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A Study of Soil Heavy Metal Pollution in the Manganese Mining in Drama, Greece

A. Argiri, A. Molla, Tzouvalekas, E. Skoufogianni, N. Danalatos

***Abstract*—**The release of heavy metals into the environment has increased over the last years. In this study, 25 soil samples (0-15 cm) from the fields near the mining area in Drama region were selected. The samples were analyzed in the laboratory for their physicochemical properties and for seven "pseudo-total'' heavy metals content, namely Pb, Zn, Cd, Cr, Cu, Ni, and Mn. The total metal concentrations (Pb, Zn, Cd, Cr, Cu, Ni and Mn) in digests were determined by using the atomic absorption spectrophotometer. According to the results, the mean concentration of the listed heavy metals in 25 soil samples are Cd 1.1 mg/kg, Cr 15 mg/kg, Cu 21.7 mg/kg, Ni 30.1 mg/kg, Pd 50.8 mg/kg, Zn 99.5 mg/kg and Mn 815.3 mg/kg. The results show that the heavy metals remain in the soil even if the mining closed many years ago.

***Keywords*—**Greece, heavy metals, mining, pollution.

I. Introduction

POLLUTION of agricultural soils by heavy metals has become a global problem [1]. Soil contamination with heavy metals is caused by human activities such as metal mining and smelting, fuel combustion, industrial and energy production, waste disposal, military activities, or agricultural application of pesticides, fertilizers, and sewage sludge [2], [3].

Because soils cannot be renewed and heavy metals are not biodegradated but accumulate in soils, the control of heavy metal concentrations is essential, in case it will be needed to prevent the contamination and for that remediation suggestions should be proposed [4].

The Drama district, during the period 1950-1994, has been the biggest Mn mine in Greece, with more than 7 Mt total ore concentrate production of Mn-oxides at the "25 km Mn-mine" ($41^0$15' 19''N, $23^0$58' 23''E) [5].

Even after the cessation of the mining works, α large amount of the mine wastes are usually found in agricultural soils which are located near the mining areas as pollutants. The accumulation of heavy metals in these areas can affect negatively not only the human health but also the production of agricultural products (reduced production, reduced food safety) [6], [7].

There are only few reports on the distribution of heavy metals in soils in the Drama district, northern Greece, where there are abandoned manganese mines [5], [7]. Thus, the purpose of this study was: (1) to determine the actual total concentration of Cd, Cr, Ni, Zn, Pb, Cu, Mn, in soils around the Drama area and (2) to assess the spatial distribution of metals.

Aikaterini Molla is with the University of Thessaly, Greece (e-mail: katerinamol38@gmail.com).

II. Materials and Methods

The studied areas are located approximately 33 km (Panaroma village) and 24 km (Grammeni village) from Drama city, Greece.

Fig. 1 The study area

From the two areas 25 soil samples, 12 from the Panorama agricultural area and 13 from the Grammeni area, were collected. The soil samples were taken from a depth of 0-15 cm from the soil surface using a steel sampler. With a Hand GPS the coordinates (latitude, longitude) were taken for every soil sample. Then, using the ArcGIS program, digital maps were made showing the concentrations of heavy metals.

Soil samples were air-dried and sieved through a 2-mm sieve. Each soil sample received a unique code.

The below physicochemical properties were analyzed: pH (1:2.5 H_2O), $CaCO_3$ (Bernard densitometer), electrical conductivity (1:1 H_2O), particle size distribution (Bouyoucos hydrometer), and organic matter (Walkley – Black wet oxidation). Also, the samples were analyzed for their "pseudo-total'' heavy metals content (Cr, Cu, Cd, Zn, Pb, Ni, Mn) by *aqua regia* (digestion at 140 ^oC for 5 hours with 3:1 concentrated HCl: HNO_3). For the measurement was used the atomic absorption spectrophotometer.

The results were analyzed by LSD test with significance 95% ($p < 0.05$) using Statgraphics plus 8.1.

III. Results and Discussion

Data on soil physicochemical properties are presented in Tables I and II for the two studied areas.

According to Table I, pH ranges between 7.6-8.3, EC between 83-328 μS/cm, $CACO_3$ between 1-29% and organic matter between 0.9-3.04%.

According to Table II, pH ranges between 7.9-8.1, EC between 109-515 μS/cm, $CACO_3$ between 28-47% and

organic matter between 0.8-5.9%.

TABLE I
PHYSICOCHEMICAL PROPERTIES OF COLLECTED SOILS IN PANORAMA AREA

	pH	Electrical conductivity (μS/cm)	$CACO_3$ %	Organic matter %	Particle size distribution
1	8,1	229	18	1,47	SCL
2	7,7	320	2	3,04	CL
3	7,6	328	1,5	2,33	CL
4	7,6	201	2	2,78	SCL
5	8,2	194	8	1,82	SCL
6	8,1	275	15	1,45	SCL
7	7,7	270	2,0	1,22	SCL
8	7,7	173	1,0	1,3	SL
9	8,3	83	9,5	0,9	SL
10	8	165	17	1,8	CL
11	8,1	260	17	2,8	SCL
12	8	205	29	2,4	SCL

TABLE II
PHYSICOCHEMICAL PROPERTIES OF COLLECTED SOILS IN GRAMMENI AREA

	pH	Electrical conductivity (μS/cm)	$CACO_3$ %	Organic matter %	Particle size distribution
1	8,2	109,0	47,0	0,8	SL/SCL
2	7,9	279,0	25,0	5,9	SCL
3	8,1	287,0	28,0	4,2	CL
4	8	329	28	3,88	CL
5	7,8	318,0	43,0	5,6	SCL
6	8,2	234,0	43,0	2,7	SCL
7	8,1	235	54	1,8	SCL
8	7,9	515,0	23,0	3,2	SCL
9	8,0	391,0	24,0	3,0	C
10	8,0	304,0	31	4,10	C
11	7,9	330,0	34,0	4,6	C
12	8,1	350,0	38,0	3,8	CL
13	8,0	296,0	42,0	3,5	CL

TABLE III
HEAVY METALS CONCENTRATION OF COLLECTED SOILS IN PANORAMA AREA

	Cd	Cr	Cu	Ni	Pd	Zn	Mn
2	1,2	11,1	21,4	32,7	42,7	95,6	776,0
3	1,4	25,3	24,3	37,4	59,3	121,9	946,0
4	1,1	23,2	24,1	36,8	53,4	109,1	894,0
5	1,0	17,2	19,4	26,1	38,4	81,7	902,0
6	1,4	22,4	22,5	35,0	67,5	116,2	936,0
7	1,4	21,4	23,8	32,6	53,1	104,5	885,0
8	1,1	19,1	23,3	27,1	41,7	86,2	869,0
9	0,6	6,4	18,1	7,2	66,7	52,8	560,0
10	0,6	2,2	16,4	8,3	86,6	51,6	546,0
11	1,1	4,8	19,4	29,0	51,3	78,5	780,0
12	0,7	3,9	21,7	31,4	47,9	82,7	765,0

According to Table III, total Cd concentration ranges between 0.6-1.4 ppm, total Cr between 3.9-25.3 ppm, total Cu between 16.4-24.3 ppm, total Ni between 7.2-37.4 ppm, total Pd between 41.7-86.6 ppm, total Zn between 51.6-121.9 ppm and total Mn between 546-946 ppm.

According to Table IV, total Cd concentration ranges between 0.3-1.8 ppm, total Cr between 4.3-25.7 ppm, total Cu between 7.9-32.9 ppm, total Ni between 13-47.9 ppm, total Pd between 19.3-70.4 ppm, total Zn between 78-169.8 ppm and total Mn between 321-1281 ppm.

TABLE IV
HEAVY METALS CONCENTRATION OF COLLECTED SOILS IN GRAMMENI AREA

	Cd	Cr	Cu	Ni	Pd	Zn	Mn
1	0,8	4,3	13,7	13,0	28,2	55,7	321,0
2	1,8	14,0	32,9	35,2	54,0	157,3	941,0
3	2,2	19,8	25,4	46,5	64,1	164,5	1281,0
4	2,0	18,6	7,9	47,9	70,4	169,8	1253,0
5	1,4	13,2	25,7	34,0	58,5	120,4	833,0
6	0,7	10,9	18,0	28,4	31,8	80,3	623,0
7	0,3	7,9	15,6	20,8	19,3	54,2	351,0
8	0,5	25,7	29,6	37,5	49,8	131,3	782,0
9	0,3	18,0	29,2	35,0	48,4	116,0	977,0
10	0,8	17,1	27,4	26,8	45,6	78,0	920,0
11	1,0	11,6	26,1	30,2	50,3	87,2	800,0
12	1,2	19,0	17,7	33,1	39,3	95,1	820,0
13	0,6	21,2	18,3	36,0	49,0	105,4	845,0

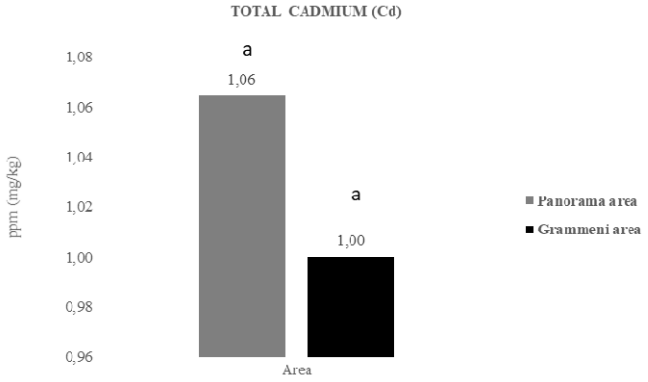

Fig. 2 Average Total Cd concentration (mg/kg) in two studied areas

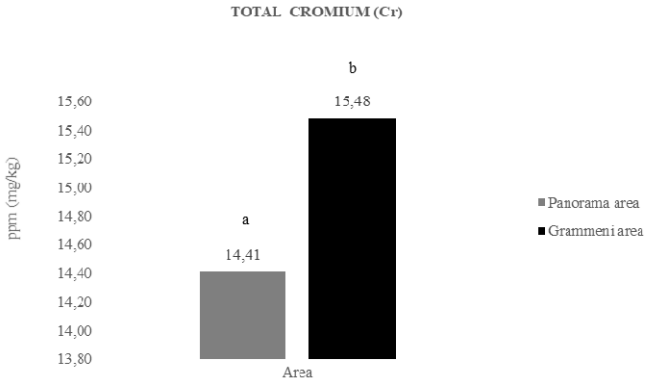

Fig. 3 Average Total Cr concentration (mg/kg) in two studied areas

According to Figs. 2-8 between the two studied areas (Panorama and Grammeni) there is statistically significant difference in the case of total chromium, copper, nickel lead, zinc, manganese concentration but not statistically significant difference in the case of total cadmium.

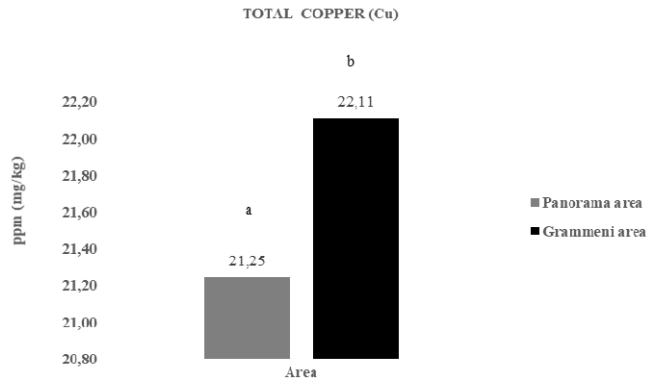

Fig. 4 Average Total Cu concentration (mg/kg) in two studied areas

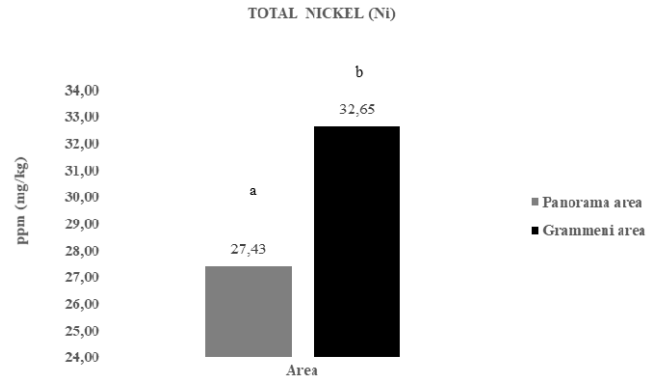

Fig. 5 Average Total Ni concentration (mg/kg) in two studied areas

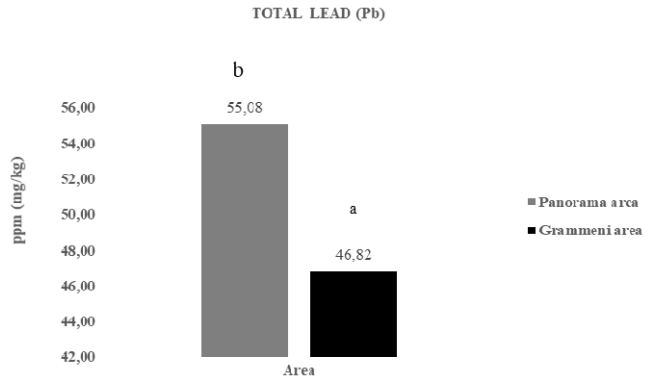

Fig. 6 Average Total Pb concentration (mg/kg) in two studied areas

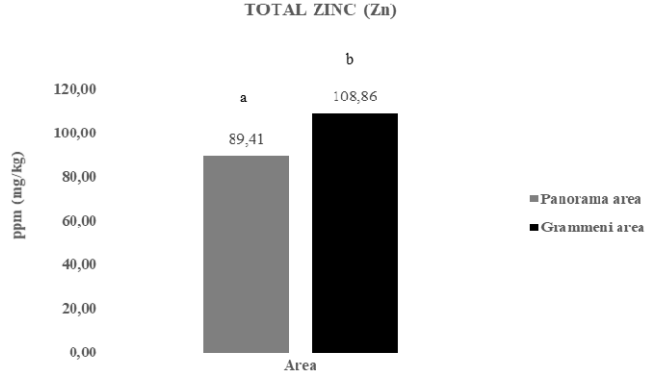

Fig. 7 Average Total Zn concentration (mg/kg) in two studied areas

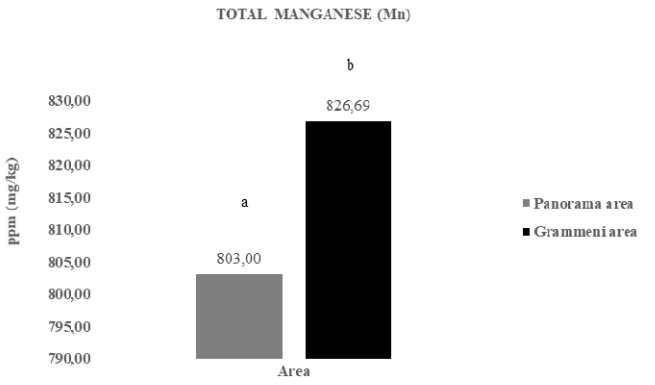

Fig. 8 Average Total Mn concentration (mg/kg) in two studied areas

The *aqua regia* extracted cadmium and lead concentrations are higher in Panorama area. While the total chromium, copper, nickel, zinc and manganese concentrations are higher in Grammeni area. Also, in this study, it was measured the contamination factor (CF) which is calculated as: $CF = C_S / C_{RefS}$ where: C_S is *aqua regia* extracted metal concentrations (mg kg^{-1} soil) and C_{RefS} is background reference element concentration in uncontaminated areas (mg kg^{-1}) [8].

The level of soil contamination can be classified as follows: low ($CF < 1$), moderate ($1 \leq CF < 3$), significant ($3 \leq CF < 6$) and very high ($CF \geq 6$) [8].

The results of the contamination factor measurement appear in Table V.

TABLE V
HEAVY METALS CONTAMINATION FACTOR (CF) OF THE STUDIED AREAS

	Cd	Cr	Cu	Ni	Pb	Zn
Panorama	1.06	7.21	0.42	0.91	1.38	0.60
Grammeni	1.00	7.74	0.44	1.09	1.17	0.73

The highest CF was observed for Cr both in two areas. According to the classification of the contamination factor, in Panorama area cadmium and lead are classified in moderate level, copper, nickel and zinc in low level and chromium in very high level. In Grammeni area copper and zinc to the low class, cadmium, nickel and lead belong to the moderate class and cadmium to the very high class.

The pollution load index (PLI) allows the levels of soil contamination to be compared between different locations. PLI is the coefficient of concentration of each metal ion in relation to the reference value of the metal in uncontaminated soil. PLI is applied by: PLI = (CF1 X CF2 X CF3 X ... x CFn) (1 / n) where n, the number of studied metals. If PLI < 1 the soil is unpolluted, if 1 < PLI < 2 the soil is moderately polluted. if 2 < PLI < 10 the soil is strongly polluted, if PLI > 10 the soil is extremely polluted [9].

TABLE VI
POLLUTION LOAD INDEX AND RISK INDEX VALUE OF HEAVY METALS IN STUDIED REGIONS

Area	PLI
Panorama	1.564
Grammeni	1.779

Although both regions belong to the second class of PLI (moderately polluted), the Grammeni area is more contaminated according to the results in Table VI.

IV. Conclusion

In the present investigation, heavy metal concentrations of Cr, Zn, Cu, Ni, and Mn are higher in Grammeni area and the concentrations of Pb and Cd are higher in Panorama area. The concentration of chromium is very high in both areas.

The PLI values of metals in the studied areas confirm that the two areas are moderately polluted ($1 < PLI < 2$).

More investigations should be done in Drama region where the manganese mines and rehabilitation suggestions must be proposed.

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