Research Article

Determination of Heavy Metals in Soil, Water Wells and Wastes After the Technological Process in the Factory Battery in Gjilan, with AAS Method

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ABSTRACT

Determinate the concentrations of heavy metals in the soil of the factory yard, agricultural and factory lands around of this site and wells in this yard, which are used in technological processes in the factory, the SAA method on May 2013. Determined elements such as: Pb, Zn, Cu, Cd, Ni, Cr, Fe and Mn, in three sampling points that land, two sampling points that the land left fallow in the courtyard of the factory, where it was a dump of material wastage, which had they remained there after the technological process and a site-sampling of working land (planted), which land planted every year and was not farther than 20 meters from the battery factory in Gjilan. We also, we analyzed heavy metals such as: Pb, Zn, Cu, Cd, Ni, Cr, Fe and Mn, in three wells yard of the factory where these wells used by factories as water for technological processes, during material processing where these wells already, are nearly surrounded by the nozzle of the factory scrap material.

Keywords: Battery Factory, Gjilan, Heavy Metals, Well, Pollution, Waste.

INTRODUCTION

Factory batteries (accumulators) in Gilan have produced batteries until the end of the last century. Production technologies of the factory, after technological processes, such as waste has remained a large amount of this material without usable junk away, where the contents such as trailer is considered to have a significant amount of heavy metals such as ; Zn, Cd, Pb, Cu, Fe, Ni, Cr, Mn, etc. Now this plant, its manufacturer activity has stopped, but the junk material is stored in one place on the right side of its yard near wells that have been used for technological processes and land planted with wheat, no later than 20m visa-line distance to the object factory. Therefore, the abandoned factory in question is the source of soil and water pollution, heavy metals, and we have estimated that the deposited material are present as elements (Pb, Cd, Cu, Zn, Fe, Mn, Cr and Ni), in the form of inorganic compounds[1]. Remains of large junk material will have a negative impact on air pollution, water and soil[2-3], where the concentration of heavy metals in landfill represents a major concern, which is also expressed to the general public[5]. The possibility of penetration of heavy metals in surface and ground waters, lands planted with different crops and through them up in the food chain are very evident[9]. So far, there have been no detailed studies about the effects of battery factory in Gjilan, the environment and health of the population of this area. To make such conclusions would be necessary to make more concise environmental studies, basic studies, socio-economic and medical. Therefore to bring real results and more reliable in this paper, we analyze the impact of residual material landfill junk, which has shed factory after technological processes, especially the concentration of heavy metals in water wells, W_1, W_2, W_3, in the courtyard of the factory and also have accurate results derived level of these elements in the soil around the plant and soil planted with wheat drawings come with this factory.

MATERIALS AND METHODS

We have done the analysis and evaluation of water and soil samples, the concentration of heavy metals in these environments, noting the impact of landfill junk material in wells within the factory yard, the yard land and land planted with wheat, we analyzed and evaluated the concentration of heavy metals in environments, water and land. Samples were taken over a period of time, from May 2013 to see the difference in the concentration of elements in different environments. During the working activity, the plant has remained substantial amount of junk material which is submitting testimony in the factory yard in the southwestern part.

All chemicals needed for the determination of physical parameters - chemical micro pollutants and parse macro pollutants water and soil samples were chemical purity. The method used for the determination of heavy metals in soil and water environments, has been SAA. Treatment method of sampling was done in the laboratory of environmental chemistry and chemical technology, in the department of chemistry, while measurements and reading results with SAA technique, were made in laboratory IHMK. Making and preparation of soil samples

for chemical analysis was done according to the standards methods that we found in the literature for the analysis of soil[6]. The amount of sample for analysis that we got was 3-5 kg at each sampling points in different layers of soil from the 5, 15 and 25 cm in depth of the landfill - land. Soil samples for analysis and scrap material, taken at three sampling points[3].

The first sample site has been; S_1-Earth - yard Factory in Gjilan, line drawings KSF-barracks, the second sample site; in battery factory yard, junk landfill material after the technological process (S_2-Land, the F.G, line drawings Lower village), and the third sample site (S_3-agricultural land), in samples soil in agricultural land planted with wheat at the factory yard, line drawings Malishevė village and turn left to the village Shillovë.

Also, water samples were taken in the factory yard wells which are used for technological processes, 25cm below the water surface, 25 cm above the bottom and a layer of middlemen in the above mentioned wells in three sampling points, (considering that wells at this time, have been nearly exhausted, perhaps not in use).

The first sample site ; (S_1–Well-$_1$, the cheese factory, the western part, visa - line with KSF- barracks), the second sample site ; (S_2–Well-$_2$, factory yard, line drawings Lower village), and the third sample site ; (S_3-Well-$_3$, inside the factory yard, line drawings Malishevė village and turn left to the village Shillovë.

Samples taken from the soil, are prepares representative samples for chemical analysis, so that the accumulated dust is mixed and well homogenized and their division into four parts, the initial amount is reduced to about 1 kg.

This amount is further mixed sample and crush the oppressor avian porcelain with sieves and sieve in the 100 to 200 mass.

Material advantage is dried at 105^{o}C until constant weight is transferred to the special container and then samples prepared in this way were used for further chemical analysis.

Samples collected from polluted water, some ingredient can be volatile, diffraction easily interact or ingredients.

For this purpose, during water sampling some parameters must be measured at the sampling sites or samples should be stored conservation and at low temperatures (about 4 ^{o}C), and conservation of sampling should be done by adding concentrated HNO_3, to pH = 3.5, and so samples should be stored in closed containers in a dark and to use necessary.

Polyethylene bottles are showing better preservation of the sample before determining the most in traced elements; therefore water samples were taken in polyethylene containers.

Analytical methods of determining the elements require that samples be in the form of aqueous solution.

During digestion of the samples should be careful that: samples digested quickly and fully, not to loss of sample by evaporation or adsorption on the walls of the container and eliminate sample contamination from the reagents used in the process from progress digestive.

Most digestion of the samples, based on the use of inorganic acids in the mixture as a solvent.

During melting, the sample digestion with sodium carbonate, the mass of melted obtained after cooling, treated with hydrochloric acid and the solution dries up in the dry.

Dry residue is added to distilled water to 50 ml.

For digestion of the elements in the soil, in order to determine heavy metals, we use mixtures of acids, nitric and perchloric acid (1:4) 0.25g sample scaled ago 105^{o}C dried and dissolved in 10 ml have mixture of perchloric acid and nitric acid.

Samples were set in sand bath in digester and are evaporated until dry.

Then the rest have dealt with 10 ml of concentrated HCl and diluted to have certain volume, the sample is made ready for SAA measurement technique.

Usually a part of silicates remains unbelted at the end of the container which leaves the filtering to avoid having obstacles in the analysis with appropriate methods.

Also in the water samples for the determination of heavy metals in the sampling point's conservation with concentrated nitric acid.

From the total volume of 1L samples measured at constant temperature and slowly evaporated to about 10 ml in volume.

Samples with a volume of 10 ml normal flow into the container 100 ml and after acidification 1 ml of HCl and mark where the sampling sites are ready for analysis.

Figure 1: Sampling points for soil, waste and water wells samples.

RESULTS AND DISCUSSION

Our results are presented in table and graphical form, are given as arithmetic average of samples analyzed. In three different sampling points, we have determined the concentration of heavy metals (Zn, Cd, Pb, Cu, Fe, Cr, Mn and Ni), in soil and water.

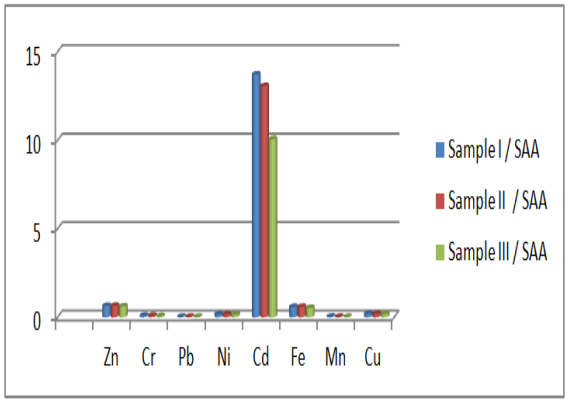

Figure 2: Soil Sampling Points

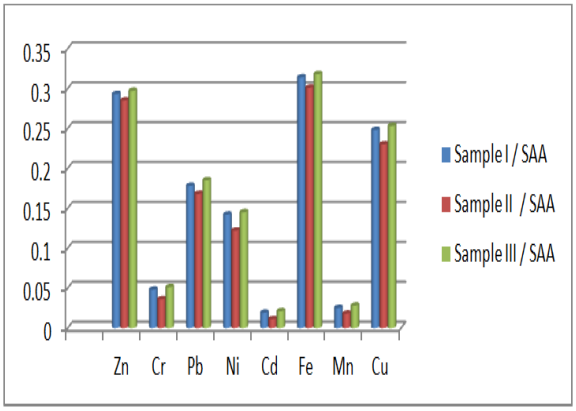

Figure 3: Water Sampling Points

Table 1: Presentation values of concentration of heavy metals in soil samples expressed in mg/kg

Elements	Sample I/SAA	Sample II/SAA	Sample III/SAA
Zn	0.628	0.635	0.605
Cr	0.076	0.081	0.051
Pb	0.014	0.018	0.015
Ni	0.158	0.161	0.148
Cd	13.71	13.06	10.06
Fe	0.573	0.583	0.521
Mn	0.025	0.019	0.011
Cu	0.196	0.189	0.180

Table 2: Presentation values of concentration of heavy metals in water samples in mg/dm^3

Elements	Sample I/SAA	Sample II/SAA	Sample III/SAA
Zn	0.293	0.285	0.297
Cr	0.048	0.036	0.051
Pb	0.178	0.168	0.185
Ni	0.142	0.122	0.145
Cd	0.019	0.011	0.021
Fe	0.314	0.301	0.318
Mn	0.025	0.018	0.028
Cu	0.248	0.230	0.253

The large amount of scrap material, has a major impact on air, water and soil, and is a potential pollutant for human health. The level of concentration of heavy metals in landfills stratified represents major troubles for the public.

The possibility of their penetration into surface waters and groundwater, the surrounding land, especially agricultural land, it is more than evident in the connection goes through the food chain. For this reason, we have analyzed the concentration of heavy metals in soil and water. Concentration of heavy metals in soil - dump, three sampling points is different, and it differs depending on the concentration of the landfill (after throwing material process technology) and real assessment of analysis of samples is extremely disturbing, especially agricultural land, perhaps it henceforth cultivated land for each year of wheat and other agricultural crops.

Also in Wells ($W_{-1, 2, 3}$), the concentration of these elements is very evident, especially in W_3, where rainfalls perhaps rinsing dump and collected directly into the foundation of the well, which also is surrounded by the junk work factory, where the physical aspect more closely the factory, not more than 20m, but can also be any other diversion of underground channels that have leaked from the factory mechanism, at a time when it has developed

its activity working. To the values of the elements, earth, environment, seen as the highest value, especially in the sampling point, S_1-earth values, Cd ; 13.71 mg/kg, Zn ; 0.628 mg/kg, Cu ; 0.196 mg/kg, Ni ; 0.158 mg/kg, and Fe ; 0.573 mg/kg, as the values of which have come about as a result of landfill material because junk in the yard of the factory, but can also be derived from the interior of the earth geology. Even sampling points S_2 and S_3 - earth values behave as related elements and most of these elements under enormous values exceed every international standard, but more disturbing is the fact S_3-ground sampling point where now this land sown with wheat every year and the related contamination in the food chain with the world of the living and deposited in the body.

The results obtained for heavy metals in water, compared with the EU standards, show an increase over the allowable limit, the concentration of these elements in the environment. In wells, the sampling points ; S_1-Well-$_1$, S_2- Well-$_2$, S_3- Well$_{-3}$, elements values are presented as ; Pb; 0.178 mg/dm^3, Zn; 0.293 mg/dm^3, Cu; 0.248 mg/dm^3, Ni; 0.142 mg/dm^3, Fe; 0.314 mg/dm^3, as higher values, which almost exceed the values according to the EU-s enormous and WHO, while elements such as; Cd; 0.019 mg/dm^3, Cr; 0.048 mg/dm^3 and Mn; 0.025 mg/dm^3, appearing as lower value in comparison with other elements analyzed.

In Figure 1, we can see that the sampling points household items were taken in most effluent, where we thought that invades pollution in water points and soil sampling, in terms of pollution from landfill scrap material is poured from the factory after technological processes therefore we have analyzed the results of the samples in these environments and have found high levels of heavy metals, especially, Cd and Zn, but Cu, Ni, and Fe, which are present in high amounts. From these results it is clear that the battery factory, has affected the concentration of heavy metals in the analyzed environments, land and water, as when it has developed its activity and now also when this activity has finished, because the material scrap has remained there ever again is not treated, controlled or removed from the place of occurrence. It should be emphasized that this material is mixed with soil land both within and outside the factory yard, which actually now on this land is planted crops such as wheat, corn and many other agricultural different, colorful world that is very disturbing and while not disastrous, causing many cancerous diseases. Therefore we think that should be the removal of the surface layer of soil, which is considered as contaminated or cover it with a layer other land although this method is rarely used because the cost of this action is very high also contaminated soil removed from the surface, deposited from the pit, a certain way or to be cleansed with thermal and chemical methods, even though these treatments damage the organic matter of soil nutrients and biomass. Should become contaminated soil coverage with a layer of soil, "healthy", be made in a thickness of at least one meter, the two layers usually are isolated from each other with a plastic sheet, but its stability is time suspicious (due to the action of roots, the life of microorganisms in soil, and various gases, etc).

CONCLUSION

Disposal of urban and industrial waste, can lead to soil contamination as a result of accumulation of aerosol particles emitted during combustion of materials containing metals, where the disposal of various metals improperly (or forbidden), by starting out as a small batteries (Ni-Cd batteries and Hg) to different parts of the car p.sh, Pb batteries in small areas, can lead to a greater concentration of heavy metals in the soil. Based on the experimental results obtained in this paper, we can conclude that the ground in the yard of landfill and land around the landfill which has been planted with wheat and other crops, is contaminated with heavy metals. On land, we have found the real value of the concentration of heavy metals, where the higher values are presented as values elements, Cd; 13.71 mg/kg, Zn; 0.628 mg/kg, Cu; 0.196 mg/kg, Ni; 0.158 mg/kg, and Fe; 0.573 mg/kg, compared to the other elements analyzed; Mn, Cr and Pb, which are recorded as low values in soil samples. It is very logical but also from scientific consciousness, that the longer the stay in terms of time, material junk in that country, the concentration of heavy metals is growing only because of heavy metals in soil completion with additional material and fissionable their time is much longer than when they are free and in a soluble form, or decomposable by vegetation, microbial decomposition and compactness with other material. While terms of the sampling points in water samples as groundwater wells, Well-$_{1,2,3}$, known to contain mineral salts and other inorganic compounds and mainly found in concentrations greater than their concentrations in surface water, ground water because of melt those substances while penetrates earth. Also, water samples were read real value of the concentration of heavy metals in the sampling points analyzed, taking into account that the values are presented as elements, Pb, Zn, Cu, Cd, Ni, Cr, Fe and Mn, where value as seen older ones, Zn, Pb, Fe, Cu, and Ni, and low value ones, Cr, Cd and Mn. Based on comparative values allowed standards with EU and WHO, groundwater's, analyzed elements have passed the limit allowed in the specified environment.

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