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Research Article

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Influence of power plants TC "Kosova", in contamination with heavy metals in the Sitnicë River, groundwater and soils in this zone

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ABSTRACT

In this research, we investigated the pollution of heavy metals that is released from power plants of Kosova in two seasons: summer and winter time. The elements that were in focus of the study are: As, Cd, Cr, Co, Fe, Mn, Ni, Pb and Zn. The study was concentrated in Sitnicë River; surface water, groundwater (wells) and soils around the region of TC''KOSOVA''. The concentration of metals in the surface water and underground water in the winter season are; Fe 0.19 mg/l, Mn; 0.258 mg/l, Pb; 0.174 mg/l and Zn; 0.238 mg/l. In the summer season, the concentration of heavy metals is increased, especially for; Co, Fe, Mn, Pb and Ni. Based on the results that we obtained, compared with international standards, some of the elements are in high concentration, more than maximum permitted allowed in both seasons, in almost every sampling point. While, metals; Cd and Co, are in permitted levels of concentrations as allowed by international standards.

Keywords: Power Plants " KEK ", heavy metals, water, river, Sitnica, soil

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INTRODUCTION

Results show that includes the representative state of the environment in the area of power plant "Kosova". The study object is Sitnicë River, delicate river that passes near coal power plants of Kosova. The focus of the study is the surface, groundwater and the soil samples around power plants of Kosova. It is a known fact, that over time, the amount of dust particles, rise from the stacks and the amount of ash, distributed by wind, contaminated more the environment with heavy metals [1]. In addition to this, coal exploitation activity as raw materials for power plants, digging excavators, transfer conveyor, separation before combustion process and storage, are sources of pollution with dust and particles coal in air, water and land surface around power stations [2]. This can be deduced from the fact that waters are polluted and without any inspection and consequently we have systematic degradation of waters without an effective system of management and protection [3].Small amounts of heavy metals may be necessary for health, but in increased quantities can cause acute or chronic diseases Discharging waste water, penetrate easily into underground layers, transferring different pollutants and heavy metals, which the plant absorbs and carries them into food chain.[4]. On the grounds that, coal has heavy metal content, which becomes more concentrated in the combustion and knowing also the potential activity of Kosovo's power plants for more than thirty years of power producing, these complexes have made uninterrupted pollution of air, soil, surface water and groundwater. The level of concentration of heavy metals in landfills stratified represents a major troubles for the public [5]. The impact of pollution from these energetic complexes, reaches several kilometres, however, we focused in the zones in most

affected by this pollution, such as Sitnicë river , which traverses the lengthwise (horizontal portion) of these territories, carrying with them the general pollution, of all types, exceeding the regional and local boundaries. Due to the fact that, power plants in Kosovo are coal fired ones, and by burning fossil material such as lignite, they leave waste ashes in landfills, tons of polluting particles in air, the residual in the soil etc., presenting the reason why these lands around Kosovo power plants should be carefully and frequently studied. Continuously monitoring enables to take appropriate steps with existing methods, the prevention and elimination of environmental pollution, where the contamination will not be a permanent risk to people's health and living organisms in general [6].

As we know heavy metals are not degraded pollutants, so they have deposit by the time in soil [7].

EXPERIMENTAL ACTION

2.1. Study zone

In the figure below (Figure 1) there is presented sampling points along the river Sitnicë (Vragoli to the village Gllavatin, in Fushë Kosova municipality); groundwater sampling points and soils sampling points of in these zones.

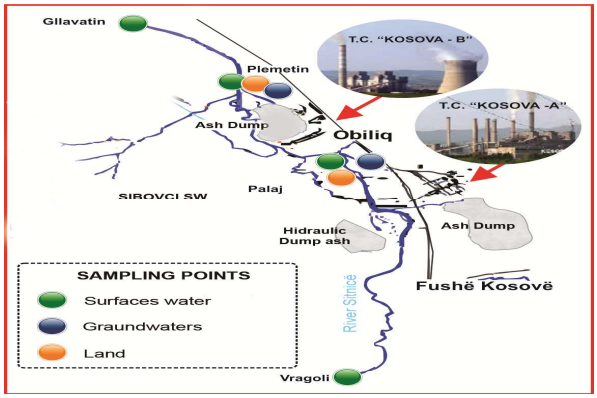

Figure 1. Schematic representation of sampling points

The samples were chosen from surface water, groundwater and soils farmland-wasteland. The samples were taken from the discharge tube, ash dumps etc., polluted from TC"KOSOVA". The goal of the study is the determination of heavy metals, whereas sampling was monitored in two season times; winter and summer of 2014.

2.2. Sampling procedure

Samples were picked carefully choosing coordinates though GPS (Magelan). Water samples were collected in polyethylene bottles (PVC), in the quantity of two liters. On the sampling points we immediately tested temperature and pH. In addition, we also preserve the samples using 1 ml of HCl per liter. For the water treatment we used method 3015. Soil samples were collected at 15-30 cm depth, in the amount of 3-5kg, which after mixing and divisions were reduced to 1 kg of mass. The soil samples initially were dried in air, and then dried in electric oven temperature in 105 ℃ to constant weight, then milled in proper dimensions using. The treatment of soil samples were done according to method 3052.

2.3. Sample preparation

In addition, water samples were first filtered, and then from each sample, we chose 50 ml and placed in teflon vessels. In each Teflon vessel were added up 1ml HCl and 5ml HNO_3, then we led the samples to mineralize in microwave digestion. After mineralization, samples drawn from microwave, filtered and then leveled up to 100 ml with distilled water.

While, for the treatment of soil samples, we initially weighted 3.5 g sample of soil and we placed in Teflon vessels, then we added 10ml of aqua for the digestion in microwave. After this phase was done, we filtered the samples and then leveled up with distillated water to 5ml.

2.4. Instrumentation

The samples were digested in microwave digestion system, berg of type and for the measurements we used different techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectroscopy (AAS) and DR 5000 UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

In the table below (Table 1) there are given the sampling points details including: coordinates and altitudes, sampling points for surface, groundwater and soil samples, the study villages etc.

Table 1. The sampling points, surface water, groundwater and soil

Winter season, January (14. 01. 2014);						**Summer season, June (10. 06. 2014)**					
Sample Places	Aer [^{O}C]	Wat [^{O}C]	pH	Coordinates	Altitude [m]	Sample Places	Aer. [^{O}C]	Wat [^{O}C]	pH	Coordinates	Altitude [m]
S_{O}.R.Sitnicë V.Vragoli	5.8	5.0	8.03	x =7 505 055 y = 4718 880	536	S_{O}.R.Sitnic ë V.Vragoli	24.1	22.1	8.12	x =7505 051 y=4718 817	537
S1.SW- River V.Palaj	5.9	8.0	8.65	x =7 505 041 y = 4726 202	532	S1.SW- River V.Palaj	24.6	22.3	8.76	x =7505 020 y =4726 299	532
S1.UG.Water Kastriot	5.9	10.0	7.60	x =7 505 519 y = 4727 132	529	S1.UG.Water M.Kastriot	25.2	12.3	7.8	x =7505 519 y =4727 132	529
S1.Wasteland V.Palaj	-	-	-	x =7 505 028 y= 4 726 460	533	S1.Wasteland V.Palaj	-	-	-	x =7505 025 y =4726 399	533
S2.SW- R.Sitnicë. V.Plemeti	5.9	7.3	8.41	x= 7 503 094 y= 4 729 746	530	S2.SWR.Sitni cë.V.Plemeti	25.4	20.6	8.62	x =7503 111 y =4729 736	530
S2.UG.W. V.Plemeti	5.9	10.02	7.74	x= 7 503 140 y= 4 729 777	528	S2.UG.W. V.Plemeti	25.4	16.0	7.54	x =7503 140 y= 4729 777	528
S2.Farmland V.Plemeti	-	-	-	x =7 503 108 y =4 729 772	531	S2.Farmland V.Plemeti	-	-	-	x =7503 101 y =4729 777	531
S3.SW–R Sitnicë.V.Glla v	4.9	6.6	7.20	x =7 501 028 y =4 732 260	524	S3.SW.R.Sitni cë.V.Gllav	26.2	20.0	8.65	x =7501 035 y =4732 258	524

The results in this paper, are presented in tabular form, for each sampling points are presented the values of the concentration of heavy metals in the environment; soil, surface water and groundwater.

Table 2. The concentration of heavy metals in water samples, with ICP-OES technique, winter 2014

Parameters [mg/l]	Sampling points for surface water and groundwater					
	$S_{0.}$ Ref	S1.S.W	S2.S.W	S3.S.W	S1.UG.W	S2.UG.W
As	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Cd	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cr	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Co	0.021	0.020	0.018	0.021	0.023	0.020
Fe	<0.001	0.086	0.097	0.094	0.170	<0.001
Mn	0.174	0.258	0.122	0.104	0.026	0.00
Ni	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Pb	<0.001	0.112	0.138	0.174	<0.001	0.052
Zn	0.164	0.176	0.238	0.188	0.238	0.168

In the tables below there are presented the concentration of heavy metals in both seasons: summer and winter for the surface, groundwater and soil samples.

Table 3. The concentration of heavy metals in soil samples, with ICP-OES technique, winter 2014

Parameters [mg/kg]	Soil sampling points	
	S1. Wasteland	S2.Farmland
As	87.35	44.20
Cd	1.25	0.26
Cr	190.39	108.94
Co	22.65	22.62
Fe	3008.68	2304.09
Mn	588.66	810.67
Ni	244.08	126.88

Table 4. The concentration of heavy metals in water samples, with AAS technique, winter 2014

Parameters [mg/l]	Sampling points for surface water and groundwater					
	S_0 Ref.	S1.S.W	S2.S.W	S3.S.W	S1.UG.W	S2.UG.W
As	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Cd	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Cr	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Co	0.020	0.028	0.020	0.026	0.027	0.029
Fe	<0.002	0.08	0.09	0.0.8	0.19	0.06
Mn	0.18	0.21	0.15	0.12	0.02	<0.002
Ni	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Pb	<0.002	0.12	0.14	0.16	<0.002	0.05
Zn	0.20	0.22	0.28	0.20	0.30	0.16

Table 5. Concentration of heavy metals in soil samples, with AAS technique, winter2014

Parameters [mg/kg]	Soil sampling points	
	S1.Wasteland	S2.Farmland
As	80.20	42.30
Cd	0.98	0.22
Cr	186.14	110.17
Co	20.82	21.24
Fe	2620.87	2201.23
Mn	540.64	780.09
Ni	212.26	130.43
Pb	170.06	68.12
Zn	306.22	130.03

Table 6. The concentration of heavy metals in water samples, with AAS technique, summer2014

Parameters [mg/l]	Sampling points for surface water and groundwater					
	S_0 Ref.	S1.S.W	S2.S.W	S3.S.W	S1.UG.W	S2.UG.W
As	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Co	0.019	0.032	0.030	0.026	0.027	0.030
Fe	0.032	0.134	0.212	0.208	0.260	0.065
Mn	0.120	0.186	0.157	0.144	0.018	0.006
Ni	0.012	0.016	0.016	0.014	<0.002	<0.002
Pb	0.00	0.078	0.114	0.094	0.00	0.048
Zn	0.22	0.24	0.23	0.21	0.21	0.18

The river Sitnicë, except the extent of the contamination of the areas covered by the grace of emissions from chimneys, there is also present the pollution that comes from the ash dusts, landfills and coal dusts from separations wards, which come out from wind and dissolve from the flushing of atmospheric water. Values and analytical techniques used: ICP-OES, AAS and spectrophotometer UV-VIS, indicate that the contamination of the water approaches the first and second degree of water quality. According to the standards developed by the Ministry of Environment and Spatial Planning of the Republic of Kosovo, water parameters are increased in these zones under restrictive allowed values, which can be discharged into water, or public sewage network. The results that were obtained for water in winter season – January (table 2 and 4) , show the presence of metals, such as Fe; 0.19 mg/l,

Mn; 0.258 mg/l, Pb; 0.174 mg/l and Zn; 0.238 mg/l. Referring to the furthest sampled point, it reflects a normal concentration of analyzed elements. From surface waters, (tables 2 and 4) , in January (winter time), R_{O-} sampling point (reference point); S1-UG.W; S2-UG.W; S3-UG.W, dominate metals; Co, Fe, Mn, Pb and Zn, whereas in groundwater the presence of Fe, at the point S2-UG.W is not detected. In soil analyzing, which refers to results from table 3 and 5, concentration of some metals are increased (S1-Wasteland- Table 3): As; four times, Cr; 3.8, Ni; 4.8, Pb; for three times and Zn in small increments. Metals Cd and Co, are in permitted levels of concentrations.

Table 7. The concentration of heavy metals in soil samples, with AAS technique, summer 2014

Parameters [mg/kg]	Soil sampling points	
	S1.Wasteland	S2.Farmland
As	75.23	41.12
Cd	0.86	0.23
Cr	142.07	84.18
Co	32.10	28.66
Fe	2620.30	1892.40
Mn	420.13	534.08
Ni	244.08	126.88
Pb	155.11	54.09
Zn	280.12	98.28

Table 8. The concentration of heavy metals in water samples, determined with SF DR 5000 method, summer 2014

Parameters [mg/l]	Sampling points for surface water and groundwater					
	So. Ref.	S1.S.W	S2.S.W	S3.S.W	S1.UG.W	S2.UG.W
As	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	0.024	0.011	0.010	0.016	0.052	0.012
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Co	0.022	0.026	0.034	0.012	0.026	0.018
Fe	0.04	0.24	0.48	0.34	0.22	0.14
Mn	0.14	0.16	0.16	0.15	0.02	0.01
Ni	0.020	0.025	0.023	0.019	<0.002	<0.002
Pb	< 0.002	0.080	0.093	0.091	< 0.002	0.036
Zn	0.21	0.22	.21	0.19	0.23	0.18

Table 9. The concentration of heavy metals in soil samples, determined with SF DR 5000 method, summer-2014

Parameters [mg/kg]	Soil sampling points	
	S1.Wasteland	S2.Farmland
As	74.02	40.15
Cd	0.79	0.3
Cr	126.11	88.09
Co	33.1	30.14
Fe	2140.4	1788.7
Mn	390.41	510.13
Ni	228.36	132.41
Pb	157.02	58.18
Zn	268.2	87.91

While, the sampling point point (S2-Farmland), it has exceeded the allowed permitted values, the concentrations in of metals are as followed: As; for twice, Cr; twice, Ni; 2.5 and Pb; with concentration exceeding 1.3 times. Metals Cd, Co and Zn, are in permitted levels of concentrations. In the summer season, (June), for water, the results from table 6 determined with AAS technique, and the same samples from table 8, determined by Spectrophotometer UV-VIS, we can conclude that there is an increase of the concentrations of heavy metals such as; Co, Fe, Mn, Pb, Ni and here is showed the presence of Ni, since last season, was not detected.

In June (summer season), the presence of Fe, is in concentrations; 0.26 - 0.048 mg/l in sampling point S2-SW, Mn; 0.16 - 0.18 mg/l in sampling points S1-SW and S2-SW; Pb; 0.093-0.114 mg/l in S1-SW and S2-SW sampling points; Ni; 0.016-0.025 mg/l, S1-SW and S2-SW in sampling area of study, Zn with concentration; 0.00-0.24 mg/l, in S1-SW and S2-SW. Also, in this season of monitoring, metals; As, Cd, and Cr in surface waters and groundwater are not detected. For sampling at June, the analysis of the soil sample, which we refer to results from table 7 and 9, the points (S1-Wasteland) and (S2-Farmland) ,we have the presence of all heavy metals such as; As, Cd, Cr, Co, Fe, Mn, Ni, Pb and Zn. According to the standards for maximum permitted levels, discharging and distribution of

pollutants in the soil, compared with table 3, we have increased concentrations at the point S1-Wasteland, as the following: As; 2.2, Cr; 2.8, Ni, 4.4, and for, Pb; 3.1 times more than is allowed. According to the standards and elements; Cd, Co and Zn, are permitted levels of concentrations. While the point S2-Farmland, have exceeded the allowed values, the concentrations of the following metals: As, for two times, Cr; 1.6, Ni; 2.5 and Pb, 1.1 times allowed concentration. Elements that do not exceed the allowed concentration are Cd, Co and Zn in S2-Farmland.

CONCLUSION

In the surroundings, near "Kosovo" power plants , it is very obvious the potential pollution with: CO_2, NO_X, SO_2, ashes, different other hazardous contaminants that release from burning of fossil material, in this case-coal. With our experimental research, we can conclude that the presence of heavy metals such as: Pb, Mn, Fe Ni and Zn in river surface water and underground water (wells), has contaminated the water up to the second degree level of pollution. Also, the analyzed soil samples, exceeded the maximum allowed concentration, comparing to the international and national standards concentration, where the contamination reaches the high degree of pollution, passing the maximum allowed values. The toxic elements enter the body mainly through water, food and air, therefore in the near future; Kosovo power plants should intervene to designs of new filters, according to European standards. Also, should minimize the capacity of the power plants that burn the fossil fuel and to make the other alternative sources of energy that can orient in the environmental friendly such as; water, wind, bio energy and solar energy.

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