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Verification of Penetration of Lead in the Profile of Soil around the Former Battery Production Factory, Berat Albania

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Abstract

The current study reports the concentration of lead in top of the soil samples and its penetration until the depth of approximately 120 cm. Representative soil samples are collected around the former Factory Production of Batteries to Berat, Albania at a distance 80 - 900 m from factory. We have chosen 12 sampling points. We have collected a total of 55 samples where 31 were soil samples (12 top of soil and 19 were profile soil samples) and 24 were random vegetation samples. All soil samples were analyzed using Atomic Absorption Spectrometry for their lead content, at the Institute of Applied Nuclear Physics, University of Tirana, Albania. From results obtained the fraction of lead in profile soil samples was in range: 78 mg/kg - 52,982 mg/kg and average concentration of lead was 2976 mg/kg, while in random vegetation samples was in range: 0.238 - 5.573 mg/kg. In general, trend of the content of lead in profile soil samples was decreasing compared to the content of lead in the respective top soil samples. The concentrations of lead which have been found in analyzed soil samples are compared with the Maximum Contaminant Levels specified by the Directive 86/278/EEC. Also, we have calculated Hazardous Quoted for each sampling point which is found very high. HQ in representative surface soil samples is 0.4 - 80.7 times higher than normal.

Keywords

Lead, Top and Profile Soil Samples, Atomic Absorption Spectrometry

1. Introduction

The presence of heavy metals in environment is dangerous because they have tendency to bioaccumulate [1].

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Also, heavy metals reach the food chain through the supply of drinking water, respiration and food consumption [2] [3]. In addition, lead is known as one of the most toxic heavy metals; it is inclined and tends to be accumulated in the environment [4]. The high level of lead has a negative impact on the natural environment and the human health. The sources of emission of lead in the environment are natural and anthropogenic [5]. Over the years lead is extracted from the mines for different purposes, such as: production of batteries, half-done production of metallic sheets and pipes, alloys, additive in benzene, in polyvinyl chloride, in ammunitions [6]. Since lead is mostly used for the production of batteries, the major pollution comes exactly from this industry. The exposure to lead in the environment results in a wide range of negative effects, depending from the level of lead and time of extended. The high levels of exposure to Pb result in biochemical and toxic effects on the people [7]. The environmental protection should be and remain the main goal and task of the society. The purpose of this study is: a) Estimate and impact of the industrial waste of lead in the profile of soil around the territory of the former Factory of Battery Production, Berat, Albania and b) determination of lead in random vegetation as well as calculation of determinate bioaccumulation factor soil to plant. This factory has begun its activity in 1970 (about 20 years) and it was designed to produce batteries for passengers' cars and trucks and technical equipment. One of the methods for determination of the total contents of heavy metals of their environmental concentrations is AAS. In this paper we present determination of lead in soil by AAS method. The level of Pb in soil samples was compared to the values recommended by the European Community according to Directive 86/278 EEC and the potential of risk HQ was calculated by USEPA, while for biological samples level of lead was compared by Directive No. 1881/2006, Brussels [8]-[10]. We have calculated the bioaccumulation factor soil to plant.

2. Material and Method

All representative soil samples are collected into and around the former Battery Production Factory, Berat. This Factory is located in the northeastern city of Berat, with respective coordinate: 400˚42'24.82"N and 190˚58'59.42"E. During the sampling we have chosen 12 stations and we have collected a total 31 samples where 19 were profile soil samples in this region. Representative soil samples are collected at the top of soil (0 - 5 cm) while profile soil sample are collected in depth 15 - 120 cm. These sampling stations are marked in map **Figure 1**, while their coordinates are presented respectively in **Table 1** with results. All soil samples are analyzed using Atomic Absorption Spectrometer, Aanalyst 800 Perkin Elmer with Atomic Absorption Spectrometry, Flame method PE [11]. Hollow cathode lamp used as radiation source for the determination of Pb according recommended conditions. Acids used for the digestion of samples, stock solutions of lead have high grade purity. Glass and Teflon vessels used were treated with solution 10% v/v nitric acid, for 24 hours and then washed with water bidistilled. Instrumental conditions for lead are based on AMAAS, from PE [11]. Three applications were carried out for the measurement of calibration standards and measurement of samples. For each element calibration curve equation is linear and passing through point zero. A quality control material IAEA-Soil_7 was analyzed in parallel with the soil samples and IAEA_336 Lichen was analyzed in parallel with the biological samples. To check the instrumental drift, an aqueous standard solution was analyzed after every three samples.
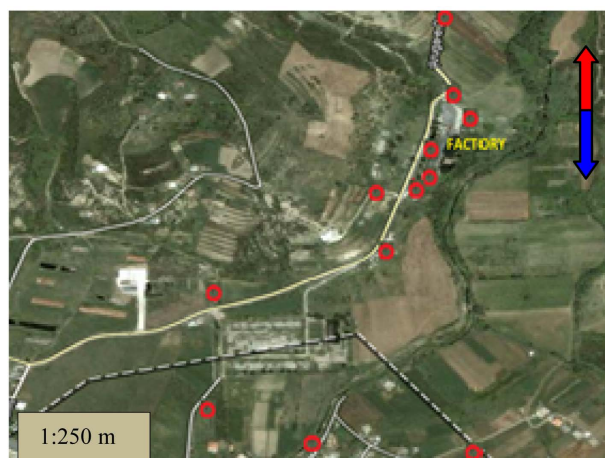
Figure 1. Map of sampling stations of soil.

Table 1. The concnetration of lead in both CRM soil and vegetation.

Element	Type of CRM	Value of CRM mg/kg	Pb mg/kg	SD	RSD%	Recovery%
Pb	IAEA-Soil-7	60 ± 8	56.8	2.8	5.7	94.9
Pb	IAEA_336_Lichen	4.9 ± 0.6	4.1	0.23	8.97	83.7

Note: (n = 3).

2.1. Digestion of Soil Samples

About 0.5 gram of dry soil sample was placed in a digestion tube and was added 10 ml of aqua regia (1 HNO_3: 3 HCl). The sample was heated for 30 - 35 min at 90˚C, and then the temperature was increased to 180˚C at which the sample was boiled for at least 2 - 3 hour until a clear solution was obtained. Concentrated HNO_3 was added to the sample, 9 ml was added at least three times and digestion occurred until the volume was reduced to about 1 - 2 ml. The interior walls of the tube were washed down with a little bidistilled water and the tube was swirled throughout the digestion to keep the wall clean and prevent the loss of the sample. After cooling, 5 ml of 2% HNO_3 was added to the sample. It was then transferred quantitatively to a 50 ml volumetric flask by adding distilled water. And finally the solution was filtered.

2.2. Digestion of Biological Samples

Each dry vegetation sample was weighed and was added a 10 ml HNO_3 solution. For the wet digestion process, an 8 hour period of digestion was provided at room temperature. After this time cold digestion period, the glass beakers were placed on a hot plate and heated for about 1 - 2 hour. Then, 1ml hydrogen peroxide (H_2O_2) was added to each beaker and the beakers were heated again until the wet digestion process was completed and a small sample volume remained. It was then transferred quantitatively to a 50 ml volumetric flask by adding distilled water. And finally the solution was filtered; their solutions were transferred to the atomic absorption lab for analysis.

3. Results and Discussions

For the accuracy of the analytical procedure for the determination of lead in environmental representative soil and vegetation samples are using certified reference material. Specifically for soil samples was used IAEA Soil-7, while for vegetation samples was used 336 IAEA. Standard reference material samples were attended the same digestion procedure with the nature of the respective sample group. In **Table 1** is presented the results obtainned form analyzed CRM for content of lead in soil and vegetation, SD, % RSD and % R. In **Table 2** is presented, sampling points, code in AAS, coordinates, mean concentration of lead in soil samples, % RSD and SD in representative top and profile soil samples. In addition, from results obtained of soil samples we have calculated HQ (US EPA 2006) [10] for representative surface soil samples. In **Table 3** is presented, sampling points, code in AAS, coordinates, mean concentration of lead in vegetation samples, SD and calculated bioaccumulation factor soil to plant in representative top soil samples. From results obtained it was observed the concentration of lead there is not unique distribution. The highest concentration of lead was found in samples which are collected in S_1 and S_14 points. By analyzing profile samples in these points the lead concentration was higher than surface. These sampling points have been selected close the factory, because in this area there are industrial solid waste thrown uncontrollably, into the environment. The Concentration of lead in the top of soil was found in the order 78 mg/kg - 24,207 mg/kg and average concentration of lead was 3523 mg/kg. While the concentration of lead in profile soil samples was found in this ranged 125 mg/kg - 52,982 mg/kg and average concentration of lead was 5614 mg/kg. The concentrations of lead in representative soil samples are compared with the MCL specified by the Directive 86/278/EEC. Maximal concentration of lead in soil recommended by the Directive 86/278/EEC is 300 (mg/kg) and was calculated HQ by USEPA. Factor of HQ was found in order 0.3 - 81. If the calculated factor of HQ in soil samples is higher than 1, than the territory is contaminated and this pollution is associated with high negative ecological and human effects. In vegetation samples the concentration of lead was found in this ranged: 0.238 - 5.573 mg/kg. The presence of lead in biological samples is high. Level of lead in vegetation samples are compared with the MCL specified by the Directive No. 1881/2006, Brussels. The dates of **Table 2** & **Table 3** are presented in the graphical forms as below. Graph in **Figure 2** is presented the

Table 2. Mean concentration of lead in the both top and profile soil samples.

Nr.	Sampling point	Code in AAS	Material	Nord	East	Pb (mg/kg)	SD	% RSD
1	S_1	P1 T1	Surface soil	40˚42'21.32"	19˚58'56.74"	3008	33.09	1.10
2	S_1	P1 T2	Profile	40˚42'21.32"	19˚58'56.74"	3052	82.41	2.70
3	S_2	P2 T1	Surface	40˚42'21.61"	19˚58'57.63"	5663	7.36	0.13
4	S_2	P2 T2	Profile	40˚42'21.61"	19˚58'57.63"	4789	76.62	1.60
5	S_2	P2 T3	Profile	40˚42'21.61"	19˚58'57.63"	4741	37.93	0.80
6	S_4	P4 T1	Surface soil	40˚42'24.18"	19˚58'58.01"	5511	22.04	0.40
7	S_4	P4 T2	Profile	40˚42'24.18"	19˚58'58.01"	821	15.59	1.90
8	S_4	P4 T3	Profile	40˚42'24.18"	19˚58'58.01"	196	7.25	3.70
9	S_4	P4 T4	Profile	40˚42'24.18"	19˚58'58.01"	135	3.78	2.80
10	S_5	P5_T1	Surface	40˚42'22.08"	19˚58'55.57"	397	3.00	0.75
11	S_5	P5_T2	Profile	40˚42'22.08"	19˚58'55.57"	424	19.93	4.70
12	S_5	P5_T3	Profile	40˚42'22.08"	19˚58'55.57"	354	13.45	3.80
13	S_6	P6_T1	Surface	40˚42'15.54"	19˚58'53.06"	856	24.81	2.90
14	S_6	P6_T2	Profile	40˚42'15.54"	19˚58'53.06"	334	12.37	3.70
15	S_6	P6_T3	Profile	40˚42'15.54"	19˚58'53.06"	352	29.23	8.30
16	S_7	P7_T1	Surface soil	40˚42'14.45"	19˚58'53.43"	333	19.32	5.80
17	S_7	P7_T2	Profile	40˚42'14.45"	19˚58'53.43"	277	26.91	9.70
18	S_7	P7_T3	Profile	40˚42'14.45"	19˚58'53.43"	199	2.79	1.40
19	S_14	P14_T1	Surface soil	40˚42'27.26"	19˚58'59.67"	24,207	11.00	18.00
20	S_14	P14_T2	Profile	40˚42'27.26"	19˚58'59.67"	26,142	0.06	11.00
21	S_14	P14_T3	Profile	40˚42'27.26"	19˚58'59.67"	52,982	9.90	3.80
22	S_15	P15_T1	Surface soil	40˚42'33.45"	19˚58"57.86"	350	3.00	5.60
23	S_15	P15_T2	Erosion profile	40˚42'33.45"	19˚58'57.86"	125	14.00	11.20
24	S_28	P28_T1	Erosion profile	40˚42'24.45"	19˚59'00.96"	78	0.20	0.10
25	S_28	P28_T2	Surface soil	40˚42'26.21"	19˚59'01.29"	10,614	3.00	0.60
26	S_31	S31_T1	Surface soil	40˚42'06.07"	19˚58'43.86"	185	2.70	1.46
27	S_31	S31_T2	Profile	40˚42'06.07"	19˚58'43.86"	218	13.50	6.19
28	S_33	S33_T1	Profile	40˚42'08.00"	19˚58'52.31"	1503	3.21	0.21
29	S_33	S33_T2	Profile	40˚42'08.00"	19˚58'52.31"	718	6.43	0.90
30	S_37	S37_T1	Surface soil	40˚42'05.09"	15˚58'59.73"	187	16.30	8.72
31	S_37	S37_T2	Profile	40˚42"05.09"	15˚58'59.73"	193	8.90	4.61

mean concentration of lead in top of soil samples, while graph in **Figure 3** is presented the probability plot of lead concentration. Graph in **Figure 4** is presented contour plot of lead concentration in top of soil samples, while graph in **Figure 5** is presented the mean concentration of lead in surface and profile soil samples, comparison of lead content in surface with profile soil samples. A graph in **Figure 6** is presented the calculated HQ for lead in top soil samples, while the graph in **Figure 7** is presented the dependence of the distribution of lead in different distance from the factory (0 - 800 m). Graph in **Figure 8** is presented the mean concentration of lead in top of soil and vegetation samples, their concentration comparison, while graph in **Figure 9** is presented the probability plot of lead concentration in vegetation samples. Graph in **Figure 10** is presented contour plot of lead concentration in vegetation samples, while graph in **Figure 11** is presented the relationship between lead concentration in surface soil samples and lead concentration in the vegetation samples. A graph in **Figure 12** is

Table 3. Mean concentration of lead in vegetation samples and BAF soil to plant.

Nr.	Sampling point	Code in AAS	Material	Nord	East	Pb (mg/kg)	SD	BAF × 10³
1	S_1	P1_BS	*Cynadon dactiyon*	40˚42'21.32"	19˚58'56.74"	3.226	2.09	1.07
2	S_2	P2_BS	*Cynadon dactiyon*	40˚42'21.61"	19˚58'57.63"	3.501	1.36	0.62
3	S_2	P2_PN	*Pinus pinea*	40˚42'21.61"	19˚58'57.63"	2.227	1.98	0.39
4	S_4	P3_BS	*Verbascum (sp)*	40˚42'24.18"	19˚58'58.01"	1.519	2.04	0.28
5	S_4	P3_PN	*Pinus pinea*	40˚42'24.18"	19˚58'58.01"	3.437	3.00	0.62
6	S_4	P3_PT	*Pinus pinea*	40˚42'24.18"	19˚58'58.01"	3.829	4.81	0.69
7	S_5	P5_F	*Ficus carica*	40˚42'22.08"	19˚58'55.57"	1.034	9.32	2.60
8	S_5	P5_BS	*Verbascum (sp)*	40˚42'22.08"	19˚58'55.57"	2.042	3.53	5.14
9	S_6	P6_BS	*Cynadon dactiyon*	40˚42'15.54"	19˚58"53.06"	2.125	5.12	2.48
10	S_6	P6_F	*Ficus carica*	40˚42'15.54"	19˚58'53.06"	0.859	2.64	1.00
11	S_6	P6_H	*Diospiros (sp)*	40˚42'15.54"	19˚58'53.06"	1.207	1.67	1.41
12	S_6	P6_V	*Ulmus canpestris*	40˚42'15.54"	19˚58'53.06"	1.141	1.61	1.33
13	S_6	P6_L	*Euphorbia (sp)*	40˚42'15.54"	19˚58'53.06"	1.134	0.67	1.33
14	S_6	P6_BS	*Cynadon dactiyon*	40˚42'15.54"	19˚58'53.06"	2.375	1.27	2.77
15	S_7	P7_BS	*Verbascum (sp)*	40˚42'14.45"	19˚58'53.43"	1.337	0.34	4.02
16	S_7	P7_L	*Euphorbia (sp)*	40˚42'14.45"	19˚58'53.43"	0.994	8.21	2.98
17	S_14	P14_BS	*Cynadon dactiyon*	40˚42'27.26"	19˚58'59.67"	2.186	0.28	0.09
18	S_14	P14_BT	*Verbascum (sp)*	40˚42'27.26"	19˚58'59.67"	4.093	2.14	0.17
19	S_15	P15_BS	*Cynadon dactiyon*	40˚42'33.45"	19˚58'57.86"	0.927	1.97	2.65
20	S_28	P28_BT	*Verbascum (sp)*	40˚42'26.21"	19˚59'01.29"	4.572	2.73	0.46
21	S_31	P32_HN	*Triticum aestivum*	40˚42"06.07"	19˚58'43.86"	0.824	1.64	4.45
22	S_33	P34_PN	*Pinus pinea*	40˚42'04.11"	19˚58'03.79"	0.642	0.43	0.43
23	S_33	P34_PN	*Pinus pinea*	40˚42'04.11"	19˚58'03.79"	0.451	3.14	0.30
24	S_37	P37_G	*Triticum aestivum*	40˚42'05.09"	15˚58'59.73"	0.238	1.19	1.27
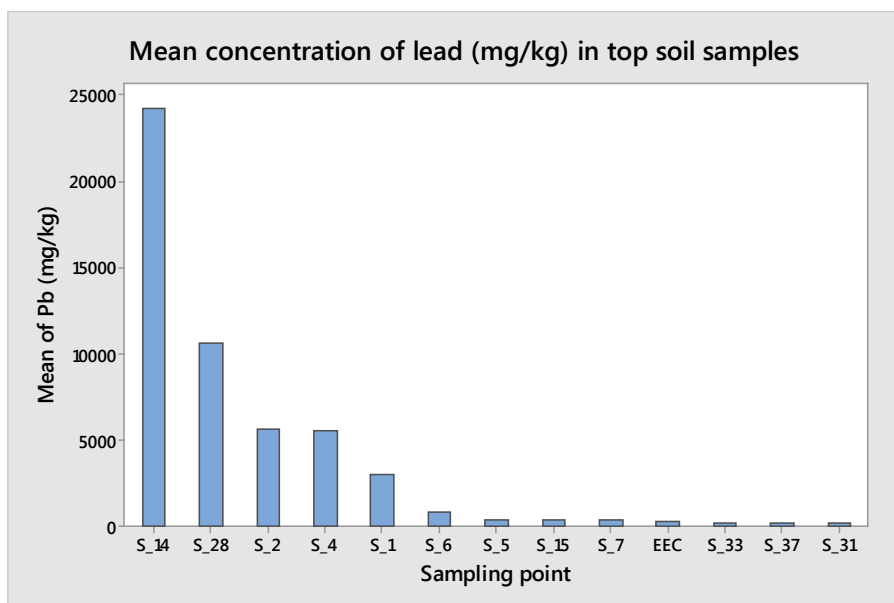
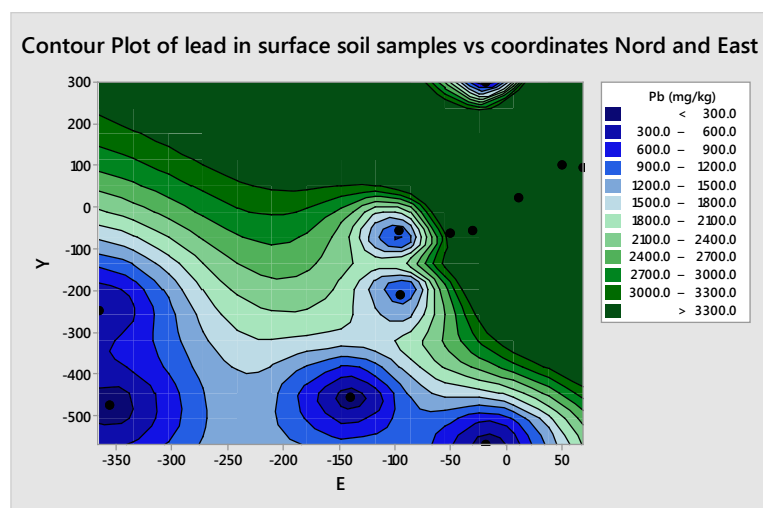**Figure 2.** Concentration of lead in top of soil.

Probability Plot of lead in surface soil samples (mg/kg)
Normal - 95% CI
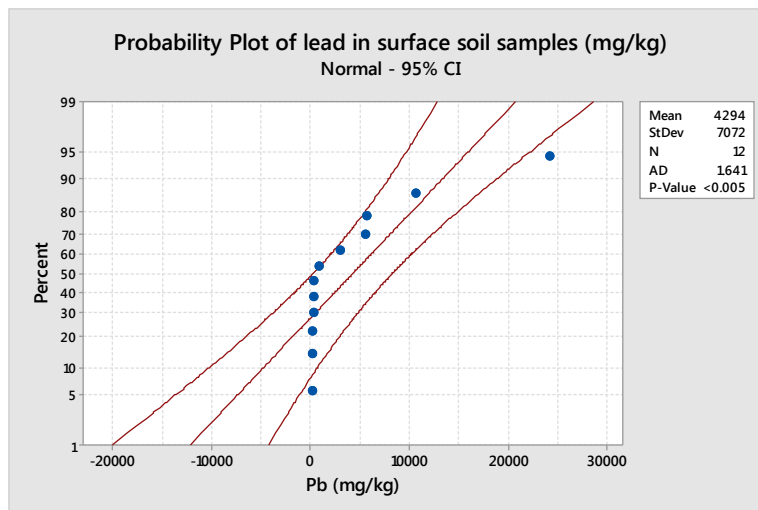
Figure 3. Probability plot of lead in top soil (mg/kg).

Contour Plot of lead in surface soil samples vs coordinates Nord and East

Figure 4. Contour plot of lead in top of soil.
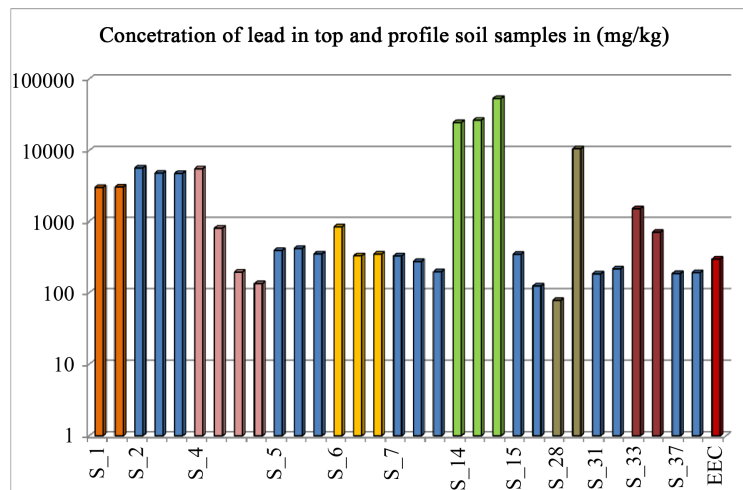
Concetration of lead in top and profile soil samples in (mg/kg)

Figure 5. Comparison of lead in surface and profile soil.

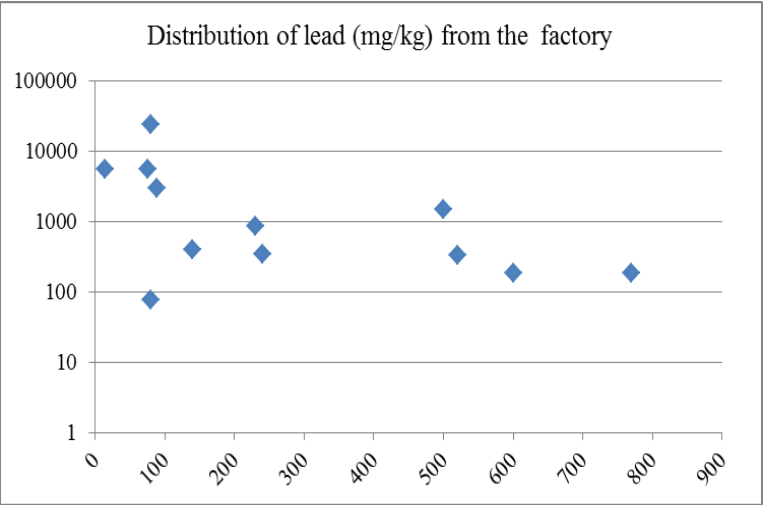## Factor of Hazardous Quoted for top soil samples
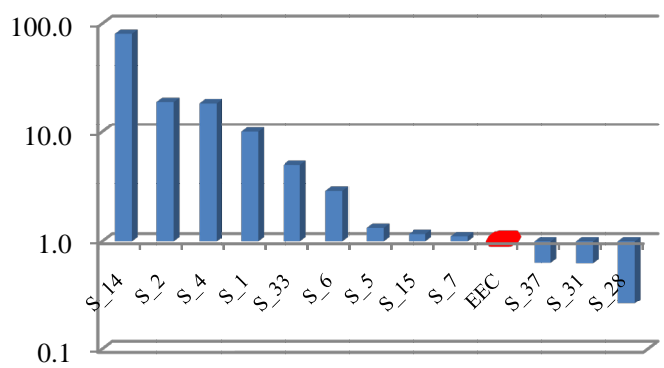
Figure 6. Calculated Hazardous Quoted of lead.

Figure 7. Dependence of lead in distance from factory.
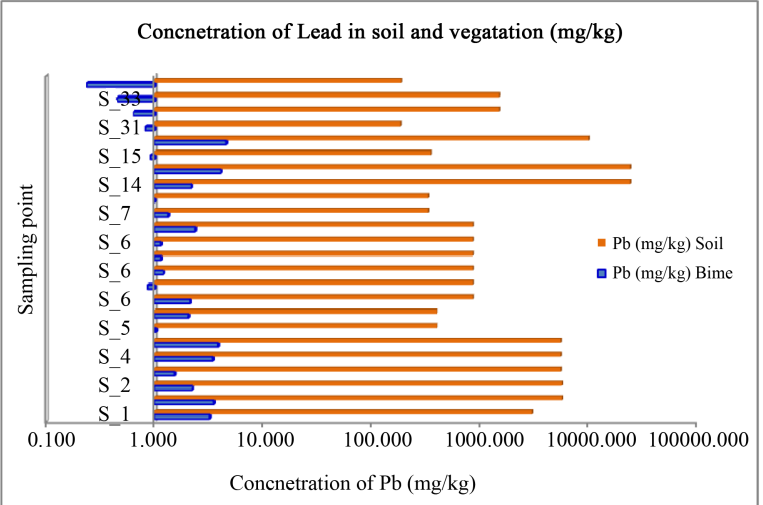
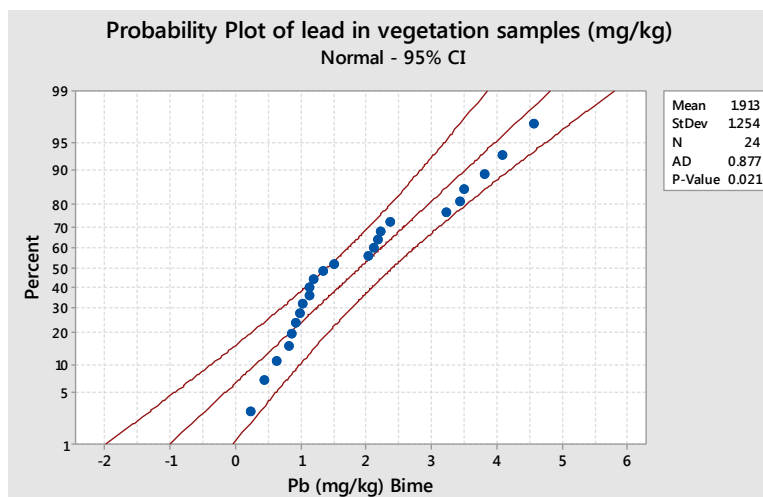**Figure 8.** Concentration of lead in soil and vegetation.
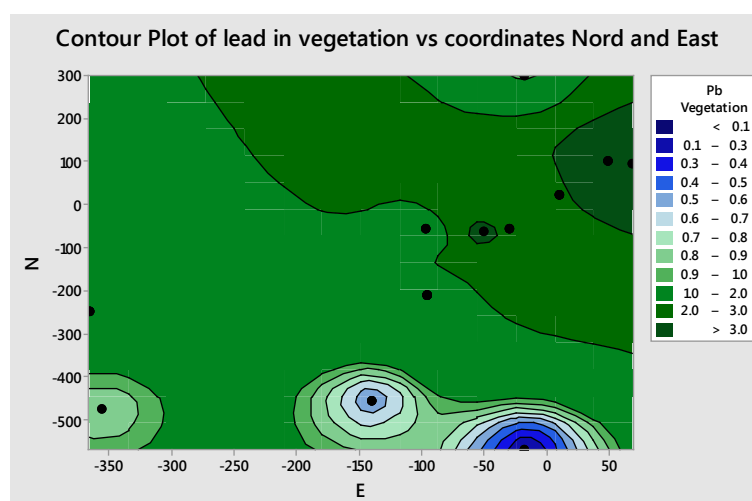
Probability Plot of lead in vegetation samples (mg/kg)
Normal - 95% CI

Figure 9. Probability plot of lead in vegetation.

Contour Plot of lead in vegetation vs coordinates Nord and East

Figure 10. Contour plot of lead vegetation.

Relationship of Pb in soil vs Pb in vegetation

$y = 3027.8x - 1643.1$
$R^2 = 0.3209$
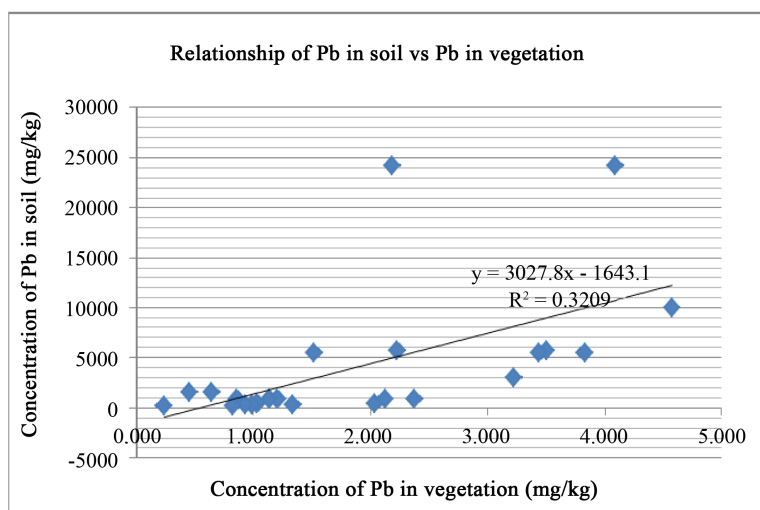
Figure 11. Dependence of lead in distance from factory.
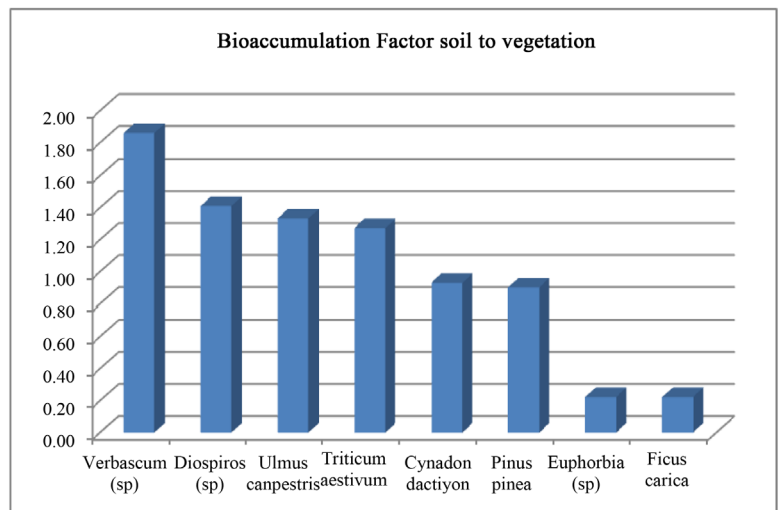
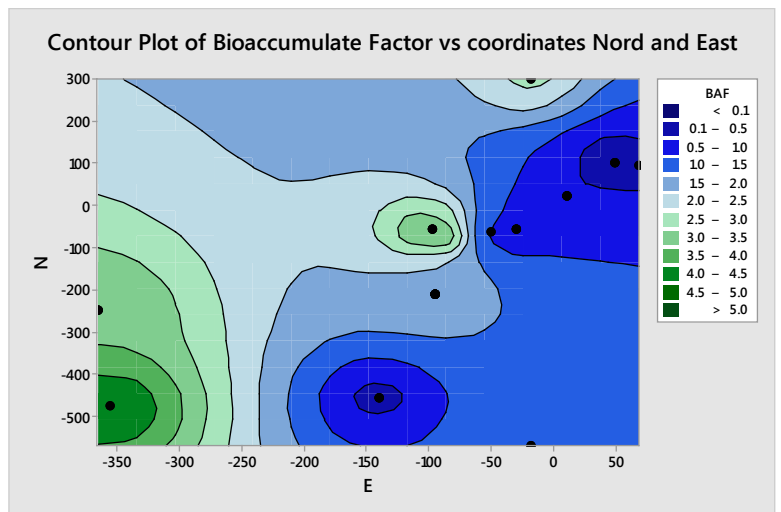**Figure 12.** The calculated bioaccumulation factor.

Figure 13. Counter plot of BAF.

presented the calculated BAF soil to plant, while the graph in **Figure 13** is presented counter plot of calculated BAF soil to plant versus coordinates, Nord and East.

3.1. Tables

Measurements obtained after analyzing CRM, soil and vegetation samples for determining the fraction of lead are presented in **Tables 1-3**.

3.2. Figures

The dates of **Table 2** and **Table 3**, the concnetration of lead in soil and vegetation which are found in respectively samples are presented in the graphical forms.

4. Conclusions

This paper presents the verification of distribution of lead concentration in the surface soil and its penetration in the profile soil samples. Lead was found present in all the soil samples. By comparing the concentration of lead in surface soil samples with MCL recommended by Directive 86/278/EEC, only three of the soil samples con-

tained lead below this concentration. The highest level of lead was found in soil samples which have been selected close the factory, S14 and S28. It was observed the lead concentration in the profile soil samples was found much higher than the level of lead in respective top soil samples. Industrial solid wastes are disposal uncontrollably, into the environment, in territory close to the factory. Thus the concentration of lead in profile soil samples (S14 and S28) was found higher than the surface soil samples for the reason that solid waste from factory were mixed with soil. Also the highest level of lead was found in top soil samples which were collected inside the factory, but in profile soil the lead has trend to decrease. Area where samples are collected is not used to cultivate plant crops but the random vegetation is used like livestock feed from inhabitants. Also, it was observed that distribution of lead depending of distance from factory is decrease, in the distance about 400 - 500 m from the factory. The bioaccumulation factor soil to plant was found in low values because the mean concentration of lead in soil was found very high. BFA depends on many factors like: the concentration of lead in soil and vegetation, duration of exposure, pH of soil, bioaccumulation ability of plants, atmospheric conditions, etc. By calculating the average of BAF soil to plant it is observed lead accumulates in plants at different levels. The ability of lead accumulation by random vegetation in descending order was: *Verbascum* (*sp*) > *Diospiros* (*sp*) > *Ulmus canpestris* > *Triticum aestivum* > *Cynadon dactiyon* > *Pinus pinea* > *Euphorbia* (*sp*) > *Ficus carica.*

The presence of lead in high concentration in representative soil samples was contributed by industrial waste as a result of the activity of the factory for about 20 years and waste disposal uncontrollably in the surrounding environment. From results obtained for concentration range of lead in soil samples collected at the area around the former Battery Production Factory, sometimes it can be observed that the measured concentrations are much higher than the MCL specified by EEC. High concentrations of lead and its duration in the environment have impacted negatively the ecosystem and human health.

Acknowledgements

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[11] (Perkin-Elmer Corperation. 1991-1999) Perkin-Elmer Corp.: 1964-2000, Analytical Methods for Atomic Absorption Spectrophotometry & Recommended conditions for THGA furnaces.

Abbreviations

AAS (Atomic Absorption Spectrometry); AAS_GF (Atomic Absorption Spectrometry Graphite Furnace); AMAAS (Analytical Methods of Atomic Absorption Spectrometry); BAF (bioaccumulation factors); CRM (Certified Reference Material); EEC (European Economic Community); HQ (Hazardous Quoted); MCL (Maximum Contaminant Levels); Pb (lead); PE (Perkin Elmer); (% R) Recovery percentage; % RSD (Relative Standard Deviation); SD (Standard Deviation); USEPA (United States Environmental Protection Agency).