

Determination of Heavy Metals in Soil in the Industrial Area

Agron Veliu*

NewCo Ferronikeli Complex L.L.C, Department of Environment and Quality Control, 13000 Gllogoc, KOSOVA

Received September 28, 2016; Accepted December 20, 2016

Abstract: Soils polluted with heavy metals have become common across the globe due to increase in geologic and anthropogenic activities. Heavy metals in the soil refers to some significant heavy metals of biological toxicity, including mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), arsenic (As), etc. With the development of the economy, more specific with the development of industry the presence of heavy metals in the soil caused by this activity have gradually increased in recent years, which have resulted in serious environment deterioration. The aim of this research study which is done in 2007 during the environmental impact assessment was to evaluate the real situation of the soil contamination with heavy metals within the industrial area of the Ferronikeli before restarting of the plant activity.

Keywords: soil, heavy metals, contamination, industrial area.

Introduction

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. Heavy metals in the soil include some significant metals of biological toxicity, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), etc. They also include other heavy metals of certain biological toxicity, such as zinc (Zn), copper (Cu), nickel (Ni), stannum (Sn), vanadium (V), and so on. In recent years, with the development of the global economy, both type and content of heavy metals in the soil caused by human activities have gradually increased, resulting in the deterioration of the environment (Han *et al.*, 2002; Sayyed & Sayadi, 2011; Jean-Philippe *et al.*, 2012; Raju *et al.*, 2013; Prajapati & Meravi, 2014; Sayadi & Rezaei, 2014; Zojaji et al., 2014). Heavy metals are highly hazardous to the environment and organisms. It can be enriched through the food chain. Once the soil suffers from heavy metal contamination, it is difficult to be remediated. The term 'heavy metal' is often used to cover a diverse range of elements, which constitute an important class of pollutants. With the industrial development, the production and emission of heavy metals have increased. Some metals, e.g. Mn, Cu, Zn, Mo and Ni, are essential or beneficial micronutrients for microorganisms, plants, and animals, but at high concentrations all these metals have strong toxic effects and pose an environmental threat.

Heavy metal pollution can be defined as an undesirable change in the physical, chemical or biological characteristics of land, water and air that may or will harmfully affect animals, plants and humans. The presence of heavy metals in different foods constitutes serious health hazards, depending on their relative levels. For example, cadmium and mercury injure the kidney and cause symptoms of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension, tumors and hepatic dysfunction. Lead causes renal failure and liver damage. Some other metals (*e.g.* chromium, zinc and copper) cause nephritis, anuria are extensive lesions in the kidney. Therefore, the problem of food contamination by toxic metals is receiving global attention. Soil adjacent to the industrial area contains the highest concentration of heavy metals.

In the past, soil contamination was not considered as important as air and water pollution, because soil contamination was often with wide range and was more difficult to be controlled and governed than air and water pollution. However, in recent years the soil contamination in developed countries becomes to be serious. It is thus paid more and more attention and became a hot topic of environmental protection worldwide.

Subject and location of the excavations of study

The main objective of this assessment study was to examine the potential risk area for a soil contamination with heavy metals, within the industrial area of Ferronikeli in the way to determine the

^{*}Corresponding: E-mail: agron.veliu@yahoo.com, Tel: +386 49 784 579

environmental situation before restarting with production process of the plant. Before starting any excavation, the location was firstly checked in the way to avoid any damage to existing underground equipment or pipeline or network (excavation locations are shown in Figure 1). In total were done 14 excavations during this assessment study.

Samples were collected on the demand of the supervisor and placed immediately in proper container. The excavations were done at a depth considered sufficient to evaluate the soil contamination. Excavation log were systematically written during excavations. These logs provide information concerning lithologic and organoleptic parameters (colour, odour). After selection, a part of the sample was sent to an independent laboratory for analyses. We have selected the laboratory ALS in Prague (Czech Republic) because of its reliability and its specialization in this kind of environmental analyses.



Figure 1: Excavation location

Description excavation and results

The table below describes potential risks checked with excavations during this study assessment. The main aim for this study was to determine total carbohydrates (TCH), polychlorinated biphenyl (PCB), polycyclic aromatic hydrocarbons (PAH) and heavy metals in these soil samples. The table 2 presents analyzed parameters for heavy metals for those samples that were more important as a subject for risk potential from the plant done during this assessment process, while in table 3 are presented results for TCH and PCB for the analyzed samples for this purpose.

ID	Location	Why	Samples	Assessment analyses
E1	In front of the 400 m ³ fuel oil tank, next to the ex steam station	Check potential spillage of fuel oil + close to the demineralization treatment plant	E1.1	ТСН
E2	Close to the area for the maintenance of the locomotive	Potential spillage of used oil	E2.1	ТСН
E3	Angle of gas pipeline for reduction station	In front of the manifold for the fuel oil delivered by railway. Gravel presents traces of spillages	E3.1 E3.2	TCH TCH
E4	West border of the main heavy fuel oil tanks (destroyed) + close to the	To check potential contamination of the surrounding soils. However, risks are minimal because of the viscosity of the fuel and because	E4.1	TCH Metals

Table	1:	Instification	of the	excavations
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ID	Location	Why	Samples	Assessment analyses
	pump station for this fuel oil	of the proper condition of the concrete basement of the bond.		Ť
	In front of the converter,		E5.1	Metals
E5	between the 2 pipes carrying slurries from the quencher scrubber	To check a potential soil contamination because of leakage from these pipelines	E5.2	Metals
E6	Cooling tower	To check potential problem coming from the close water treatment plant	E6.1	-
E7	South-West site, close to surface water effluent	-	E7.1	-
E8	Internal scrap disposal, close to the smelting department	Check potential leakage of used oil if this place was used also as an internal garbage disposal'	E8.1	-
E9	West corner primary electric station	Immediate downstream from electric transformer and information that oil of 1 of this transformer were spread during the bombing	E9.1	TCH PCB
E10	East corner primary electric station	Next to old barrels left on the ground. These barrels could have contained used oil and leaked on the naked ground	E10.1	-
E11	Old small electric transformer	Presence of used oils on the soil	-	-
		To estimate the depth of buried slag and	E12.1	Metals
E12	Internal slag disposal	evaluate potential metal contamination of the surrounding soils	E12.2	Metals
E13	Marshy area downstream to primary electric station	Potential soil contamination by the proximity to the transformer station	E13.1	Complete
E14	Ex garage	Potential fuel and used oils contamination by the maintenance of the vehicles	E14.1	-

Doromotor	E5 1	E5 2	E12 1	E12.2	E13	Unit		Soil	
Falameter	E3.1	EJ.Z	E12.1	E12.2	E13	Unit	Guio	leline valu	es (1)
Dry matter at 105 °C	85.7	76.8	80.1	77.2	70.5	%	VDSS	VCI (1)	VCI (2)
As	9.8	11	5.0	14	10	mg/kg of dw	19	37	120
Ba	260	260	62	450	100	mg/kg of dw	312	625	3125
Cd	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	mg/kg of dw	10	20	60
Со	39	34	380	71	13	mg/kg of dw	120	240	1200
Cr (total)	130	130	1600	140	80	mg/kg of dw	65	130	7000
Cr (VI)	5.1	0.24	< 0.080	21	-	mg/kg of dw	ND		ND
Cu	26	28	24	34	19	mg/kg of dw	95	190	950
Hg	0.26	< 0.13	< 0.12	< 0.13	< 0.14	mg/kg of dw	305	7	600
Мо	1.6	1.2	<1.0	<1.0	<1.0	mg/kg of dw	100	200	1000
Ni	290	170	6800	320	120	mg/kg of dw	70	140	900
Pb	46	31	5.6	41	8.2	mg/kg of dw	200	400	2000
Sn	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	mg/kg of dw			
Zn	130	69	63	76	44	mg/kg of dw	4500	9000	ND
ТСН	-	-	-	-	<dl< td=""><td>mg/kg of dw</td><td>2500</td><td>5000</td><td>25000</td></dl<>	mg/kg of dw	2500	5000	25000

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<u>Note:</u> French BRGM - Guideline value soils - BRGM - Annex 5 - 2002 (1) - VCI sensible use; (2) - VCI non sensible use Guideline values from Kosovo for environment were not available at the time of this study.

Discussion of the results

The results presented in tables 2 and 3 shown:

- Samples E5.1 and E5.2 are riches with chromium in the soil but below 'usage sensible' (residential) of the land, also high nickel in the soil but below 'usage non sensible' (industrial and commercial).
- Sample E12.1: High cobalt and chromium but below 'usage non sensible' (industrial and commercial), and very high nickel content, above usage sensible.

• Samples E12.2: Nickel content is decreasing compared to the above sample (low migration of the nickel in the soils)

All samples have shown chromium = geological background. Nickel is also present in the soil but it is most likely from geological background. Only 1 sample shows very high content of nickel (E12.1). But this is very coherent because this sample contains slag from electric furnace (internal slag disposal). Also, TCH, PCB and PAH are in very low level (below detection limit). No major contamination is analyzed in the tested samples.

Parameters	TCH	PCB	PAH, pesticides	Unpolar extractable aliphates			
Unit	mg/kg dw	mg/kg dw	mg/kg dw	mg/kg dw			
E1.1	<dl< td=""><td></td><td></td><td></td></dl<>						
E2.1	210						
E3.1	<dl< td=""><td></td><td></td><td></td></dl<>						
E3.2	<dl< td=""><td></td><td></td><td></td></dl<>						
E4.1	<dl< td=""><td></td><td></td><td><21</td></dl<>			<21			
E5.1	-						
E5.2	-						
E9.1	<dl< td=""><td><dl< td=""><td></td><td><21</td></dl<></td></dl<>	<dl< td=""><td></td><td><21</td></dl<>		<21			
E12.1							
E12.2							
E13	<dl< td=""><td><dl< td=""><td><dl< td=""><td></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td></td></dl<></td></dl<>	<dl< td=""><td></td></dl<>				
DL - Detection limit							

Table 3: Soil analytical results for TCH, PCB and PAH

Conclusions

Globally, soils within the industrial area of Ferronikeli do not show contamination from oils, fuel or metal. These field results are 'in conformity' with what we could expect from this site. The Ferronikeli process is not a polluting process. Main pollutants are oils or fuel oils. This site is not an old site (built in the 80's) and proper constructive measures and standard were then adopted. All fuel oil storage is included in concrete bond for example. For the primary electric station is exists an underground tank collecting potential leakage of oils from transformers. No major contamination is analyzed in the tested samples.

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