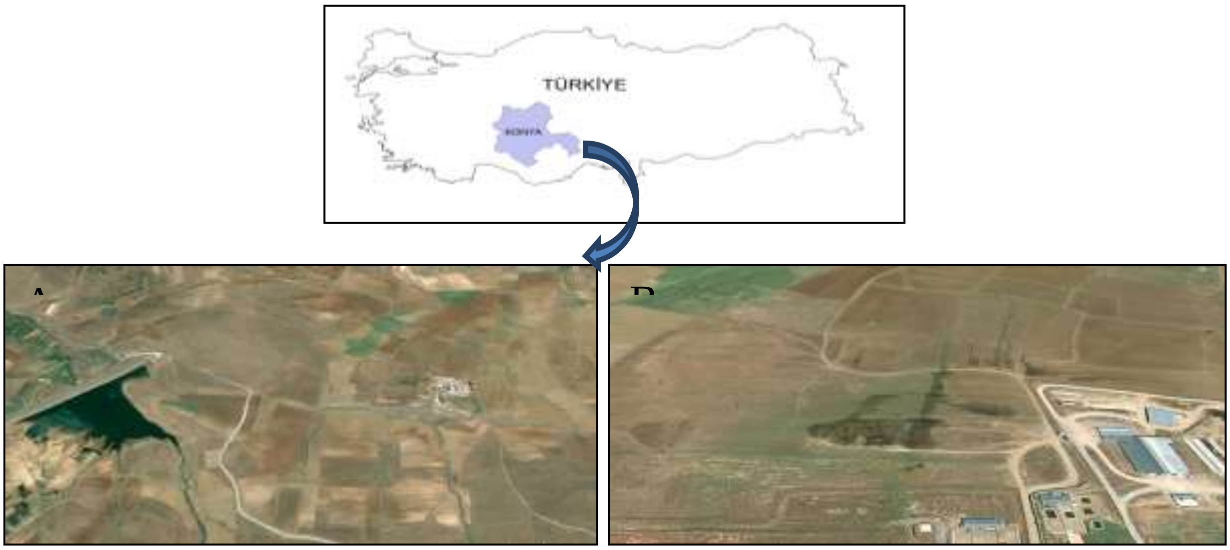

Fig. 1: Soil sampling area of around the dump site located near an old mercury mine site in Konya province of Turkey

3. Result and Discussion

The descriptive statistics of pH, EC, carbonate content, organic matter, particle size analysis, Zn, Cu, Mn, Fe, Ni, Co, Mo, Pb, As, Cd, Sb, Cr, Al and Hg levels (mg/kg) in these surface soils are summarized in Table 1. The pH of soils (*n* = 68) varied between 6.70 and 7.59 with a median value of 7.16. It is concluded that the pH of soils from the mining area is neutral. Electrical conductivity of soils varied between 54.8 and 294.0 (µS/cm) with a median value of 124.49 µS/cm. Particle size analysis (USDA classification system) indicates that majority of soils have sandy loam texture. The median carbonate content of the soils was (3.82%) .

Table 1. Descriptive statistics of pH, EC, particle size,organic matter,$CaCO_3$ and some element and heavy metal contents of reseach area soils (n=68)

Soil Properties	**Statistics**			
	Mean	**St.Deviation**	**Minimum**	**Maximum**
pH	7.16	0.20	6.70	7.59
EC(µS/cm)	124.49	60.99	54.80	294.00
$CaCO_3$(%)	3.82	4.55	0.91	21.85
Sand(%)	63.78	10.16	48.00	89.20
Loam(%)	24.93	10.66	4.00	41.20
Clay(%)	11.29	6.56	4.20	28.80
Org.Mat.(%)	2,89	0,21	0,22	8,39
Zn(mg/kg)	107.21	18.20	78.00	152.00
Cu(mg/kg)	52.86	19.64	19.60	109.70
Mn(mg/kg)	1132.6	419.1	491.0	2677.0
Fe (%)	4.59	1.32	2.28	7.71
Ni (mg/kg)	98.47	38.15	30.20	169.50
Co (mg/kg)	25.43	10.04	10.30	46.50
Mo (mg/kg)	1.39	0.77	0.60	3.40
Pb (mg/kg)	58.96	36.35	18.80	184.80
As (mg/kg)	74.16	76.17	21.00	382.00
Cd (mg/kg)	0.94	0.90	0.20	4.90
Sb (mg/kg)	492.6	669.3	8.8	3386.0
Cr (mg/kg)	160.78	78.26	50.00	333.00
Al (%)	7.61	1.19	4.50	9.15
Hg(mg/kg)	22.23	24.56	0.60	100.00

The total elemental data allowed us to elucidate the ranges of metal contamination in the area (Table 1). The observed median concentrations in the soils (*n* = 68) as determined by four-acid digestion were 107.21, 52.86, 1132.6, 4.59(%), 98.47, and 25.43 mg/kg, respectively for Zn, Cu, Mn, Fe, Ni, Co. Also other heavy metal concentrations were 1.39, 58.96, 74.16, 0.94, 492.6,160.78, 22.23 mg/kg and 7.61(%) respectively for

Mo, Pb, As, Cd, Sb, Cr, Hg and Al. Concentrations of all the metals ranged widely. The values are mostly within the usual range observed for similar kind of environmental settings [1].

Table 2. Correlation matrix for physico-chemical characteristics and total metal concentrations in soils *(n* = 68*)*

Soil Pro.	pH	EC	$CaCO_3$	O.M.	Sand	Clay	Silt	Cu	Fe	Zn	Mn	Pb
pH	1											
EC	0,155	1										
$CaCO_3$	0,293*	0,621**	1									
O.M.	-0.357**	0,277*	-0.102	1								
Sand	-0,031	-0,349**	-0,282*	-0.292*	1							
Clay	-0,360**	0,143	-0,100	0.159	-0,245*	1						
Silt	0,251*	0,244*	0,330**	0.180	-0,803**	-0,382**	1					
Cu	-0,146	-0,127	-0,164	0.045	-0,174	-0,153	0,260*	1				
Fe	-0,151	-0,580**	-0,521**	-0.105	0,208	-0,188	-0,082	0,508**	1			
Zn	0,097	0,101	-0,043	0.114	0,141	-0,131	-0,054	0,172	-0,050	1		
Mn	0,056	-0,135	-0,319**	0.084	0,162	-0,049	-0,124	0,373**	0,544**	0,391**	1	
Pb	0,223	0,434**	0,542**	0.105	-0,291*	0,049	0,247*	0,045	-0,524**	0,167	-0,283*	1
Ni	-0,070	-0,386**	-0,313**	-0.124	0,087	-0,304	0,104	0,802**	0,772**	-0,097	0,354**	-0,266*
Co	-0,176	-0,388**	-0,285*	-0.031	0,021	-0,253	0,135	0,777**	0,818**	-0,063	0,336**	-0,302*
As	0,325**	0,290*	0,306*	-0.074	-0,304*	0,234	0,146	0,044	-0,396**	0,001	-0,288*	0,796
Cd	0,228	0,355**	0,400**	0.021	-0,322**	0,101	0,245*	0,125	-0,414**	0,123	-0,279*	0,925**
Sb	0,262*	0,357**	0,395**	0.019	-0,353**	0,100	0,275*	0,088	-0,385**	0,065	-0,294*	0,907**
Cr	-0,190	-0,368**	-0,256*	-0.017	-0,010	-0,243*	0,159	0,759**	0,775**	-0,096	0,213	-0,263*
Al	-0,201	-0,530**	-0,757**	0.056	0,357**	0,063	-0,379**	0,033	0,605**	-0,035	0,490**	-0,645**
Hg	0,028	0,453	0,562**	0.161	-0,439**	-0,008	0,423**	0,429**	-0,290*	0,174	-0,078	0,612**
	Ni	**Co**	**As**	**Cd**	**Sb**	**Cr**	**Al**	**Hg**				
Co	0,935**	1										
As	-0,175	-0,194	1									
Cd	-0,158	-0,204	0,859**	1								
Sb	-0,156	-0,182	0,873**	0,977**	1							
Cr	0,915**	0,979**	-0,155	-0,170	-0,142	1						
Al	0,297*	0,268*	-0,531**	-0,517**	-0,506**	0,216	1					
Hg	0,088	0,045	0,369**	0,480**	0,427**	0,054	-0,716**	1				

** Correlation is significant at the 0.01 level; *aCorrelation is significant at the 0.05 level

To examine the statistical correlations between physico-chemical characteristics and total metal concentrations Fe,Zn,Mn,Pb,Ni,Co,As,Cd,Sb,Cr,Al and Hg in soils were calculated (Table 2). It was observed that pH, sand,loam and clay were not significantly correlated with these elements. But EC and calcium carbonate were significantly correlated with these elements ($P<0.01$ and $P<0.05$)except Zn and Cu. Cu,Fe,Pb,As,Cd,Sb,Al and Hg levels were significantly correlated with the same element levels.

4. Conclusions

The analysis result of soils took from abandoned mine area showed that soils have especially very high concentrations for Ni, Co, As, Cd and Hg. These values are very higher the limit values often reported by the Turkey Soil Pollution Control Regulations adopted. The soils have neutral, calcareous, low total organic matter.$CaCO_3$ contents and Fe, Mn, Pb, Ni, Cd, Sb, Al, Hg contents of soils were closely correlated ($P<0.01$) and also $CaCO_3$ contents and Co, As, Cr contents of soils were correlated ($P<0.05$).Besides Fe contents with Pb, Ni, Co, As, Cd, Sb, Al, Hg contents in soils were closely significantly correlated ($P<0.01$) .As contents with Cd, Sb, Al, Hg contents of soils were correlated ($P<0.01$).This study demonstrates that correlation matrix methods can provide important and useful tools for source apportionment of elements in polluted soils. Mercury has relatively higher levels in the study area. Considering the high levels of As, Sb, Cr and especially Hg, further research efforts should be addressed to enhance our understanding of processes controlling metal speciation and bioavailability in soils.

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