Spatial distribution and source identification of heavy metals in surface soils in the city of Elbasan

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Abstract

In this study we investigated the pollution degree and spatial distribution of heavy metals and determined their sources in topsoil in Elbasan a typical industrial city. We collected 15 soil surface samples in different areas of Elbasan city.The soil samples were analyzed for Zn, Cd, Cu, Pb, As, Mo, Mn, Fe, Ni, Co and Cr. Soil samples were taken around the area of the metallurgical factory and in a radius of 20 km far from it. It was taken soil samples in two diagonal directions every 1 km (0-30 cm and 30-60 cm).
The average contents of all heavy metals were lower than the Soil Quality Standard for industrial area which are describe in Legislative Decree 152/2006 "Limit values of soil and subsoil concentrated" and higher for a lot of those heavy metals than the standard for public and private areas.The reading for the elements and heavy metals and metals was done with the IPC-MS device. Based on a data analysis and outcomes, the concentration of Cr, Mn, Co, Ni, Zn, Pb, Fe, etc., are related to industrial pollution and near the industrial area, while in relation to the content of Ni, Cu, Zn, and Pb there is no regularity with increasing distance from the object. The results showed that the source contributions in soil pollution are atmospheric deposition, industrial activities, agricultural activities, erosion, car cemeteries, heavy traffic and uncontrolled garbage collection.

Keywords: Heavy metals, soil, soil distribution, source apportionment, Elbasan.

Introduction

Soil heavy metal contamination attracts great attention around the world due to rapid urbanization and industrialization (Chen et al., 2009). In a large number of soil pollutants, heavy metals already turn into an important contaminant because of their toxicity and difficult degradation (Zhong et al., 2014). Heavy metals accumulate in soils as time goes on, which can lead to the loss of soil nutrient component and the degeneration of soil biology and function (Zhang et al., 2016). Heavy metals in the ecosystem resulting from natural and anthropogenic inputs may pose considerable threats to the aquatic environment. These metals harm human health through various pathways, due to their bioaccumulation, acute and chronic toxicity and persistence (Mclaughlin et al., 1999; MacDonald et al., 2000; Salmanighabeshi et al., 2015). Heavy metals are a major environmental problem around the world due to rapid industrial growth and urbanization. The problem is driven by inadequate environmental management and lack of strict adherence to environmental protection policies.

For instance, if the Fe concentration in soils is too high, it will affect the growth of rice. Additionally, high contents of soil heavy metal cause a serious threat to human and animal's health, because heavy metal ions can easily enter human and animals bodies by inhalation, dermal absorption or ingestion (Sun et al., 2010). For example, Cu in soils can be absorbed by the roots of crops, when Cu accumulates to a certain extent in the human body, it will be harmful to human health (the normal Cu content in soils is 2e200 mg kg_1). Chronic exposure to heavy metals and metalloids even at relatively low levels can cause adverse effects such as pulmonary disease, bone defects, lung cancer, liver damage, decreased lung function, airway constriction, and difficulties in breathing (Dockery et al., 1994; Morais et al., 2012). It is generally considered that natural and human activities are the two major origins of heavy metals. Natural sources of soil heavy metals are mainly controlled by the geological parent material (Liu et al., 2015). In addition, anthropogenic inputs of soil heavy metals are attributed to metalliferous industries, mining, vehicle exhaust, agricultural practices, coal combustion and atmospheric deposition (Alloway, 2013; Zhang, 2006). Therefore, it is very necessary to identify metal inputs before taking effective measures to protect soil quality. The spatial distribution of heavy metals in topsoil is largely influenced by natural inputs and human activities (Lu et al., 2012). In the city of Elbasan the main source of pollution in agricultural lands for years is considered the Metallurgical Factory and less the others industrial agents. The erosion and deregulation is another problem that is often encountered in the Elbasan lands. The Elbasan city enters in the second group of erosion sensitivity with a value of 37 ton / h / year degradation. Land plots have affected housing damages in the nearby villages of the city. The land pollution is also result of uncontrolled storage area of waste construction as well as the exercise of "car cemetery" activities which damage the landscape and pollute the land with oils and fuels and also affect the collection of plastic and metal wastes.The aim of this study is ; (1) to estimate the contamination extent of heavy metals in soils; (2) to ascertain the spatial variation characteristics of soil heavy metal concentration; (3) to quantitatively identify various sources of soil heavy metals. This work will provide effective information to prevent further heavy metal pollution in soils.

1. Materials and methods

1.1. The study area

The study area is the area of Metallurgical Factory and up to a 20 km radius from this place. Elbasan area, according to the climatic division of Albania, is part of the Mediterranean hilly area and the central hilly Mediterranean sub-area. The variety of relief forms and the wide north-south extension of this sub-zone affect the regime of climate elements. The average air temperature varies from 6.7^{o}C in January to 23.4^{o}C in July. Wind is another important climatic element for which in general it can be said that the Elbasan area is characterized by high silence values (about 53%) and average speeds of 1.2m / s during summer and average maximum speeds of 2.1 - 2.4m / S in winter. As for rainfall, most of them fall in the second half of the year and less in the warm half due to cyclone activity. Specifically, during the coldest half it falls to 65.8%

of the annual rainfall and during the cold half it falls 34.2%.The city of Elbasan has been built on a part of the Elbasan field and specifically in the Labinot - Paper sector, in a gorge constructed by molosic formations. This area of more than 5 decades has been under the influence of the Metallurgical Factory and of other plants such as ferrochrome, cement factories, etc. These industries and other activities are closely related to the pollution of heavy metals in the soil in the city of Elbasan.

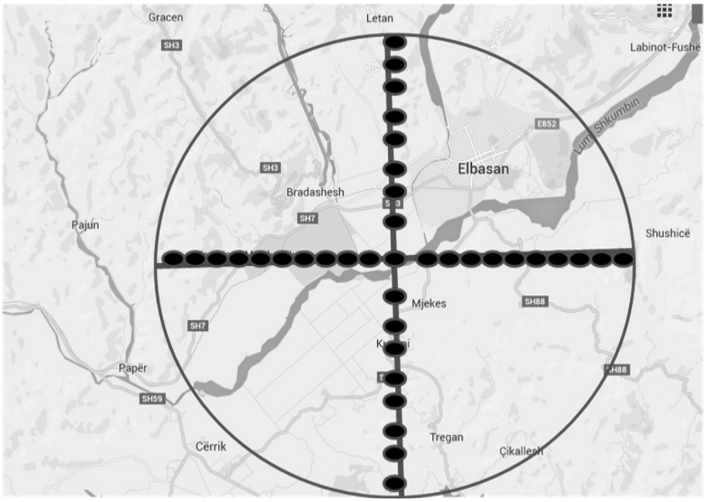

Fig. 1: Schematic presentation of the study area.

1.2 Sample collections and concentration determination

A total of 15 land samples were collected in different locations around the Metallurgical Factory area (table nr. 1). These soil samples were taken in depths 0-30 cm and 30 - 60 cm. Each of the ground samples was thawed and then placed in a 2 mm porous site. To make soil mineralization (soil destruction to see the presence of minerals in them) use the Multiwave ECO Digestion System. Initially we weighed one gram of soil for each of the samples taken for study. Then, in each of the experiments we had set 10 ml of nitric acid (65%). We put our product into the above-mentioned device for a time of 20 minutes in the temperature of 200 ^{O}C. After the completion of the procedure, we made the dilution at 1:200. There was collected 5 μl of each tube and we added 10 ml of nitric acid HNO_3 and 100 μl of standard. The standard solutions includes (Bismuth, Germanium, Holmium, Indium, Litium, Radium, Scadium, Terbium, Yttrium). At the beginning, in the new test tubs which are empty we throw 100 μl of the standard solution, then we add 5 μl of sample from soil samples taken in the study and 10 ml of HNO3 2%.

Photo no. 2: Microwave device which enables the nitric acid to warm up in the tubes and allows the organic matter present in the soil and other elements to enter the nitric acid solution and then read by IPC-MS.

After the reading of the dates from the device for the identification of the heavy metals we use the formula to make the proper calculations for each of the heavy metals:

HM (mg/kg) = (C/1000)x V) / P

HM = heavy metals

C = concentration of the elements in mg L^{-1}

V = volume

P = weight

Matrix	Area Definition	Depth	Coordinates	
			Width	Height
Soil	Paper 1	0 - 30	41.0522871	19.9702752
Soil	Paper 1[1]	30 - 60	41.0522871	19.9702752
Soil	Paper 2	0 - 30	41.0552857	19.9452093
Soil	Paper 2[1]	30 – 60	41.0552857	19.9452093
Soil	Paper 3		41.0563139	19.9500339
Soil	Xibrake 1	0 – 30	41.1511694	20.1638904
Soil	Xibrake 2	0 – 30	41.1623239	20.1959841
Soil	Kurum 1	0 – 30	41.1024793	20.0242945
Soil	Kurum 1[1]	30 – 60	41.1024793	20.0242945
Soil	Ferrokrom	0 – 30	41.0944218	20.0273586
Soil	Labinot – fushe	0 – 30	41.1437394	20.15515
Soil	Belerbe	0-30	41.106307	20.107006
Soil	Kraste	0-30	41.110896	20.100079
Soil	Near Cemetery	0-30	41.105263	20.097903
Soil	Serat	0-30	41.118295	20.095342

Table no. 1 Geografical coordinates of the soil samples obtained

2. Results and discussion

2.1. Degree of heavy metal contamination

In the following table gives the results of the analyzes made on soil samples taken in the city of Elbasan to observe heavy metal contamination. From the table it is noted that for heavy metals such as Cr, Ni and Co kemi nje tejkalim te standartit per zonat industrial ne vleren 4 here me shume per Cr, 6 here me shume per Ni si dhe 2 here me shume per Co nisur nga vlerat e tyre mesatarde.Ndersa duke iu referuar standartit per zonat publike vlerat e metaleve te renda kalohen shumfish ne te gjitha rastet e marra ne studim.

The lands subject of the study	Cr mg/kg	Co mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Cd mg/kg	Pb mg/kg
Paper 2"	2209.02	462.54	2430.33	210.34	601.10	61.80	1.66	183.4208
Paper 2	2177.20	241.49	1966.72	195.45	582.59	52.62	1.14	154.1048
Xibrake 1	2496.44	329.86	2789.55	790.19	1120.04	63.40	1.70	205.8162
xibrake 2	2347.38	361.61	4620.13	321.63	586.40	39.98	1.72	96.84497
Paper 1	2980.36	386.61	3315.91	308.46	764.89	67.74	1.75	215.7114
Bradashesh	1550.81	214.91	2383.33	262.34	759.92	43.56	3.26	148.1109
Lab.Fushe	2382.61	319.93	2935.88	598.84	1053.67	54.69	2.20	176.8273
Ferrokrom	4321.54	278.94	3793.55	592.74	1884.82	70.73	4.49	354.649
Paper 3	3344.83	263.29	3246.89	540.27	922.57	61.08	2.05	130.5918
Kurum	1973.77	232.90	2693.01	283.78	809.27	47.95	2.69	123.2992
Paper 1"	2610.53	370.53	2766.32	238.95	564.21	52.63	1.20	156.8421
Belerbe	2102.06	236.71	2559.84	426.48	960.55	54.78	1.77	134.0076
Kraste	1798.45	259.25	2300.67	508.73	1208.37	53.15	4.04	222.3657
Afer Varrezave	1921.66	223.16	2249.73	574.11	1145.37	77.25	2.42	206.9482
Serat	2233.64	229.09	2480.81	390.86	894.26	52.25	1.93	158.756
Mean	2430.02	294.05	2835.51	416.21	923.87	56.91	2.27	177.89
Min	1550.81	214.91	1966.72	195.45	564.21	39.98	1.14	96.84
Max	4321.54	462.54	4620.13	790.19	1884.82	77.25	4.49	354.65
S.D	689.7742	74.16476	681.0937	176.9422	342.2782	10.11494	0.97588	61.10947
Standard for the public lands	**150**	**20**	**120**		**150**	**20**	**2**	**100**
Standard for the industrial lands	**800**	**250**	**500**	**600**	**1500**	**50**	**15**	**1000**

Table no 2. The content of the heavy metal in the lands

Conclusions

In the city of Elbasan, the agricultural land is formed on the Quaternary formations where the carbonate lands prevail. Typical are the red clay soils formed on carbonate rocks in Kraste. From a pedological point of view and bonity: all the lands of valleys surrounding the city of Elbasan are considered to be the soils of the first to the fourth category. The main source of pollution in agricultural lands of Elbasan in years is considered the Metallurgical Factory and with less industrial agents. Monitoring of agricultural lands is done for heavy metals and the content is assessed as negative for the case of Chrome, Cobalt, Lead and Nickel in almost all inhabited areas compared with the standard for public places of Legislative Decree 152/2006 "Legislative Decree 152/2006 "Limit values of soil and subsoil concentrated". The dates and the results of the concentration of Cr, As , Co, Ni, Zn, Pb, etc. indicate that they are related to industrial pollution and being near the industrial zone of ferrochrome and Kurum but in some cases regarding the content of Ni, Cu, Zn and Pb in two or three sampling points indicate that there is no regularity with increasing distance from the object. The results indicate that the source contributes to soil contamination, industrial activities, agricultural activities, erosion, car cemeteries, heavy traffic and uncontrolled garbage collection. The content of heavy metals in the soil layers is also characterized by spatial diversity (Alexandrovskaya and Alexandrovskiy, 2000; Birch et al., 2011). The changes in the content of pollutants in each stratum of the soil can be related to the morphology of the space, the type of soil texture and its mineral composition (Engovatova and Golyeva, 2012; Manta et al., 2002). The presence of heavy metals in the soil layers on urban soils can also be influenced by the presence of the amount of organic material in it (Lehmann and Stahr, 2007). The ability to accumulate heavy metals is related to the type of soil (ie, its physical texture, especially the content of clay parts) of the chemical properties as well as the nature of heavy metals (Kabata-Pendias, 2011). Heavy metals are characterized by high stability in the environment and are generally not biodegradable. The mobilization of heavy metals on earth occurs under anaerobic conditions (Akan et al 2013). Moreover, the accumulation of heavy metal in the soil breaks down the usual biochemical processes occurring therein, which can cause effects that have a negative effect on the biological activity of the soil. The highest content of heavy metals is generally found in the top soil; surface layers, especially organic horizons, characterized by the ability to bond heavy metals. Accumulation of heavy metals in the surface layers of the earth is also related to human activity in a direct and indirect way.

References

Jie Liang a, b, *, Chunting Feng a, b, Guangming Zeng a, b, Xiang Gao a, b, Minzhou Zhong a, b, Xiaodong Li a, b, Xin Li a, b, Xinyue He a, b, Yilong Fang a, b Spatial distribution and source identification of heavy metals in surface soils in a typical coal mine city, Lianyuan, China.

Lin Zhua, Jianwei Liua,⊚, Shiguo Xua, Zaigang Xieb (2017).Deposition behavior, risk assessment and source identification of heavy metals in reservoir sediments of Northeast China.

Lasun T. Ogundelea, Oyediran K. Owoadea, Philip K. Hopkeb,c,⊚, Felix S. Olisea Heavy metals in industrially emitted particulate matter in Ile-Ife.

Zhang Jun Shena,b, De Cong Xua,⊚, Yan Song Chena, Zhen Zhangc Heavy metals translocation and accumulation from the rhizosphere soils tothe edible parts of the medicinal plant Fengdan (Paeonia ostii) grown on a metal mining area, China.
Alexandrovskaya and Alexandrovskiy, 2000; Birch et al.,2011.
Engovatova and Golyeva, 2012; Manta et al., 2002.
Lehmann and Stahr, 2007.
Mmolawa et al.,2011; Steinnes et al, 1997. Wei dhe Yang, 2010; Zhao et al.,2013b.
Gu et al 2016;.. Parzych et al, 2012.
Karczewska dhe Kabala, 2002; Zawadzka dhe Łukowski, 2010.
Acosta et al.,2015; Chen et al, 1997. Wei dhe Yang, 2010.
Kabata-Pendias, 2011.
Mmolawa et al., 2011.
Akan et al 2013;.. Zadro_zny et al, 2015.