Analysis of Research of Heavy Metals On Ground In "Kosova-A" Thermal Power Plant

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Abstract: Obiliq which is located in Kosovo is known as an industrial city, with significant energy and coal activities. Kosovo Energy Corporation is an industrial complex based in Kosovo, which includes surface mining for coal extraction as well as electricity generation as well as a large number of secondary axiliary equipment. KEK JSC is the only corporation in Kosovo that produces electricity. And based on the existing environmental situation and the primary impact on the environment that includes the impact on land, water and air as well as legal obligations to the environment, in KEK JSC, there is a need to determine and committment to take measures to improve this condition as well as the continuous protection of the environment in the spaces in which it conducts its activities. Due to the long time of these activities without any special care for the environment, today is one of the most polluted cities in Kosovo. Although now these activities are no longer intense their consequences are obvious. Environmental damage continues to be aggravated not only because of the production units that are still active, but also because the polluted areas continue to cause pollution through dust, industrial waste and water discharge, making it a constant environmental threat. The purpose of this paper is to research heavy metals in the Kosovo A Power Plant when it is known that coal contains heavy metals and other elements. And these metals despite small concentrations, they can cause damage to the environment and human health. Most heavy metals such as (As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn, V) are released as compounds (for example oxides, chlorides, etc.) bound to the particles. Only Hg and Se are partially present in the vapor phase. Mercury (Hg) is the heavy metal that causes the biggest problems, in terms of emissions from the coal combustion process. Part of the lignite mercury stops in the vapor phase, which means it does not condense on the surface of the ash particles, so its removal from the particle emission control device is very volatile. Most heavy metals are associated with fly ash at operating temperatures of boiler equipment.

Keywords: environment, soil, heavy metals

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1. Introduction

The electricity sector in Kosovo is supported by coal-fired power plants (about 97%) and is considered one of the sectors with the greatest potential for economic development. The first production unit of the power plant Kosova A, started operating in 1962 with a production capacity of 65 MW. The last A5 unit was built in 1975.

2. Pollution

Pollution is the introduction of a foreign chemical substance or energy (radioactivity, noise, heat) in a permanent form, into the environment, in concentration or quantity, which at a time causes direct damage to the environment, parts of nature, living,

beings or human health. Pollution is also a long-term detrimental, often irreversible impact on the well-being of the environment and its material or aesthetic values. Pollution is required to be prevented by controlling the sources of pollutants. Human actions endanger and pollute the soil, air and water. Pollution can cause disease and even death (in chronic patients). Pollutants that pollute the environment are increasing nowadays. The main characteristics of hazardous waste are toxicity, reactivity, flammability and corrosion. Infectious and radioactive waste are also classified as hazardous waste. Although disposing of hazardous waste on land is not always the best option, it still is done. Hazardous solid waste or containers can be disposed of by burying in secure landfills, while hazardous liquid waste can be disposed of underground if the geological properties of the soil permits. Soil pollution has major consequences that can be catastrophic for the environment and the living world. There are several possible consequences, most of which are as follows: Depending on the soil and if chemicals are improperly dumped into the ground, they can end up in groundwater. The process is known as rinsing. It can occur on farms, industrial areas and landfills. Chemicals, such as nitrogen, pesticides and alike, which are often used on farms, are washed from the ground and reach the water, polluting them.

Fig: 1/1 View from the Power Plant "Kosova A"

Pollution or contamination is the presence of a foreign pollutant in the environment, in a concentrated or volatile form that does not cause direct damage to human health or other living organisms in a short time. Tens of thousands of different chemical compounds bring industrial activity to the beginning of the 21st century, especially the production of chemicals, drugs and auxiliaries for processing raw materials, in the environment, whether through direct release, consumption or use of products. These are metals and metal compounds (salts), organic compounds from simple to complex, especially halogenated organic compounds, gases, mainly nitrogen and sulfur oxides and their compounds with hydrogen, fluorine and chlorine. There are ways of polluting the land where we are mentioning some.

3. Land monitoring in power plants Kosovo A

The purpose of land monitoring in the area of TPP Kosova A is to determine the degree of soil pollution from the operation of the power plant. In order to enable regular and safe production in order to protect people, flora, fauna and the environment, the protection of the soil from pollution is implemented, issues that must be implemented by KEK. Protection of soil from pollution is done by prohibition, restriction and prevention of direct transfer, transfer through water and air of harmful substances and taking measures to preserve and improve the soil. The release of harmful and dangerous substances, which damage and change the productive capacity of the soil, is prohibited. In order to protect the soil from pollution, continuous research and monitoring of the condition and degree of soil pollution from harmful substances should be done. For each month, chemical-physical analyzes of 5 soil samples are performed in a pedological profile (sampling site) in depth: 0 ÷ 20 (cm), 20 ÷ 40 (cm) 40 ÷ 60 (cm), 60 ÷ 80 and 80 ÷ 100

(cm). After air drying, grinding and sieving in a 2 (mm) sieve, chemical analyzes were performed.
We present some data which may be harmful in the process of their activity such as:

1. Agricultural Chemicals-One of the biggest sources of soil pollution is modern agriculture. Today agricultural lands occupy large areas. In our country, they make up more than 60% of the total territory. Agricultural soils are directly chemically contaminated - with pesticides and excessive use of artificial fertilizers. Pesticides are used to control weeds and other pests.
2. Industrialization- The Industrial Revolution led to significant positive changes in the economy and society, but at the same time led to significant land pollution. Through unsafe procedures of disposal of chemicals used in production, poor regulation and a large number of industries and factories that pollute the land on a daily basis, industrialization has become one of the main factors of pollution.
3. Mining-Ore mining can lead to the creation of large open spaces beneath the earth's surface, which threatens the integrity of the earth. Excavations also release harmful chemicals, such as uranium, into the environment.
4. Municipal and Industrial Waste Landfills- Fertilizers in landfills contain toxins that eventually penetrate the soil. During rain, toxins leak into other areas and pollution spreads. As the human population grows, so does the amount of waste.
5. Wastewater - Untreated municipal waste can produce toxic gases that can enter the soil. In addition, the land is directly polluted by numerous quarries, artificial accumulation lakes that pollute fertile soil, excessive and inadequate urbanization and alike.

Indirect sources of soil pollution are acid rain as well as polluted water (polluted river flood, polluted water flood,etc.). Almost all pollutants pollute surface and groundwater by flowing from land and reaching the seas of the world, and through food chains to humans as food. Waste materials that cause soil pollution can be classified into: municipal waste, including non- dangerous waste from households, institutions, commercial facilities and industrial facilities; contains wet and degradable food waste as well as dry materials such as paper, glass, textiles, plastics;

Construction debris includes wooden and metal objects, wall tiles, concrete rubble, asphalt and other materials created during the demolition of structures; Hazardous waste consisting of harmful and hazardous liquid, solid or gaseous substances created in the chemical industry, oil refineries, paper mills, foundries, dry cleaners, car repair shops and many other industrial and commercial plants;

4. Materials and methods

Sampling from the soil profile and its physico-chemical properties

Soil layers are obtained as a result of the slow destruction (erosion) of waste rock formations and coal, due to the action for a very long time of climatic factors, vegetation and organisms. Soil formation is a very slow process, e.g., it is estimated that the formation of a soil layer with a thickness of 30 cm requires 1,000 to 10,000 years, therefore, the soil can be considered as a non-regenerative natural resource. In the process of rock erosion, which leads to the formation of the soil layer, two mechanisms are distinguished, which act simultaneously and reinforce each other: physical (mechanical) erosion and chemical erosion. The interaction of organic compounds,

obtained from the action of microorganisms with minerals of rock formation and soils is the predominant factor that determines the speed of soil formation processes. The presence of water is a condition for many rocks erosion processes, where the action of water is more intense in the presence of hydrogen ions because the acidic environment facilitates the digestion of many minerals. The soil profile can ideally be composed of a series of layers with different compositions called horizons.Different degrees of soil are formed as a result of complex processes that occur simultaneously during erosion, such as rinsing the soil from rainwater, which is associated with the transport of solutes and suspension to the deeper layers, biological processes such as bacterial decomposition of bio-mass, various chemical reactions, etc.

5. Origin of heavy metals- Soil monitoring

The research of pollution sources is done by observing possible sources of pollution, identification of hotspots and surrounding areas, reviews of scientific materials and official reports related to the field of study. In this case it was concluded that the potential sources of environmental pollution with MR in and around the industrial zone of Mitrovica, are landfills created during metallurgical and hydro-metallurgical processes

6. Soil sampling

As a consequence of industrial waste and their impact on soil pollution in and around the industrial area, after determining the area for monitoring, the soil sampling site was determined in order to determine the content of MR in the soil as Pb, Zn, Cd and As. Soil sampling sites are designed so that some of them belong to hotspots near polluting sources and some to places where the concentration may be lower due to the distance from the polluting source. Sampling stations should form a network that covers the entire surface to be investigated as it deals with diffuse pollution from distant or non-point sources. Composite samples may also be used, unless changes in the color or structure of the soil are observed in different areas of the surface being studied. In determining the direction of sampling points should be taken into account wind direction as well as topographic terrain constraints. Usually, pollutants deposited from the atmosphere do not show visible mobility and remain in the surface layer of the earth. A total of 12 samples were taken for a study at a depth of 20 cm, from 4 samples at each point near the power plant Kosova A.

7. Preparation of samples for analysis

Soil samples are taken from the respective stations and placed in sterile bags marked on the basis of the sampling site. They are brought to the laboratory where they are cleaned of stones or root parts of plants. Due to the structure of the soil that may contain large aggregates, the sample is ground in mortars or mills as the concentration of many pollutants is higher in fine particles (90% of pollutants are expected to appear in fine particles). Then they are opened on a clean flat surface by dividing it into four almost equal parts and the sample which we will treat for analysis to be as homogeneous as possible, two parts are selected opposite each other and treated as a single one (quaternization method) . Given the microbiological activity that can take place, care for drying soil samples is understandable, so drying is often done in air at room temperature, for at least 24 hours. So initially the soil samples are pre-treated to fine powder.Finally, all soil samples are dried at 105 (° C) for 2 to 3 hours before analytical treatment. Environmental monitoring usually requires the total metal

content in the soil, so disgusting is often used in harsh conditions such as with mixtures of concentrated acids, containing hydrofluoric acid and perchloric acid. Their analysis was done in an atomic absorber which is possessed by the laboratory of INKOS Institute in Obiliq (attention: analysis technique and laboratory in which the analysis of samples was done are certified with the accreditation agency and with European standards ISO 9001/2015).The comparison of the results was done with the values of the Canadian list and the administrative instruction of Kosovo.

8. Analysis of sample results

The results obtained from the research conducted in the INKOS Institute JSC in two periods divided into that of January and that of June 2021 where these data are researched according to the depth of the profile expressed in mg / kg of soil, and according to research the data are presented in the table.

		Profile depth					
Parameters	Unit%ppm	0-20	20-40	40-60	60-80	80-100	mg/kg of soil
pH-H_2O	100% ppm	7.3	7.3	7.2	7.3	7.2	
Ca		2.21	1.48	1.43	1.54	1.37	
K		0.47	0.41	0.42	0.29	0.3	
Mg		0.38	0.37	0.36	0.36	0.37	
Na		517	325.3	339.85	311.4	302.45	
As		36.9	36.6	37.35	34.3	34.9	
Cd		14.9	16.25	16.75	15.5	16.35	
Cr		92.5	88.6	87.25	89.8	92.15	
Hg		<1ppb*	<1ppb*	<1ppb*	<1ppb*	<1ppb*	
Ni		125.79	111.7	112.55	120.9	122	
Pb		40.85	37.85	39.4	41.35	41	
S		125.55	93.4	109	80.7	51.75	

Table # 1. Analysis of some elements together with the pH and the degree of soil contamination in January 2021 in the power plant Kosova A.

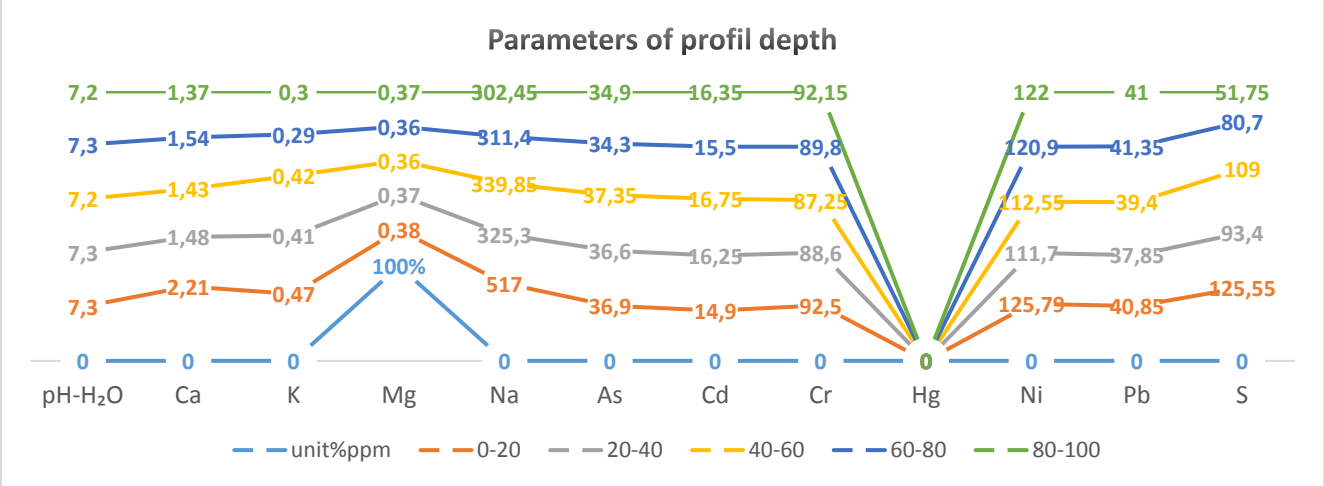


Table #2 Descriptive statistics of month January 2021

	Descriptive Statistics

Variable	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Std.Dev.	Coef.Var.	Standard Error	Skewness	Kurtosis
Ca	5	1.6	1.4	2.2	1.4	2.2	0.34	21.38	0.15	2.05	4.35
K	5	0.4	0.3	0.5	0.3	0.5	0.08	20.95	0.04	-0.23	-2.51
Mg	5	0.4	0.4	0.4	0.4	0.4	0.01	2.27	0.00	0.51	-0.61
Na	5	359.2	302.5	517.0	302.5	517.0	89.34	24.87	39.96	2.10	4.50
As	5	36.0	34.3	37.4	34.3	37.4	1.33	3.70	0.60	-0.54	-2.42
Cd	5	16.0	14.9	16.8	14.9	16.8	0.74	4.64	0.33	-0.66	-0.94
Cr	5	90.1	87.3	92.5	87.3	92.5	2.26	2.51	1.01	-0.10	-2.14
Ni	5	118.6	111.7	125.8	111.7	125.8	6.18	5.21	2.76	-0.21	-2.49
Pb	5	40.1	37.9	41.4	37.9	41.4	1.46	3.63	0.65	-1.13	0.04
S	5	92.1	51.8	125.6	51.8	125.6	28.13	30.55	12.58	-0.46	-0.01

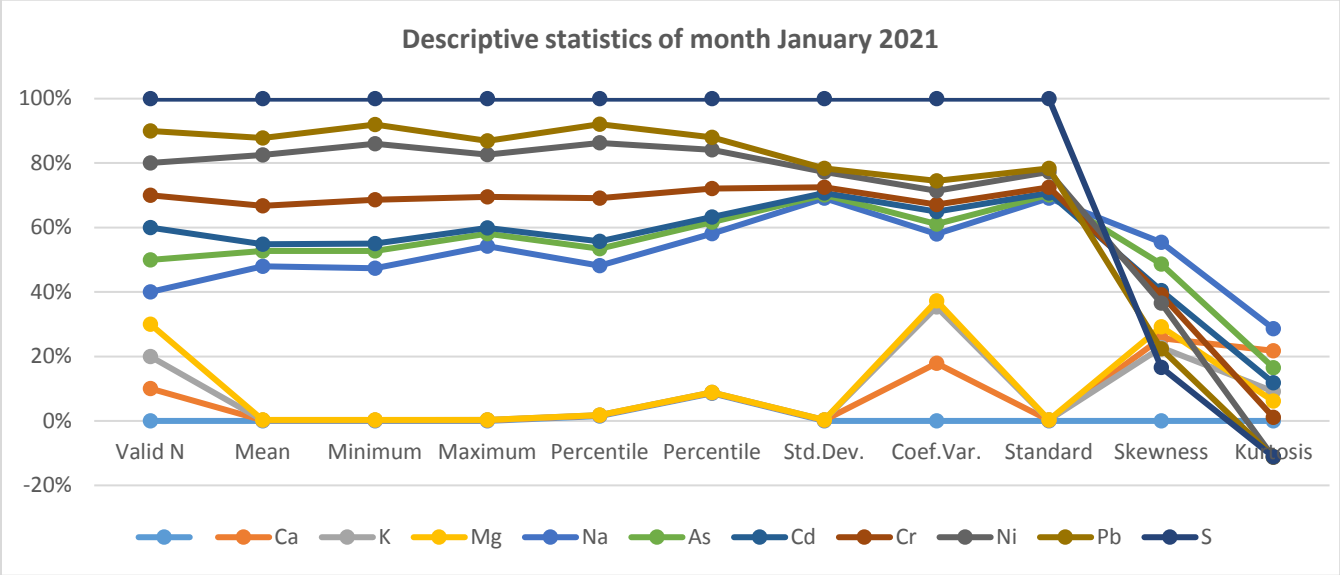
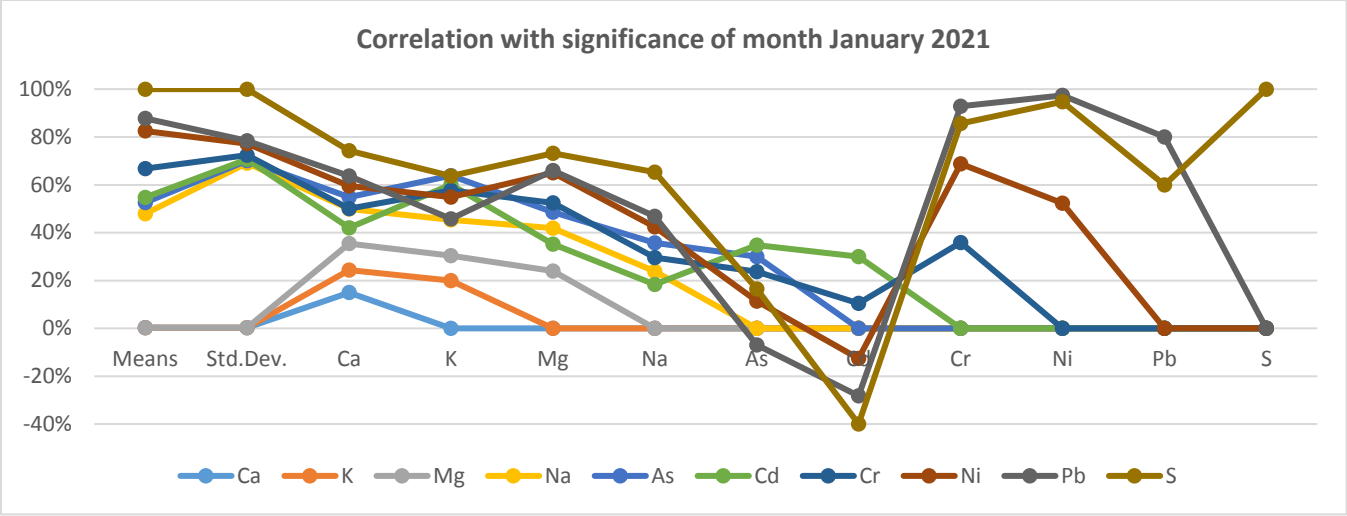


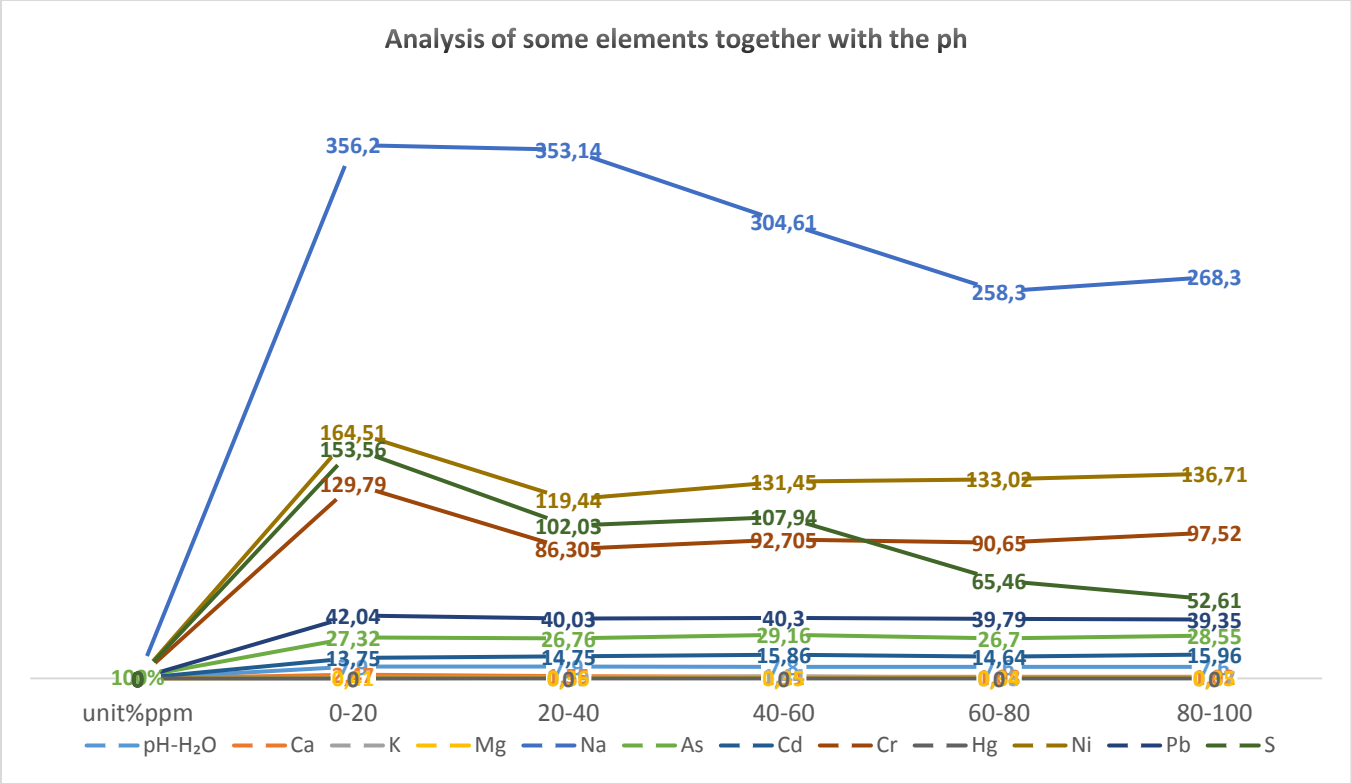
Table #3 Correlation with significance of month January 2021

Variable	Correlations. Marked correlations are significant at p < .05000. N=5											
	Means	Std.Dev.	Ca	K	Mg	Na	As	Cd	Cr	Ni	Pb	S
Ca	2	0.3	1.00									
K	0	0.1	0.63	1.00								
Mg	0	0.0	0.74	0.52	1.00							
Na	359	89.3	0.97	0.75	0.75	1.00						
As	36	1.3	0.33	0.93	0.28	0.50	1.00					
Cd	16	0.7	-0.86	-0.19	-0.56	-0.73	0.16	1.00				
Cr	90	2.3	0.54	-0.12	0.72	0.47	-0.37	-0.65	1.00			
Ni	119	6.2	0.63	-0.14	0.53	0.54	-0.41	-0.77	0.92	1.00		
Pb	40	1.5	0.28	-0.46	0.04	0.19	-0.61	-0.52	0.67	0.86	1.00	
S	92	28.1	0.71	0.90	0.30	0.77	0.78	-0.39	-0.20	-0.05	-0.25	1.00



		Profile depth					
Parameters	unit%ppm	0-20	20-40	40-60	60-80	80-100	mg/kg.of soil
pH-H_2O	100% Ppm	7.9	7.9	7.8	7.6	7.6	
Ca		2.47	1.55	1.11	1.08	1.02	
K		0,44	0.39	1.44	0.33	0.37	
Mg		0.41	0.36	0.35	0.34	0.35	
Na		356.20	353.14	304.61	258.3	268.3	
As		27.32	26.76	29.16	26.70	28.55	
Cd		13.75	14.75	15.86	14.64	15.96	
Cr		129.79	86.305	92.705	90.65	97.52	
Hg		<1ppb*	<1ppb*	<1ppb*	<1ppb*	<1ppb*	
Ni		164.51	119.44	131.45	133.02	136.71	
Pb		42.04	40.03	40.30	39.79	39.35	
S		153.56	102.03	107.94	65.46	52.61	

Table# 4Analysis of some elements together with the pH and the degree of soil contamination in June 2021 in the power plant Kosova A.



Table# 5 Descriptive statisticsfrom data of month June 2021.

Variable	Descriptive Statistics										
	Valid N	Mean	Minimum	Maximum	Percentile 10	Percentile 90	Std.Dev.	Coef.Var.	Standard Error	Skewness	Kurtosis
Ca	5	1.4	1.0	2.5	1.0	2.5	0.61	42.18	0.27	1.673	2.51
K	5	0.6	0.3	1.4	0.3	1.4	0.47	79.90	0.21	2.197	4.86
Mg	5	0.4	0.3	0.4	0.3	0.4	0.03	7.67	0.01	1.881	3.77
Na	5	308.1	258.3	356.2	258.3	356.2	45.87	14.89	20.51	0.069	-2.89
As	5	27.7	26.7	29.2	26.7	29.2	1.10	3.99	0.49	0.578	-2.23
Cd	5	15.0	13.8	16.0	13.8	16.0	0.92	6.16	0.41	-0.218	-1.41
Cr	5	99.4	86.3	129.8	86.3	129.8	17.47	17.57	7.81	1.945	3.97
Ni	5	137.0	119.4	164.5	119.4	164.5	16.67	12.17	7.46	1.356	2.80
Pb	5	40.3	39.4	42.0	39.4	42.0	1.03	2.56	0.46	1.603	3.03
S	5	96.3	52.6	153.6	52.6	153.6	39.71	41.23	17.76	0.508	-0.30

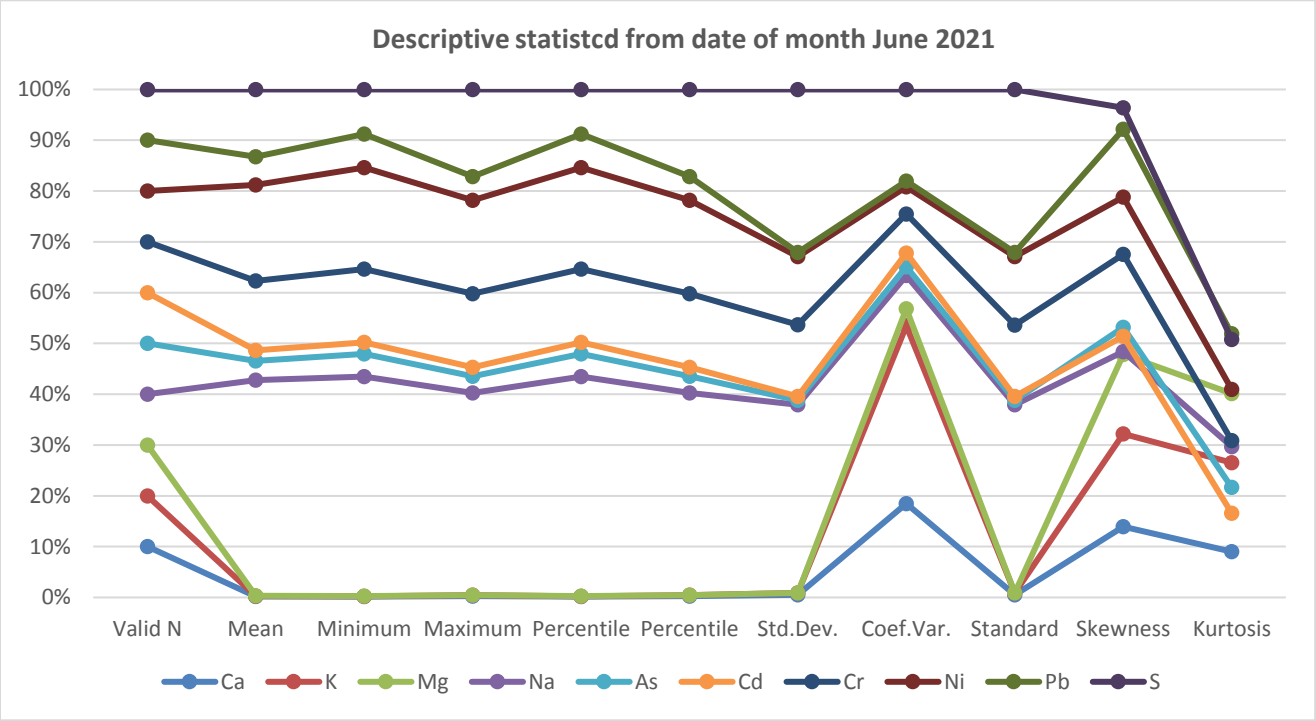


Diagram 1.1. Descriptive Statistics

Table# 6 the correlation between the researched elements and the significance during the research of June 2021.

Variable	Correlations. Marked correlations are significant at p < .05000. N=5											
	Means	Std.Dev.	Ca	K	Mg	Na	As	Cd	Cr	Ni	Pb	S
Ca	1	0.6	1.00									
K	1	0.5	-0.23	1.00								
Mg	0	0.0	0.98	-0.16	1.00							
Na	308	45.9	0.81	0.03	0.75	1.00						
As	28	1.1	-0.36	0.74	-0.18	-0.25	1.00					
Cd	15	0.9	-0.83	0.49	-0.72	-0.56	0.77	1.00				
Cr	99	17.5	0.85	-0.15	0.92	0.44	-0.02	-0.61	1.00			
Ni	137	16.7	0.73	-0.13	0.82	0.25	0.02	-0.55	0.98	1.00		
Pb	40	1.0	0.93	0.07	0.93	0.71	-0.15	-0.74	0.87	0.80	1.00	
S	96	39.7	0.88	0.24	0.86	0.86	-0.09	-0.64	0.70	0.58	0.95	1.00

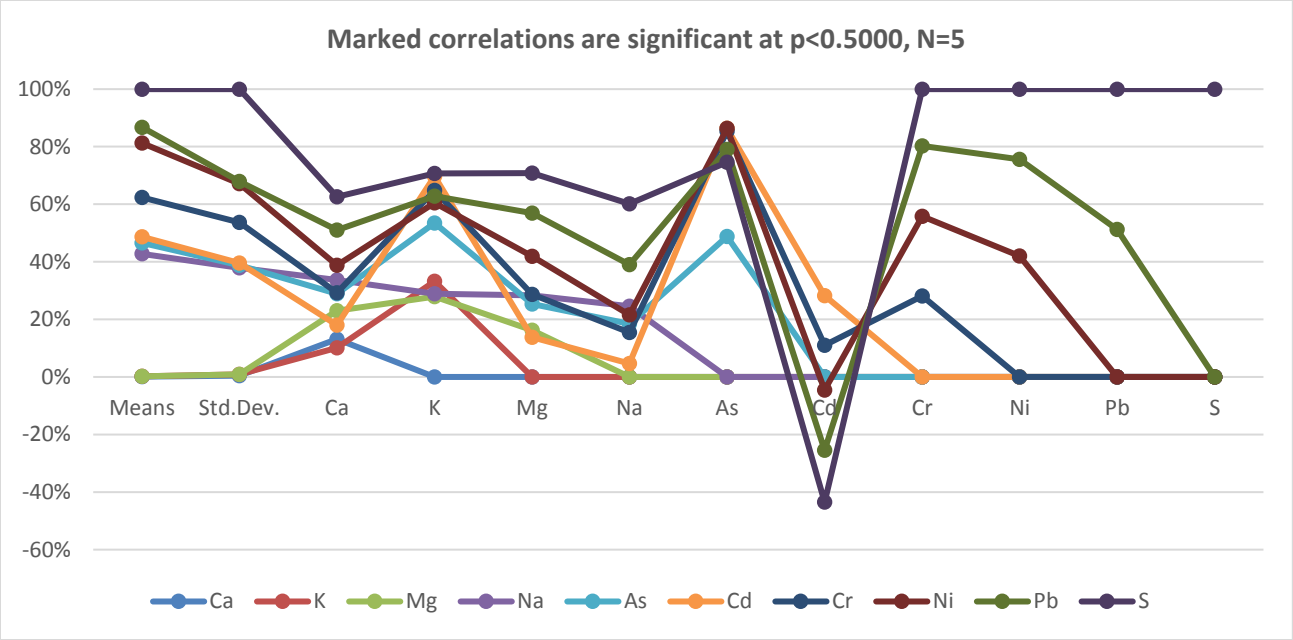


Diagram.1.2 correlations between the researched elements and the significance during the research of June 2021.

9. Results and conclusions

Samples taken near the Power Plant "Kosova A" in two time periods in January 2021 and June 2021 at depths of 0-20, 20-40, 40-60, 60-80 and 80-100 [cm]. All the results obtained during January are presented in figure # 1 as well as the correlation statistics in tables # 2 and # 3.

10.Analysis in January 2021

The results of physico-chemical analysis of soil samples at the depth presented above in January 2021 where these results will be commented separately while their comparison with the maximum allowed values was made based on the deutch list.

From the data presented in table # 1 we conclude that the values of the active reaction of the soil (pH in H_2 O), in special samples taken according to the depth are in the range of 7.7-7.3 and thus we ascertain or classify in the class of weak soil alkaline.

- the content of the number of interchangeable cations in Ca, K, and Mg are expressed in% Na in mg / kg (ppm) as well as the total sulfur content,
- The obtained values show that the content of these elements is within the optimal limits and is in proportion to their dynamics in the agricultural land.
- Ca content was in the soil reaction values (pH).
- High values are presented at a depth of 0-20cm 2.21% and at a depth of 60-80cm 1.37% of the analyzed samples.

- in terms of cations are recorded as follows Mg 0.36-0.38%, and K 0.29-0.47% while the content of Na ranges around 302.45-517.00ppm while in terms of the content of total S sulfur it ranges in the range of 51.75-125.55 ppm as presented in table 1 and in terms of heavy metals As, Cd, Cr, Hg, Ni, and Pb from the obtained results and their comparison with the values determined by the deutch list the values of these elements are among the lowest and optimal values.
- High values are presented at a depth of 0-20cm 2.21% and at a depth of 60-80cm 1.37% of the analyzed samples.
- in terms of cations are recorded as follows Mg 0.36-0.38%, and K 0.29-0.47% while the content of Na ranges around 302.45-517.00ppm while in terms of the content of total S sulfur it ranges in the range of 51.75-125.55 ppm as presented in table 1 and in terms of heavy metals As, Cd, Cr, Hg, Ni, and Pb from the obtained results and their comparison with the values determined by the deutch list the values of these elements are among the lowest and optimal values.

Table 3 shows the correlation between the elements extracted in a systematic way where it is seen that between Na and Ca there is a signification and also between As and K such a thing is also shown between S and K and Ni and Cr.

11.June 2021

From the samples taken in June the results presented in tab no. 1 we can conclude that the values of the active reaction of the soil (Ph and H_2 O) in specific samples taken according to the depth range from 7.6 to 7.9 respectively soil researched can be classified into weakly alkaline soils.

- the content of the amount of exchangeable cations Ca, K, Mg are expressed in% and Na in mg / kg (ppm) as well as the total content of S. The values obtained show that the content of these elements is within the optimal limits and is in proportion to the dynamics of tare on agricultural land,
- The exchangeable Ca content was in correlation with the soil reaction values (pH). The highest values were observed at the first depth (0-20cm) 2.47% while the lowest were at depth (80-100cm) 1.02%.
- to the cations of Mg (0.34-0.41%) and K (0.33-0.44% while the content of Na is around (258.34-356.20) while in terms of sulfur S it is in the range (52.61-153.56ppm).
- Regarding the content of chemical elements (heavy metals) As, Cd, Cr, Hg, Ni, and Pb from the research done in comparison with the values determined by the Deutch list we can conclude that the number of samples analyzed is in the range from lower.
- Regarding the correlation between the elements based on the extracted statistics it turns out that the correlation between Mg and Ca represents a significance such a thing has been observed between Pb and Ca and S with Ca,also a significance is presented between Cr and Mg and Pb with Mg, also Ni with Cr and S with Pb. All of these can be found in tab no. # 6.

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