# **Research Article**





# Impact of the Cement Factory in "ElezHan" in Pollution of the Water of River Lepenc and Agricultural Soil around of This Area

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#### ABSTRACT

During this research, we have analyzed heavy metals in three different environments, such as: the water of the river Lepenc, fallow land around the river and fertile land that are included in this area. Samples were analyzed carefully and are defined elements such as Pb, Zn, Cu, Ni, Fe and Mn. In the three areas analyzed, are found in trace elements of these metals, exceeding each level allowed under international standards for heavy metals in the environment (samples) were examined. So we very carefully, we have analyzed and researched, the presence of trace elements and their impact on the environment, so that the results achieved and the values presented in these environments are extremely distressing for the ecosystem.

Keywords: 'Sharrcem ElezHan', Heavy metals, Water, Sludge, Soil, Lepenc.

#### **INTRODUCTION**

ement factory in Elez Han, has produced cement in the last three decades. Production technologies of the factory, after technological processes, such as waste has remained a large amount of scrap material, and still unusable, where the contents such as trailer, is considered to have a large amount of heavy metals as; Zn, Pb, Cu, Fe, Ni, and Mn, and by tracking the channel, around 200 meters, this material is thrown directly into the river Lepenc, which causes pollution reliable, and more so this pollution affects when now known that the improved capacity of the factory production increased after privatization. Geographic location of the factory, enabling you to waste after the shutdown process free pass through the channel tracking directly on the river Lepenc, untreated properly and with a nice large contamination of different chemical elements. Accordingly, the when we consider that Lepenc found near the river and agricultural areas surrounding villages where residents grow fruit and vegetables, the irrigation of these types of fruit and vegetables, from Lepenc do then this gives us understood that one aspect of the food chain, residents are directly attacked by this pollution, especially from heavy metal presence, where these toxic elements can accumulate in the body and cause various diseases carcinogenic. Elements that we have analyzed, the samples taken on the environmental, soil, water and sludge have as source remains after technological processes of factory, especially limestone, which can be as impurities; MgCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO<sup> $\perp$ </sup>. Therefore, the factory in question is the source of water pollution, sludge and soil, with heavy metals, in this locality and we have estimated that in the analyzed environments, are present elements as, (Pb, Cu, Zn, Fe, Mn, and Ni) in the form of inorganic compounds<sup>2</sup>. The first case of mixed material, between limestone, clay and other allowances, after baking, will result in the benefit of a delicatessen product, clinker, with certain chemical composition and usually this ratio between mixing, limeclay is 3:1, where after technological processes, residual material (debris-free usable), will have a negative impact on air pollution, water, sludge and soil<sup>3</sup>, where heavy metals associated with various forms complex junk material, pose a pollution environments analyzed. Therefore to bring concrete results and more reliable in this work, we have analyzed the impact of the factory, we have carefully analyzed the concentration of heavy metals in water, river sludge and agricultural areas Lepenc, with three sampling points, for each environment.

## **MATERIALS AND METHODS**

We have done the analysis and evaluation of water samples, sludge and soil, the concentration of heavy metals in these environments. Samples were taken in the period June-2013. All chemicals needed for the determination of physical parameters - chemical micro pollutants and parse macro pollutants samples were chemical purity "pro analysis" (free). The method used for the determination of heavy metals has been SAA methods. Treatment of samples was done in the laboratory of environmental chemistry and chemical technology, in the department of chemistry, while measurements and reading results with SAA technique, are made in the laboratory of hydro-meteorological institute of Kosovo.

Making and preparation of soil samples for chemical analysis was done by methods which we found in the literature for soil analysis. The amount of sample for analysis that we got was 3-5 kg at each sampling points in



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different layers of soil from 10, 20 and 30 cm in depth agricultural areas. Soil samples for analysis were taken at three sampling points.

The first sample site has been;  $S_1$ -agricultural areas, neighborhood Rana, 2km before you depleted Sharrcem factory junk in the river waters Lepenc as reference points.

The second sample site;  $S_2$ -agricultural areas, village Seqishtë, 1 km after the factory junk in the river waters pour Lepenc. The third sample site,  $S_3$ -agricultural areas, 3-km neighborhood Lloka, after the factory junk in the river waters pour Lepenc, in order to see the ability of self-purification, ( autopurification ) river water.

Also, water samples were taken at the same sampling points on river Lepenc, 25cm below the water surface, 25 cm above the bottom and a layer of intermediaries, given that the river at this time, we were packed bed trailer and a normal stream.

The first sample site: the river,  $S_1$ -Lepenc visa-line with Rana neighborhood. The second sample site: the river  $S_2$ -Lepenc line drawings Seqishtë neighborhood, and the third sample site. The River,  $S_3$ -Lepenc visa-line with the neighborhood (area) Lloka. Also, the sludge samples were taken at the same sampling points, such as:  $S_1$ -sludge,  $S_2$ sludge and  $S_3$ -sludge, which are taking water samples, ie at the end of the river and on the shore of river Lepenc.

In Figure 1, we can see that the sampling points were obtained in the effluent points, where we thought that invades the pollution in the sampling points of water, sludge and soil, in terms of pollution from factories with junk material after gaining technological process of cement.



Figure 1: Sampling points for soil, sludge and water samples

From soil samples taken are representative prepares samples for chemical analysis, so that the accumulated dust is well mixed and homogenized and their division into four parts, the initial amount is reduced to about 1 kg. This further amount of sample is mixed and crushes the oppressor avan porcelain with sieves and sieve in the 100 to 200 mass. The material obtained was dried at 105  $^{\circ}$ C until constant weight is transferred to the special

container and then, samples prepared in this way were used for further chemical analysis. Ways of taking samples and sludge treatment has been the same as to soil samples.

Samples collected from polluted water, some components can be volatile, easily interact distributed across 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 °C), and conservation of samples should be done by adding HNO<sub>3</sub> concentrated up to pH = 3.5, and so samples should be stored in closed containers and dark place for use as necessary.

Polyethylene bottles are showing better preservation of the sample, before the determination of most elements track, 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 to digested samples 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 digestive process.

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

During melting, ie 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 soil and sludges, in order to determine heavy metals, we use mixtures of acids, nitric and perchloric acid (1:4). Sample scaled 0.25g ago 105°C dried and dissolved in 10 ml have mixture of perchloric acid and nitric acid. Samples were set in sand bath in digestor and are evaporated until dry.

Then the rest've 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 un melted 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 points conservation with concentrated nitric acid.

From the total volume of 1 L and slowly samples measured at a constant temperature, evaporated to about 10 ml in volume. Samples with a volume of 10 ml poured into 100 ml of normal container and then acidification with 1 ml of HCl and mark where the sampling sites are ready for analysis.



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## RESULTS

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, Pb, Cu, Fe, Mn and Ni), in soil, sludge and water.

**Table 1:** Presentation values of concentration of heavymetals in soil, samples expressed in mg/kg

Elements	Sample I / SAA	Sample II / SAA	Sample III / SAA
Pb	0.516	0.700	0.435
Zn	0.394	0.547	0.447
Cu	0.248	0.379	0.273
Ni	0.142	1.024	1.011
Fe	0.963	1.241	1.125
Mn	0.516	0.627	0.546

**Table 2:** Presentation values of concentration of heavymetals in water, samples in mg/dm<sup>3</sup>

Elements	Sample I / SAA	Sample II / SAA	Sample III / SAA
Pb	0.049	0.094	0.058
Zn	0.169	0.190	0.172
Cu	0.168	0.196	0.181
Ni	0.060	0.074	0.067
Fe	0.537	0.573	0.549
Mn	0.025	0.035	0.029

 Table 3: Presentation values of concentration of heavy

 metals in sludge, samples expressed in mg/kg

Elements	Sample I / SAA	Sample II / SAA	Sample III / SAA
Pb	0.621	0.789	0.695
Zn	0.791	0.803	0.797
Cu	0.267	0.275	0.270
Ni	0.902	0.984	0.938
Fe	0.675	0.691	0.683
Mn	0.384	0.393	0.388

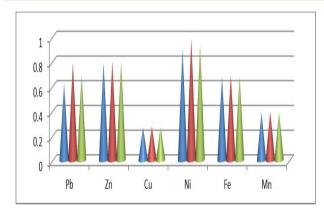


Figure 2: Samples of Soil Sampling Points

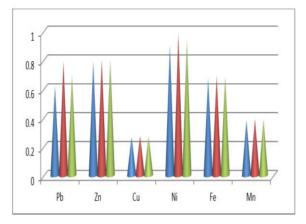


Figure 3: Samples of Water Sampling Points

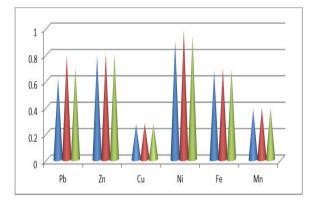


Figure 4: Samples of Sludge Sampling Points

Concentration of heavy metals in agricultural areas, in three sampling points is different and it varies depending on the concentration of the material after molding process technology and real assessment results presented to the analyzed samples, is extremely disturbing, especially agricultural areas, where these lands are cultivated with wheat every year and other agricultural crops. Also in the river water Lepenc, the concentration of these elements is very evident, especially in the S<sub>2</sub>-water, where behind depleted of solid-liquid material, encounter waste collected directly in the river bed, where the physical aspect is more near the factory, not later than 200m, but could be any other diversion of underground channels that have leaked from the factory mechanism, when the factory operates its working. Also in the sludge samples analyzed, read the values of concentration of heavy elements, especially after rains where the atmospheric accumulation of silt becomes large in the river bed and bank of contamination. To the concentration of elements in the environment of agricultural areas, are seen as higher values, especially in the sampling point, S2- agricultural areas, values of Ni; 1,024 mg/kg, and Fe; 1,241 mg/kg, as high values which consequently have come due to pollution from the factory junk material, which flows into the river, which is located on the bottom side of the factory, but another quantity, can also be geological origin of the interior of the earth, because this land lies with the large mass of various forms of limestone and clay structures, but do not forget the other facts, that the

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bed of the river on both sides of the trailer are located landfills various large scrap metal, which consequently impact these may have on their own, with heavy metal contamination, especially after the corrosion reactions and rinse after heavy weather. Even at the sampling point, S<sub>3</sub>- agricultural areas, values behave as related elements and most of these elements exceed enormous values by any international standard, but more disturbing is the fact S<sub>2</sub>- agricultural areas, sampling point where it now sown with land each year wheat and related contamination in the food chain with the living world and deposited in the body. While in the sampling point, S<sub>1</sub>agricultural areas, (Sample Reference) values are recorded as elements of high value, but the S2agricultural areas, values increase significantly as the impact of the factory is directly on the river and the land around contamination. The results obtained for heavy metals in the river water Lepenc, compared with the EU standards, show an increase over the allowable limit, the concentration of these elements in the environment. In the sampling point; S<sub>1</sub>-water, S<sub>2</sub>-water and S<sub>3</sub>-water, as the value with the highest concentrations are presented as elements; religion; Fe; 0.573 mg/dm<sup>3</sup>, Cu; 0.196 mg/dm<sup>3</sup>, Zn; 0.190 mg/dm<sup>3</sup>, especially in the second sampling point, S2-water, where the factory is a direct impact on the river. Therefore, these high values, almost enormous values exceed EU standards and WHO's, while elements such as; Pb; 0.094 mg/dm<sup>3</sup>, Ni; 0.074 mg/dm<sup>3</sup> and Mn; 0.035 mg/dm<sup>3</sup>, as presented lower values in comparison with other elements analyzed. Also to sludge samples are read, the values of concentration of heavy metals, especially the values of elements such as, Ni; 0.984 mg/kg, Zn; 0.803 mg/kg, Pb; 0.789 mg/kg, and Fe; 0.691 mg/kg, as values that exceed every international standard for permissible levels of the element in this environment, while elements such as Cu; 0.275 mg/kg, and Mn; 0.393 mg/kg, lower values are compared with the concentration of elements such as; Ni, Zn, Pb and Fe. From these results it is clear that cement factory has a potential impact on the concentration of heavy metals in the analyzed environments, soil, sludge and water, because the material spilled junk after the process it directly affects Lepenc river pollution and agricultural areas, especially heavy metals, for which the results speak extracted from samples analyzed.

# DISCUSSION

Based on the experimental results obtained in this work, we can conclude that; agricultural areas surrounding the cement plant, which is planted with wheat and other crops, is polluted with heavy metals. On land, we have found the real value of the concentration of heavy metals, especially at the sampling point, S<sub>2</sub>-agricultural areas, where the highest values are shown as elements, Ni; 1,024 mg/kg, and Fe; 1241 mg/kg, compared with the other elements of the analyzed; Mn, Zn, Cu and Pb, which are recorded as the lowest value in the sampling points; S<sub>1</sub> and S<sub>2</sub>, in agricultural areas. It's very logical, but also from scientific consciousness, that the longer the residence time, junk material in various forms couplings, the concentration of heavy metals is growing only because the heavy metals in the soil, with complex additional material and half time degradation is much longer than when they are free and in a soluble form, or of biologically decomposable by vegetation, microbial decomposition and compactness with other material.

Also, water samples were read real value of concentration of heavy metals in the sampling points analyzed;  $S_1$ -water,  $S_2$ -water and  $S_3$ -water, taking into consideration that the values are presented as elements, Pb, Zn, Cu, Ni, Fe and Mn, where values increased as they are seen; Fe; 0.573 mg/dm<sup>3</sup>, Cu; 0.196 mg/dm<sup>3</sup> and Zn; 0.190 mg/dm<sup>3</sup>, as higher values in the second sampling point,  $S_2$ -water, where the impact is direct factory in the river, while elements such as; Pb; 0.094 mg/dm<sup>3</sup>, Ni; 0.074 mg/dm<sup>3</sup> and Mn; 0.035 mg/dm<sup>3</sup>, appear as lower values in comparison with other elements analyzed in these sampling points.

Do not forget that one of the EU's criteria for admission of Kosovo to the EU, it is also the treatment and regulation of transboundary surface water infrastructure (lakes and rivers), so anyway our country must also meet this standard because well as from the neighboring state, we often receive complaints beautiful for this phenomenon.

While, in terms of concentration of heavy metals in the sludge samples, the sampling points;  $S_1$ -sludge,  $S_2$ -sludge and  $S_3$ -sludge, read values are high concentrations of heavy metals, especially in the second sampling point, the values of the elements as, Ni; 0.984 mg/kg, Zn; 0803 mg/kg, Pb; 0.789 mg/kg, and Fe; 0.691 mg/kg, as values that exceed all international standards for permissible levels of the element in this environment, while elements such as, Cu; 0.275 mg/kg, and Mn; 0.393 mg/kg, values are lower compared to the concentration of elements such as Ni, Zn, Pb and Fe.

Therefore, based on comparative values, allowed under EU standards and WHO, for heavy metals in agricultural areas, surface waters and sludge's, elements analyzed in these environments, have passed the limit allowed by any international standard.

# REFERENCES

- 1. Shehu E. Fundamentals of Chemical Technology and Environmental, University of Tirana, Faculty of Natural Sciences, Tirana-Albania, u-6, 2006, 103-119.
- Chirenjet T, Ma Q. Heavy metals in the Environment. J. Environmental, University of London-London, u-28, 1999, 760-773.
- Pula Xh. Beqiri L. Chemical Technology, University of Pristine, Faculty of Mathematics and Natural Sciences-Pristine-Kosovo, u-14.3.1, 2010, 244-252.
- 4. Fernandez L, Lopez A. Trace elements in coal and there behaviour in large station up during Combustion. Fuel, University of Cambridge-UK, u-74, 1995, 331-339.



Available online at www.globalresearchonline.net

- 5. Manahan S. Environmental Chemistry, 7<sup>th</sup> Edition, Boca Raton, Florida, USA, 2007, 492-566.
- Çullaj A. Theory, exercises and laboratory work, Environmental Chemistry, University of Tirana, Faculty of Natural Sciences, Tirana-Albania, u-7&12, 2010, 128-280.
- Fulek Ar H, Dave M. Deposal of fly ash. Environmental problem. International Journal of Environmental Studies, 26, 1986, 191.
- Demaku S, Shehu I, Jusuf S, T Arbneshi, Dobra B. Heavy Metals in Coal Ash, Soil, Water and sludge near the Two Coal - Fired Power Stations in Kosovo, Chemistry Department, University of Valencia, str. Mother Teresa 5,10000 Pristine, Kosovo, 2011, 412-416.
- Btu Lowicz K, Kotlinow No T, Sto Biecki M, Dechnik K, Obtu Lowicz M, Manecki A Manecki M, Schejbal - Chwastek M. Environmental Air Pollution and Pollen allergy, Annals of Agricultural and Environmental Medicine, 3(2), 1996, 131.
- 10. Daka S. & Ahmad F. Hydro in Kosovo yesterday, today and tomorrow. Collection of papers. The second seminar of hydro Pristine, 2002, 41-58.
- 11. Filipovic i & S. Lipanoviq. General chemistry and inorganic, ISBN, 1995,-954 -0- 30905-8.
- 12. Gjorgieva D, Kadifkova P, Tatjana A, Ruskovska T, Bačeva K, and Stafilov T. Influence of Heavy Metal Stress on Antioxidant Status and DNA Damage in Urtica dioica, Biomed Res Int, 10, 2013, 276-417.
- Shehu I, Demaku S, Morina M, Malsiu A, Bytyqi H, Behrami A. Heavy metals in soil and vegetables in anadrinia region as a result of the use of pesticides, herbicides and fertilizers, Journal of Chemical and Pharmaceutical Research, 7,8, 2015, 923-927.

- 14. Athar M. Vohora S. Heavy Metals and Environment, New International, Wiley Eastern, New Delhi, 1995, 31–38.
- Shehu I, Demaku S, Bytyqi H, Malsiu A, Musliu D, Behrami A. Pollution of the Toplluha River from Human and Industrial Activity in the Town of Suhareka J. Int. Environmental Application & Science, 9, 2014, 487-492.
- Pančevski Z, Stafilov T, Bačeva K. Distribution of heavy metals in some vegetables grown in the vicinity of lead and zinc smelter plant, Section of Natural, Mathematical and Biotechnical Sciences, MASA, 35, 2014, 25–36.
- 17. Pula Xh, Beqiri L. Chemical Technology, unit-University of Prishtina, Faculty of Mathematics and Natural Sciences-Pristina-Kosovo. 1985, 244-252.
- Elezaj Z, Kodra A. Geology of Kosovo unitUniversity of Prishtina, Faculty of Mathematics and Natural Sciences, Pristine, Kosovo, 2007, 2007, 189-214.
- 19. Çikatovo Goles, Investing in Nickel Mines Glogovc-Kosovo, 2013.
- Demaku S, Shehu I, Rysheni E, Dobra B, Jusufi K. Impact of Industrial Complex "Ferronickel" in Pollution with Heavy Metals in Soil, Surface and Ground Water of this Location. International Journal of Pharmaceutical Sciences Review and Research. 35(2), November - December 2015, 43, 240-244.
- http://www.epa.gov/wastes/hazard/testmethods/sw846/p dfs/3015a.pdf, METHOD/3015A Microwave assisted acid digestion of aqueous samples and extracts, Environmental Protection Agency, USA.
- 22. http://www.epa.gov/wastes/hazard/testmethods/sw846/p dfs/3052.pdf,METHOD/3052 Microwave assisted acid digestion of siliceous and organically based matrices, Environmental Protection Agency, USA.

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