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Assessment of Toxic Trace Metals Emitted from Industrial Sources in East of Turkey

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In this study, four trace metals including nickel, copper, manganese and zinc and as a major element iron were determined in solid samples taken around industrial regions including thermoelectric power plant, copper mining plant, ferrochrome plant, cement factory and other probable polluting sources in east of Turkey. The solid samples were collected from 29 different points and trace metals were extracted from matrix by aqua regia by using wet ashing method. Trace metals were determined by flame atomic absorption spectrometry (FAAS). The metal concentrations in soils were found in ranging as mg/kg; 11-89 for Ni, 6-35 for Cu, 77- 893 for Mn, 58-122 for Zn and 10343-32226 for Fe and in industrial samples were found to be in ranges as mg/kg; 25-1942 for Ni, < detection limit (DL) of 4.5 ng/mL - >4000 for Cu, 22-768 for Mn, 14-6580 for Zn and 2300- >80000 for Fe.

Key Words: Toxic trace elements, Soils, Bottom and Fly ash, Power plants, Industrial pollution.

INTRODUCTION

Trace elements are commonly classified as essential or non-essential and toxic elements, depending on their effects on human health. Soil is the permanent source of most biologically active trace elements that reach human through plants and animals. Many of essential trace elements can be toxic if their concentrations exceed certain limits[1]. The levels of trace elements in soil largely depends on some factors such as pH, organic matter content, cation exchange capacity, chemical structure, calcium carbonate equivalent and microorganisms. Furthermore, levels of toxic elements such as As, Cd, Pb, Be, Hg and Ni in soils have been increased from day to day due do industrial and human activities. Waste discharges of metal processing plants, burning of fossil fuels, mining of ores, wood preservation and agricultural use of pesticides and fertilizers can contribute high concentrations

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in environment of toxic elements described above. In addition, coal fly ash, land disposal of sewage sludge and other industrial wastes may increase levels of toxic elements in soil. For instance, high amount of fly ash emitted from coal-fired power plants have riched in many toxic metals. Depending on the origin of coal, heavy metals have been released to environment in significant levels from power plants without filters. Finally, trace elements in soil have gradually raised because of salvation effects of acid rains on various environmental factors such as rock, mica and granite[2].

The metals including As, Cd, Be, Hg, Ni and Cr(VI) were classified as carcinogenic to human, according to information published by International Agency for Research on Cancer (IARC) and World Health Organization (WHO)[3,4].

The emissions of burned coals include bottom and fly ash. Remaining of trace and minor elements in bottom and fly ash highly depend on air/ coal rate, burning temperature as well as the kind of coal[5]. It has been reported that 70 % of elements in coals leave from bottom ash by flying. For instance, up to 70 % of As, Pb, Mn, Hg and Se could be removed in burning processing[6]. The more contents than expected levels of trace element in soil and other environmental samples were attributed to emissions of fly ash, which could be detected even at an 8 km distance from emission sources. In fact, it is suggested that the dust may be deposited on ground at distances ranging from several to hundreds of kilometers from the emission point[5].

In Turkey, the factories of cement and many other plants are generally near to end even in middle of the cities and so, large amounts of dusts and fumes are emitted from these factories. As a result, citizens living in these cities are directly exposed to toxic elements. Therefore, determination and evaluation of toxic metal levels in soils and other environmental samples have high importance because of very low allowable concentrations of some toxic metals.

Maximum allowable concentrations of toxic metals in agricultural soils were settled depending on pH of soil. In Turkey, these levels for pH = 6 and pH > 6 were described as mg/kg (dry basis) 30 and 75 for Ni, 50 and 140 for Cu and 150 and 300 for Zn, respectively[7]. However, the standards differ among different countries. For example, limits of Netherlands[8] are 300, 75 and 30 for Zn, Cu and Ni, respectively. The allowable metal concentrations in soil samples under grass are suggested as 330, 130 and 80 mg/kg for Zn, Cu and Ni, respectively[9]. On the other hand, the maximum permissible topsoil concentrations of Zn, Cu and Ni were reported to be 200, 50 and 50 mg/kg, respectively[9]. According to US EPA[8], limits of Zn, Cu and Ni in biosolids are 2800, 1500 and 420 mg/kg, respectively.

In this respect, analytical techniques with high sensitivity, sufficient reproducibility and accuracy are required for detection of these metals.

For this purpose, methods such as flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), anodic stripping voltametry (ASV), differential pulse polarography (DPP) and inductively coupled plasma mass spectrometry (ICP-MS) have been commonly used.

In laboratory, FAAS has been successfully used for the determination of very low levels (as low as 5 ng/mL) of various metals in different matrices such as soil, water, biological, food, fruit and vegetable samples[10-20].

In this study, trace and minor element levels in solid samples such as soil, coal, coal-bottom ashing of Elbistan Power Plant, slag of copper mining and the cement raw materials such as clay, gypsum and limestone taken from Elazig city in east of Turkey, were determined. Fort his purpose, the metals were extracted in aqua regia and element levels in clear solutions were determined by FAAS.

EXPERIMENTAL

An ATI UNICAM Model 929 flame atomic absorption spectrophotometer (FAAS), equipped with ATI UNICAM hollow cathode lamps and deuterium background correction, was used for the determination. The optimum conditions for FAAS are given Table-1.

TABLE-1
OPERATING PARAMETERS FOR FAAS

Parameters	Ni	Cu	Mn	Fe	Zn
Wavelength (nm)	232.0	324.8	279.5	248.3	213.9
HCl current (mA)	7.5	3.0	11.5	15.0	9.5
Slit width (nm)	0.2	0.5	0.2	0.2	0.5
C_2H_2 flow rate (L/min)	0.5	0.5	0.5	0.5	0.5
Air flow rate (L/min)	4.0	4.0	4.0	4.0	4.0

Unless stated otherwise, all chemicals (Merck) used were of analytical-reagent grade. Throughout all analytical work, double distilled water was used. All Pyrex glassware was kept permanently full of 1 M nitric acid when not in use. In digestion works, aqua regia was used. For each element, stock solution of 1000 mg/L of metal was prepared by dissolution of their salts in 1 M of HNO_3.

Collection and preparation of samples: Four sites were selected from major industrial areas in the east of Turkey. These areas are Elbistan thermoelectric power plant, plant of Maden copper mining at 70 km distance from Elazig city (in the south-east), ferrochrome plant at 70 km distance from Elazig (in the east) and cement factory in middle of Elazig city and surrounding of Hazar lake in Elazig in the east of Turkey.

The soil samples were collected from the areas that were thought to be contaminated by the industrial resources mentioned above. The soils samples were taken with the sampling at a depth of about 10 cm below the surface. Then, about 1 kg of soil was put into a PET container and transferred into laboratory. Soils and industrial residues samples were dried at 100 ºC in an oven and subsequently grinded in a porcelain mortar and sieved from 100 mesh (Tylor). Thus, the grain size of the samples prepared for analysis was less than 1 mm.

Digestion procedure: 0.200 g of dried samples were placed into a Pyrex flask and digested by adding 2 mL of aqua regia. The mixture was heated by occasionally stirring on a hot plate near to dryness. This process was repeated. Finally, the residue was dissolved in 4 mL of 2 M nitric acid. After centrifugitation, the clear solution was analyzed by FAAS. A blank digest was carried out in the same way.

RESULTS AND DISCUSSION

The effect of the matrix components on the determination of the studied elements by FAAS was investigated. In order to overcome the probable enhancement or suppression due to the presence of other matrix components, the calibrations were performed within the sample matrix itself. The solutions for calibration graphs were contained matrix components at the following concentrations (as mg/L); Ca^{2+}: 1000, Mg^{2+}: 500, Al^{3+}: 100, Cl^- and SO_4^{2-} : 200 and PO_4^{3-}: 100.

The accuracy of the method was studied by examining the recovery of the metals from solid samples fortified with various amounts of the studied elements. The following metal amounts were added: 10 mg/kg of Ni, 2 mg/kg of Cu, 5 mg/kg of Zn, 100 mg/kg of Fe and 5 mg/kg of Mn. After digestion as mentioned above, the recoveries were found to be at least 90 % for all studied metals.

The possibility of sample contamination was examined by subtracting the values obtained for blanks. Adsorption losses can be excluded as the procedure was followed in exactly the same way, using the same glassware and the same reagents throughout the work. The results showed that there was no contamination or adsorption loss at the studied conditions.

Levels of the metals including Ni, Cu, Zn, Fe and Mn in the reagent blanks in total analytical steps were found to be 25; 10; 50; 50 and 50 ng/mL with standard deviations of 3.0; 1.5; 6.0; 5.0 and 7, respectively. Therefore, the detection limits for these elements, defined as three times the s values of blanks were calculated as 9; 4.5; 18; 15 and 21 ng/mL. As related with precision, the standard deviations for 10 replications of the same solid samples were found to be less than 10 % for all studied elements.

Calibration curves were obtained by using solutions of the studied elements at different concentrations. The graphs obtained were linear in the concentration range and the equations of the curves are described as follow:

$Y = 72.0X + 1.5$ $R^2 = 0.999$ for Ni^{2+} (0.25-5 mg/L)
$Y = 97.1X + 6.0$ $R^2 = 0.997$ for Cu^{2+} (0.25-5 mg/L)
$Y = 57.3X + 3.7$ $R^2 = 0.997$ for Fe^{3+} (0.25-5 mg/L)
$Y = 123.3X + 3.3$ $R^2 = 0.997$ for Mn^{2+} (0.25-5 mg/L)
$Y = 243.6X + 4.2$ $R^2 = 0.998$ for Zn^{2+} (0.05-2 mg/L)

Trace elements concentrations in the studied solid samples: From the Table-2, Ni concentrations in solid samples were found (as mg/kg) in range of 25-110 for the samples around ETPP (sample no; 1-4), 98-257 for the samples around MCMP (sample no; 5-8), 21-1942 for the samples around FF (sample no; 9-11), BDL-163 for the samples around cement (sample no; 12-20) and 37-111 for the soil samples (sample no; 21-27) taken from different points.

Cu concentrations in solid samples were found (as mg/kg) in range of 6-23 for the samples around ETPP, 770- >4000 for the samples around MCMP, BDL-6.5 for the samples around FF, BDL-17 for the samples around cement and 6-35 for the soil samples taken from different points.

Mn concentrations in solid samples were found (as mg/kg) in range of 50-173 for the samples around ETPP, 49-666 for the samples around MCMP, 22-768 for the samples around FF, 22-462 for the samples around cement and 77-893 for the soil samples taken from different points. Yaman *et al.*[10] reported Mn concentrations in agricultural soils in same region in range of 360-1100 mg/kg.

Fe concentrations in solid samples were found (as mg/kg) in range of 8515-37367 for the samples around ETPP, 2300- >80000 for the samples around MCMP, 2635-550 for the samples around FF, 2806-25926 for the samples around cement and 10343-32226 for the soil samples taken from different points.

Zn concentrations in solid samples were found (as mg/kg) in range of 57-96 for the samples around ETPP, 404-6580 for the samples around MCMP, 20-362 for the samples around FF, 14-180 for the samples around cement and 58-122 for the soil samples taken from different points. Yaman *et al.*[13] reported Zn concentrations in agricultural soils in same region in range of 31-100 mg/kg.

It was shown that a portion of trace elements in coal may be released as a part of dust in flue gas[5].

In the literature, the concentrations of trace elements vary remarkably in soils. The concentrations of Zn, Cu and Ni in worldwide soils are 10-300, 20 (mean) and 40 (mean) mg/kg, respectively. The concentrations of Zn, TABLE-2

OBSERVED ELEMENT CONCENTRATIONS (mg/kg) IN VARIOUS SOLID SAMPLES (THE RESULTS ARE THE MEAN VALUES ± STANDARD DEVIATION; n = 3)

No	Sample	Ni	Cu	Mn	Fe	Zn
1	Dusts suspended on ETPP internal walls	55 ± 18	7 ± 2	83 ± 33	18317 ± 898	96 ± 37
2	Slage of ETPP	110 ± 21	23 ± 7	173 ± 13	37367 ± 3950	83 ± 25
3	Dusts outward ETPP	60 ± 11	6 ± 1	136 ± 7	19622 ± 840	57 ± 16
4	Lignite coal used in the ETPP	25 ± 1.4	14 ± 2	50 ± 2	8515 ± 452	74 ± 25
5	Grinded crude mineral used in MCMP	235 ± 4	770 ± 105	312 ± 14	5200 ± 350	406 ± 120
6	The Residue water*of MCMP	252 ± 33	> 4000	49 ± 1	> 80000	6580 ± 62
7	Chimney of MCMP	98 ± 9	1703 ± 96	366 ± 31	2700	1115 ± 27
8	Dusts suspended inside MCMP	257 ± 18	3195 ± 41	666 ± 26	2300	404 ± 16
9	Chromite ore	848 ± 38	BDL	100 ± 7	5550 ± 37	20 ± 2
10	Slag in FF	21 ± 3	BDL	365 ± 9	2635 ± 213	362 ± 17
11	Ferrochromium	1942 ± 45	BDL	768 ± 18	3365 ± 418	28 ± 2
12	Native gypsum for CF (plaster stone)	46 ± 9	6.5 ± 2.2	22 ± 5	2806 ± 285	14 ± 4
13	Limestone	BDL	BDL	201 ± 10	4664 ± 246	27 ± 4
14	Dusts around CF	69 ± 24	17 ± 2	376 ± 20	22583 ± 615	180 ± 34
15	Alloyed cement	48 ± 3	BDL	424 ± 11	25926 ± 1863	61 ± 2
16	Cement clay	163 ± 15	BDL	462 ± 8	21237 ± 2545	80 ± 5
17	Cement	73 ± 2	BDL	327 ± 7	19053 ± 1168	49 ± 2
18	Turla tras	51 ± 6	BDL	794 ± 84	37285 ± 2845	67 ± 7
19	Karatas tras	81 ± 17	BDL	842 ± 6	30058 ± 1163	49 ± 3
20	Kizlartasi tras	87 ± 17	BDL	702 ± 120	39956 ± 1573	67 ± 7
21	Soil of agricultural field near ETPP-1	89 ± 11	35 ± 4.0	562 ± 65	17100 ± 1440	76 ± 28
22	Soil near slag of ETPP-2	73 ± 4	32 ± 4.0	77 ± 2	10343 ± 474	112 ± 4
23	Agricultural soil near FP-3	111 ± 2	21 ± 2.0	780 ± 32	22057 ± 1030	94 ± 28
24	Soil (near Hazar lake)-4	80 ± 10	14 ± 2.0	754 ± 40	25706 ± 3080	122 ± 38
25	Soil (turpol)-5	78 ± 21	29 ± 2.0	797 ± 32	32226 ± 1250	102 ± 4
26	Soil-6	37 ± 12	6 ± 0.4	404 ± 28	21138 ± 6851	58 ± 14
27	Soil of beet field-7	56 ± 14	33 ± 5.0	893 ± 90	11215 ± 1305	118 ± 9

ETPP: Elbistan Thermoelectric Power Plant, MCMP: Maden Copper Mining Plant, FF: Ferrochromium Factory, BDL: Below detection of limit, CF: Cement Factory, *This water runs down to Tigris river.

Cu and Ni in metal-rich soils are >1 %, >2000 mg/kg and 800-8000 mg/kg, respectively[21]. The content of Cu in rural soils is in range of 2 to 100 mg/kg and natural levels of Zn in soils are reported in range of 30-150 mg/kg[22]. The concentrations of Cu, Ni and Zn in igneous and sedimentary rocks are in range of 2-160, 0.2-410 and 2-240 mg/kg, respectively[8].

Jing *et al.*[21] reported Cu concentrations over 5000 mg/kg in mine soils and over 500 mg/kg in a soil used for disposing tail wastes from nearby a refinery. Gritsand and Babiy[23] determined 30, 22000, 10, 20 and 30 mg/kg for Mn, Fe, Ni, Cu and Zn, respectively, in the Ukraine soils. Meness *et al.*[24] reported 423, 17 and 98 mg/kg Mn, Ni and Zn, in soil samples, respectively. Mielke[25] determined 11.1, 164, 3.9 and 3.9 mg/kg in Spillway samples and 130, 138, 3.8 and 12.7 mg /kg for Zn, Mn, Ni and Cu in urban soils, respectively. Llobet *et al.*[26] determined 224 and 8.7 mg/kg Mn and Ni in soil samples, respectively. Götzl and Riepe[27] reported 1000-16700, 30-250 and 15 mg/L Zn, Cu and Ni in Galvanic sludge samples and 250-2800, 3-70 and 50-350 mg/L Zn, Cu and Ni in Filter cake samples, respectively. Ovari and co-workers[28] measured 18.9 and 16.4 g/kg Fe and Ni in flying ash emitted by Szazhalombatta power station. According to information published by the USA Clean Air Act Amendment of 199029, the concentrations of Cu, Mn, Ni and Zn in Australian Export Coals are in range of 6-27, 5-700, 4-23 and 3-26 mg/kg, in other Internationally Traded Coals are < 1-23, 7-117, 2-22 and 4-23 mg/kg, in Earth's Crust are 55, 950, 75 and 70 and in Earth's Shales are 50, 850, 70 and 100 mg/kg, respectively.

It can be seen that Ni level in soils is higher compared to global average values[8,9,21-24,26-29]. However, the concentrations of Cu, Mn, Zn and Fe in the soil samples are similar to global averages[8,9,21-29].

Conclusion

In conclusion, it could be seen that levels of Cu, Mn, Zn and Fe in soils are near to global averages, but levels of nickel in soils are higher than allowable levels. On the other hand, the analysis results of the industrial samples show variations in very wide ranges.

The results confirm that toxic metal accumulation in industrial residues and nickel level in soils beyond acceptable safe limits. High level of environmental pollution is the result of various economic and human activities.

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