Ecotoxicity of the leachate chemical analysis of the trace elements in natural sources of surface water Kosovo

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Abstract
The main factor for the existence of life on our planet is water. Water is the essential substance of living on earth. Water was created much earlier than his life .The quality and quantity of water for man throughout history were a vital factor in determining his welfare. In many countries, especially in countries with low standards are very prevalent disease with disastrous consequences, due to pollution and water shortage Supplying the population with drinking water and hygienic clean view is a prerequisite for good health result of industrial waste, toxic metals often exceed the permitted limit toxic and eco-caused serious physical changes in living organisms. For this reason analytical methods should be used with high sensitivity for the determination of their concentration because of heavy metal ions in natural waters are contaminated at very low concentrations (approximately 1 μg per dm ^{3}).

Keywords: Of heavy metals in waters.

Introduction
Clean Water pollution is any deviation Natural qualitative and quantitative chemical composition and natural qualities, physical and biological characteristics of which have adverse consequences for human health, the economy and the ecosystem in general [12].

Reasons of natural surface water pollution can be found in urban development and intensive industrialization of human society.

Today rivers have become collector of all wastewater influent, urban and industrial.

Nature is different pollutants: organic matter, inorganic (that decomposed stages), synthetic materials (not biologically decomposed) and heavy metals that are not subject to decomposition [11].

Water discharged from the various technological processes contain a large amount of heavy metals such as Pb, Cd, Cu, etc.. which are highly toxic to living organisms, and they become dangerous when considering the fact that some of their body accumulate and concentrate having fatal in high concentrations and even cause death.

Sources of heavy metals except that the genesis of the various departments of industry, they also come from other sources such as mining, urbanization, agriculture etc. To reduce the environmental consequences of water before discharge must undergo several cleaning processes in physico-

mechanical, chemical and recently biological. Në study of heavy metals is given special importance for two reasons, as a result raising awareness of environmental protection on the one hand and on the other the development of new methods made possible the identification and measurement of their concentration.

For realistic assessment of the degree of pollution of a natural ecosystem (air, water, soil) is necessary to know the exact concentrations of heavy metals [14].

An element is considered toxic if it causes a reduction of the metabolic activity of living cells or reduce the population of the species, when present in relatively small concentrations because many substances that are non-toxic under normal conditions, if the organism toxic amounts included in large [15].

Often in natural waters belongs some elements that have toxic chemical effects [21].

Lead and its soluble salts are poisonous substances. They show a tendency to accumulation in living organisms, and mostly affect the central nervous system.

Biologically more susceptible to lead poisoning, in any circumstances and exposure doses are newborn children [22]. It was found that acute lead poison is strong, which is easily absorbed if it is in the form of soluble compounds. [23] However, the compounds less soluble and insoluble toxic substances that cause chronic poisoning. Lead acts detrimental to enzyme blood, respiratory system, cardiovascular system and cellular.

In drinking water quantity allowed is 10 μg for dm^3. concentration the top causes of death.

Cadmium and its compounds are highly toxic. The main sources of cadmium contamination are: burning oil, tires, plastics and other materials. The effects of acute cadmium poisoning in humans are very serious as high blood pressure, kidney damage, cancer, etc. Toxic effect of cadmium in water decreases with increasing water hardness, due to increased water carbonates. It is known that heavy metal carbonates are less soluble in water and thus a part of dissolved cadmium removed from the water. Copper is an important chemical element for human life and other living things, having an important role in metabolic processes, affects a number of enzymes and synthesis of hemoglobin. Copper taken with food and daily necessities are 2-5mg. In high doses is toxic and deadly, especially in children that causes liver disease [18].

Irritates the respiratory system and causes disease in the thorax, reduces hemoglobin and erythrocytes in the blood, hinders the healing of wounds, reduce concentration, etc. [19]. Zinc is found in natural waters in large quantities and therefore industrial waters contain higher concentrations of it. It is an essential and indispensable element for 160 enzymes. Daily necessities are 2-15mg zinc. Under these values, the body reacts with physical fatigue, depression, anemia, loss of appetite, diarrhea and slow healing of wounds.

Mercury is an essential element of respiratory cells, red blood cells and enzymes. Deal with food, daily necessities are 2-5mg, no toxic action, in high doses, especially in children causes liver disease, irritates the respiratory system, reduces blood hemoglobin and red blood cells and causes difficulties in endocrinological system. Mercury difficult to heal wounds and reduce concentration and memory. Manganese is found in nature in the form of oxides, silicates, carbonates, etc. Manganese is an essential element and enters in the composition of enzymes and negatively affects

their physiological function. Manganese is protective of biological cells from the damaging actions of free radicals.

Values under physiological quantities adversely affect the formation of teeth and bones. But on the contrary increase the amount of manganese adversely affects the respiratory system, cardiovascular, hematological, immunological and neurological. Surface and underground waters contain up to 0.3mg dm ^{3}.

The presence of arsenic in water comes as a result of the large collection of waste industriale.Arseni able elementary is not poisonous, but its ours +3 Neither is highly toxic, more than ours Neither +5. Arsenic compounds are highly carcinogenic and harmful act in living cells and in rind .According to EU directives (1990) normal doses of arsenic allowed in drinking water is 10μg per dm^3. Arsenic in small amounts is an essential element. Consumption of arsenic under physiological requirements quantity causes anemia and other health problems. Consumption during the arsenic causes cancer. Because of the advantages that presents such as low detection limits for many elements, very good selectivity and high accuracy. ICP-MS (kopuluar induction of plasma-mass spectroscopy) and ICP-OES (kopuluar induction of plasma-optical emission spectroscopy), are the most important fundamental analysis. Analysis of elements with ICP-MS method is implemented in commercial laboratory "ACTLABS" in Ontario Canada. As the atom samples and ionized plasma serves Torch. For the analysis of liquids, aerosol samples put into a state. The plasma torch earned positive metal ions, which through a special device placed in MS four polar. Acquired spectra are very simple, similar to optical spectra. They consist of a series of points of isotopes of each element that is in the sample. ICP-MS spectra used for qualitative analysis and quantitative analysis. Sampling of river water Lumbardh is made with 16.04.2013. The water level was quite convenient for sampling. Sampling points were selected, taking into account characteristic of countries which have received pollution from anthropogenic activities (traffic, sewage, agricultural land, etc.)

Preparation of water samples for chemical analysis

According to international standards on chemical and biological indicators of 1978, the water quality of the river is classified Lumbardhi grade II ..

Preparation of samples for analysis is done so that from each sample was divided by a quantity for determining various parameters.

The rest of the water is conserved with concentrated HNO_3 where (1 dm^3 sample was treated with 1 cm^3 HNO_3, 63%) and is sent for analysis multielementare (100 cm^3).

Sample	Location	Time	Dissolved substances TDS/λ	Date / time ofsampling	Type of relief	The water level	Land Use	Potential Pollutants
L1	Haxhaj	sunny	47	16.04.2013 12^{50}	Steep	The above	Residence, forests, traffic	Little credibility
L2	Kuqishtë	Sunny	111	16.04.2013 13^{35}	Steep	The above	Residence, forests, traffic	Residence, forests, traffic
L3	Pejë (te kisha)	Sunny	114	16.04.2013 14^{30}	Steep	The above	Residence, forests, traffic	Residence, forests, traffic
L4	Pejë (te tregu)	Sunny	116	16.04.2013 15^{10}	Soft	The above	Residence, forests, traffic	Residence, forests, traffic
L5	Klinë (para ure)	Sunny	140	16.04.2013 16^{10}	Soft	The above	Residence, forests, traffic	Residence, forests, traffic
L6	Volliak	sunny	158	16.04.2013 17^{10}	Soft	The above	Residence, forests, traffic	Holiday

Table 1. River water sampling points Lumbardh with detailed descriptions

Physico - chemical parameters of water river Lumbardhi

Water temperature was measured at sampling points digital thermometer, pH was measured with pH meter "HANNA" is measured electrical Conductivity "inolab" and the turbidity value is measured turbitimetrin "HACH" 2100P ISO. The parameters are presented in Table 3.

As in Table 1 and 2 are presented alkalinity in the presence and in the presence metiloranzhit fenolftaleinës, general hardness (total and transient), the concentration of chloride ions, the concentration of calcium oxide and potassium permanganate spending and . table. presented nitrates, sulphates, nitrites and phosphates.

Sampling location	Temp. and Water / ° C	Dissolved oxygen	electrical conductivity/Ms cm-1	pH	Turbidity / NTU
L1	10.3	8.9	95	7.31	1
L2	10.9	9.63	218	7.95	1.1
L3	11.1	9.60	220	7.78	1.8
L4	12.0	9.72	226	7.83	2
L5	13.2	9.25	282	8.01	41
L6	11.3	11.3	240	7.90	27.7

Table 2. Temperature, conductivity, pH and turbidity in the sample rate

Sampling location i	Alkalinity mA	Alkalinity pA	Total hardness/°D	Transitional strength../°D
L1	11.9	1.5	7..12	1.22
L2	23.7	3.08	7.13	1.66
L3	23.8	3.15	7.41	1.68
L4	23.5	2.0	8.77	1.65
L5	15.4	3.5	8.84	1.42
L6	27.6	3.06	7.36	1.35

Table 3. Alkalinity, total hardness passerelle

Sampling location i	γ(CaO) /mg dm^{-3}	γ(MgO) /mg dm^{-3}	Expenditure i $KMnO_4$ /mg dm^{-3}	γ (Cl^-) /mg dm^{-3}
L1	16.8	5.5	3.08	3.45
L2	57.68	7.28	6.17	1.41
L3	56.95	5.9	6.17	1.43
L4	54.32	15.22	7.71	2.12
L5	66.08	5.6	7.71	2.13
L6	66.09	5.40	9.26	2.18

Table 4. Calcium and magnesium oxide, permanganate concentration and expenditure of chloride ions in water samples.

Sampling location i	SO_4^{-2} /mg dm^{-3}	NO_2^-/mg dm^{-3}	NO_3^- /mg dm^{-3}	PO_4^{-3} /mg dm^{-3}
L1	7.07	0.02	0.0	0.051
L2	3.68	0.02	0.0	0.002
L3	1.76	0.032	0.1	0.009
L4	7.94	0.03	2.9	0.017
L5	9.976	0.065	1.4	0.011
L6	10.03	0.089	1.2	0.010

Table : 5 determination of sulphates and nitrates

ICP-MS analysis AND ICP-OES, micronutrients in river water Lumbardhi

Multielementeve analysis is performed with ICP-MS techniques and ICP-OES commercial laboratory "ACTLABS" in Ontario, Canada. 67 elements are defined, which are presented in Table 8. . Elements such as Li, Be, Sc, V, Cr, Ge, Se, Br, Mo, Ru, Pd, Ag, Sn, In, The, Tm, Lu, Hf, Ta, W, Os, Pt, Au, Hg , Ti and Bi are found below the limit of detection with appropriate techniques.

Element μg/ dm^3	**Sampling location**					
	L1	**L2**	**L3**	**L4**	**L5**	**L6**
Ca	12400	39500	39800	51200	32300	56600
Na	927	806	1370	2110	730	2180
Li	<10	<10	<10	<10	<10	<10
Be	<1	<1	<1	<1	<1	<1
Mg	1560	3810	3600	4740	2770	3990
Al	<20	55	62	248	57	240
Si	2100	<2000	<2000	2400	<2000	<2000
K	640	550	530	630	330	710
Sc	<10	<10	<10	<10	<10	<10
Tl	<1	1.1	<1	1.5	<1	<1
Cr	<5	<5	<5	<5	<5	<5
Mn	1.7	8.2	9.3	51.4	4.4	12.3
Fe	<100	130	100	490	<100	
Co	<0.05	0.11	0.18	0.65	0.06	0.99
Ni	<3	<3	<3	3.5	<3	5.6

Table 5. The concentration of elements in 6-sampling points in the river water

Element μg/ dm^3	Sampling location					
	L1	**L2**	**L3**	**L4**	**L5**	**L6**
Er	<0.01	0.01	<0.01	0.04	<0.01	0.07
Tm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Hf	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ta	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
W	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Re	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
Os	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pt	<3	<3	<3	<3	<3	<3
Au	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Hg	<2	<2	<2	<2	<2	<2
Ti	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	36.7	10.7	8.74	22.9	5.82	13.6

Th	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
U	0.04	0.12	0.16	0.24	0.11	<0.22

Table 6. The concentration of elements in 6-sampling points in the river water Lumbardhi

- ✓ The experimental results obtained during tests in the river water are important indicator Lumbardh and realistic picture of water quality in the river. From the analysis of river water Lumbardh water temperature varies from 10.3 (L1) -13.2 (L5)
- ✓ Temperature of water with low sampling recorded in L1 and L5 higher. Registered dissolved oxygen ranges from 8.9 (L1) -11.3 (L6) mg / L.
- ✓ Përqueshmëria registered electrical ranges from 95 (L1) -282 (L5) μs / cm, përqueshmëria with low sampling is registered in L1 and L5 higher.
- ✓ The concentration of hydrogen ions registered PH ranges from 7:31 (L1) -8 (L5), with low PH is in L1 and the highest in L5.Turbiditeti ranges from 1 (L1) -27.7 (L6) NTU.
- ✓ dissolved substances TDS / λ ranging from 47 (L1) -140 (L5) TDS / λ.Vlera with low L1 is high and the total L5.Fortësia ranging from 7:12 (L1) -8.84 (L5) OD , the above value is in the lower L5 and nëL1.
- ✓ transition strength ranges from 1:22 (L1) -1.68 (L3) OD, with the lowest values in L1 and L3 higher. The growth of these parameters along the river flow resulting from Lumbardh added salts in water and other primes.
- ✓ alkalinity of the water in the presence of indicator metiloranxh varies from 11.9 (L1) -27.6 (L6), whereas in the presence of indicator fenolftaleinë values ranging from 1.5 (L1) -3.5 (L5). Since resorts.Saranda river flow have different algal organic preparations, but not in large quantities, potassium permanganate spending has been rising along the river flow.
- ✓ The amount of chloride ranges from 1:41 (L2) -3.45 (L1) mg / dm^3, the amount of sulphate varies from 1.76 (L3) -10.03 (L6) mg / dm^3, the amount of nitrate ranges from 0.0 (L1) -2.9 (L4) mg / dm^3 and the quantity of nitrites ranging from 12:02 (L1) -0.08 (L6) mg / dm^3 and the amount of phosphate ranging from 0.002 (L2) -0.05 (L1) mg / dm^3. Heavy metals that are determined by ICP-MS method and ICP-OES are presented in Table 8, 9, 10 and 11.
- ✓ Our measurements show that the concentration of Mn ranging from 1.7 (L1) -51.4 (L4) μg / dm^3, Cu concentrations ranging from 3.4 (L3) -35.9 (L5) μg / dm^3, Zn concentrations ranging from 9.7 (L6) -59.2 (L3) μg / dm^3, Cd concentrations ranging from 0.17 (L4) -2.86 (L1) μg / dm^3, Pb concentration varies from 5.82 (L6) -36.7 (L1) μg / dm^3, etc..
- ✓ According to Croatian and Slovenian standards on the quality of surface water and drinking, we are serving to assess river water quality in Table 12 Lumbardh as some trace metals are classified in this class, according to the River Zn is classified Lumbardh mainly in class IItë, III, and IVtë, according Cd mainly in class IItë, III, and IVtë according to class IVtë Pb and Cu in class by IItë, III, and IVtë.
- ✓ The first category: no anthropogenic contamination with metals
- ✓ The second category: the concentration of toxic metals are more pronounced than usual concentrations of their natural.

- ✓ The third category: the toxic metal concentrations are lower than those of their permanent level.
- ✓ The fourth category: temporary metal concentrations are more pronounced than those of their permanent level of toxic and do not cause permanent toxic effects.
- ✓ The fifth category: metal concentrations are higher than the level of their permanent acute toxic and polluting permanent

Conclusions and recommendations

- Based on the experimental results of this study can be deduced. Methods applied for determining the physico-chemical parameters and the determination of trace elements in river water Lumbardh proved to be successful even require precision equipment used quite great job during analysis.
- Results show Lumbardh ot the river water is soft water.
- The level of concentration of several heavy metals that are determined by ICP-MS technique and ICP-OES eg Cu, Zn, Cd, Pb etj.kanë shown their concentrations increased. According to WHO and EU standards for drinking water, high pëqendrimet some elements are under the maximum permissible value (MAV).
- The aim of this study was the analysis of pollutants in the river water Lumbardh. The comparison of experimental results for samples of river water samples Lumbardh with countries in the region shows that the amount of pollution of river Lumbardh is not too high and that this water is classified according to several elements in the class who, by the River Zn Lumbardh is mainly classified into class IItë, III, and IVtë, according Cd mainly in class II, III and IV according to Pb in class IV and class according to Cu II, III and IV.

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