Chemical characteristics of lignite ash from Power Plant Kosova A and local geological settings in Kosova near Prishtina

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Abstract **-** Because of poor maintenance of the power plant (PP) Kosova A this study reports and discusses the results of reconnaissance work carried out in the vicinity of ash disposal site from PP in relation to the geochemical assessment of ash. The regional geology Kosova is rich in ore and lignite deposits. For about 100 years lignite has been exploited in one of the largest lignite deposits in Europe near Prishtina. Currently 97 % of the power demand of Kosova is generated by the power plants Kosova A and B near Prishtina. The aim of this study was to estimate environmental impacts which are caused by the ash disposal site of power plant Kosova A and to assess geological conditions within this work. The chemical and physical properties of ash differ from each other in relation to disposal age and technique. Ash and surrounding soils were analyzed for knowledge of chemical properties and mineralogy. Additional the data were analyzed to assess environmental impacts caused by ash and geology.

Key-Words: Kosovo, lignite ash, lignite, heavy metals, fluorine, soil

1 Introduction

This industrial complex is located about 3 km northwest from the capital Prishtina near settlement Obiliq Fig. 1. All facilities and disposal sites of Kosova A and B are close to the river Sitnica, which is the major surface run off in this region.

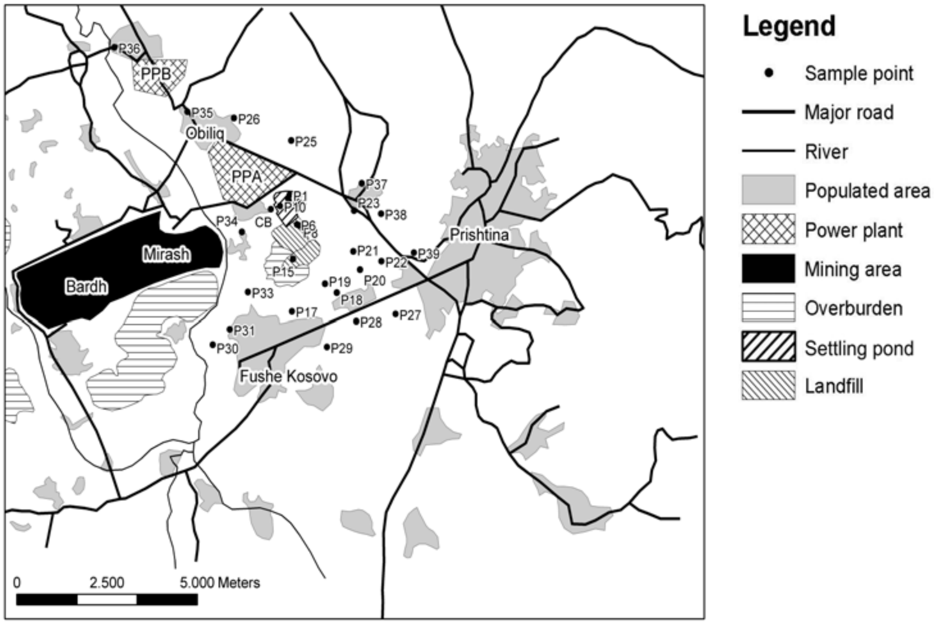


Figure 1: Disposal sites and facilities near Prishtina

The first activities of lignite exploration have started about 100 years ago [1]. With approximately 10.000 billion tons the estimated lignite resources in Kosova are one of the largest in Europe [2]. In the early 1960s the first power plant units were started with power generation, exploitation of lignite in open mines and deposition of overburden and ash. Dust emission of ash during disposal and dry season could be a main factor for contamination of water, air and soil. According to rough estimates, 26 million m^3 of ash have been deposited from the beginning of the operation [3]. Fly ash from the combustion units A1 and A 2 of power plant Kosova A was deposed as pulp on settling ponds (wet disposal technique). Bottom ash, slag and fly ash from the remaining combustion units have been transported on open conveyor belt systems to disposal sites (dry disposal technique). No technique was available to prevent wind erosion of ash from ash deposits. Ash and soil samples were analyzed for the elements considered to be hazardous to human health (Cu, Pb, Zn, Cr, Co, Cd) as well as for several elements that make up matrix structure of ash and soil (Na, K, Ca, Mg, Mn, Fe, Al) . For this study ash samples were taken from the conveyor belt, from old and new disposal sites, in addition top soils of near surrounding area were sampled. The chemical and physical properties of ash differ from each other in relation to disposal age and technique. New ash has very high pH values of 12.5 and very low contents in $CaCO_3$ down to 1.1 %. The weathering of ash causes the decrease of pH to 8.2 and the increase of contents in $CaCO_3$ to 24.6 % [4], [5]. The ashes are highly concentrated with Ba, Cl, Cr, F, Mn, Ni and Sr. Regionally soils are neutral to alkaline with an approximate $CaCO_3$ content of 1.7 %. Due to local geological settings the soils are naturally enriched with Ba, Cr, Ni, F and Mn. The ash and soils are geologically enriched with Cr, Ni and F, due to the high contents of $CaCO_3$ leaching of heavy metals and F can be prevented, excluding Cl [4], [5]. All these pollutants which have effect in river Sitnica also have influence in soil and water pollution in region of Mitrovica [6].

2 Study area

The study area is located in central eastern Kosova near the capital Prishtina. The climate of this region is characterised by an annual precipitation sum of 595mm per year and a mean annual temperature of 10°C, summer maximum temperature of 39°C, winter minimum of -27°C [5], [7], [8]. Therefore the local climate is classified as humid and mild continental (Fig. 2).

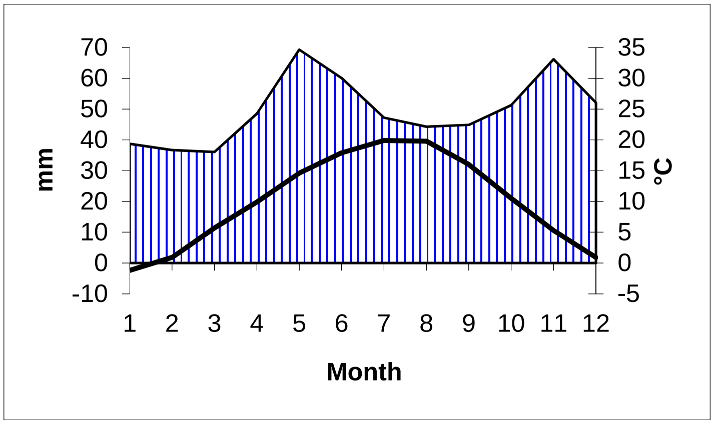


Figure 2: Climate diagram of Prishtina (1949 – 2003)

The main wind direction is NNE, but the strongest winds come from NW [8].

The geology is described by [9], [10], [11] and similar within geological conditions in Greece [12], [13], [14]. In these locations the formation of metal enriched minerals with higher contents in heavy metals Cr, Mn, Co, Zn and Ni, Tab. 1, is likely in contact zones between Harzburgiten, Serpentinite and limestones.

Table 1: Typical trace element contents of heavy metal enriched minerals

Element	Greece[a]	Kosova
	%	
Co	03 – 1,6	0,07 – 0,7[b]
Cr	2,3 – 9,1	3,5[b, c]
Mn	0,3- 1,1	n d a
Ni	1,5 – 16,0	1,2 – 1,3[b]
Zn	0,06 – 0,85	n. d. a.

n d a: no data available

Commonly these deposits are over talc-serpentinite schists or massiv silcrete with abundant chromit contents. The serpentinites and biotite containing slates and their weathered products can be enriched with Cr, Ni and F [15], [16], [17]. Higher amounts of F are attributed to apatite, which can have contents up to 5.5 % of F.

2.1 Lignite

Currently lignite is the most important energy source in Kosova [2]. The estimated lignite reserves are distributed all over the area of Kosova. The main lignite deposit is in the Kosova lignite basin near Prishtina with approximately 12 billion tonnes of exploitable lignite [12]. Other deposits are in the Dukagjini lignite basin in the West and in the centre of Kosova located Drenica lignite basin. Lignite from the Kosova lignite basin belongs to upper Miocene and has an age of about 9 million years [2]. A wide range of physical properties and chemical composition of the lignite from Kosova lignite basin is shown by a variety of authors [1], [2], [18]. However, the lignite has a range of ash content from 12 to 21 % whereas the mean average values range from 14 to 17 %. The sulphur content is approximately 1 % including an average content of combustible sulphur of 0.35 %. Because of sufficient contents of $CaCO_3$ significant amounts of SO_x could be absorbed. The lignite has a density of 1.14 g/cm^3 and a CO_2 emission factor of 1.39 kg/kg.

2.2 Ash

The incineration of lignite results in waste products, mainly fly ash and additional bottom ash and slag [19], [20]. Every year 150 million tons of fly ash is produced worldwide [20]. Fly ash is used in cement and construction industry. Unused fly ash is disposed into landfills or settling ponds [20], [21]. The disposal of ash results in significant environmental problems, therefore ash and fly ash is classified as a hazardous residue [20], [22]. Trace elements are enriched during combustion of lignite as a result of carbon loss as carbon dioxide [9], [20]. The chemical and mineralogical qualities of fly ash are related to coal qualities and combustion techniques. During combustion fly ash can absorb trace elements [20], [23]. The major elements Ca, Mg, Na and K can be leached in high amounts, whereas Ca can precipitate partially as sulphate and/or carbonate [20]. Cr and Cu are precipitated as hydroxides [15]. In total maximum leaching rates have been determined for Ca, Na, K and S. Otherwise it have been analysed for Cd, Mg, Cu, Cr, Zn and Co a minimum leaching rate and the leaching rate for Mn and Pb depends by the leaching activity of Iron [20].

2.3 Soil

According to several authors, lignite ash can cause significant impacts to surrounding environments. Wind and water erosion can transport ash particles to surrounding environments [21]. Salts as well as toxic substances can be leached and pollute soils as well as surface and ground waters [20], [23], [24]. Another environmental risk is the pollution with phenols in this region. One of the major pollutants in Kosova was the industrial complex Obiliq with its open pit lignite mines, heating plants and in 1988/89 closed down gasification and fertilizer plants [25]. Because lignite is a source of phenols and Cl [26], likely formed chlorophenols are strong fixed to soil matrix [27] and highly toxic [25].

3 Materials and methods

All samples of about 1 kg were taken in May 2004 see Tab. 2. On the ash disposal areas samples were taken from four areas of different age and disposal technique.

3.1 Sites of investigation

Soil samples were taken around an ash disposal site between three major settlements.

Table 2: Sample number and Location

	Ash				Soil	
Site	Location (UTM)		Type	Site	Location (UTM)	
	X	Y			X	Y
P1	508062	4724379	OAWD	P17	508129	4721447
P2	508027	4724291	OAWD	P18	509374	4721916
P6	508027	4724291	OADD	P19	509044	4722141
P8	508027	4724291	OADD	P20	510016	4722495
P10	507800	4724100	NAWD	P21	509829	4722958
P15	508161	4722767	OADD	P22	510610	4722706
				P23	509849	4723981
				P25	508109	4725755
				P26	506528	4726323
				P27	511002	4721378
				P28	509912	4721201
				P29	509100	4720555
				P30	505938	4720617
				P31	506408	4721001
				P33	506912	4721931
				P34	506742	4723450
				P35	505235	4726482
				P36	503211	4728107
				P37	510065	4724675
				P38	510599	4723908
				P39	511509	4722922

Four ash types from Power Plant A (Tab. 3) and several surrounding soils were investigated. New ash from a dry disposal technique (NADD) was collected directly from conveyor belt system.

Table 3: Ash types from disposal area from Power Plant A

Type of ash	Age	Description
NADD	< 1 day	New ash which has been disposed of on young landfills
NAWD	< 1 week	New ash which has been disposed of on young settling ponds
OADD	app. 7 years	Old ash which was disposed of on old landfills
OAWD	app. 40 years	Old ash which was disposed of on old settling ponds

New ash from a wet disposal technique (NAWD) was sampled from one investigation site on a currently used settling pond. Old ash from landfills (OADD) was collected from three investigation sites and old ash from settling ponds (OAWD) from two investigation sites. At each investigation site soil profiles were investigated and samples were collected from each horizon with respect to sedimentological layer except for FADD.

To compare chemical properties of soils and ash, topsoil samples were taken within an area between settlements of Prishtina in the east, Obliq in the north and Fusha Kosova in the west. Soil samples were taken in depths at 0 to 10 cm according to the German Federal Soil Protection Act and Ordinance [28].

3.2 Methods

All samples were dried at 40°C and stored in clean polyethylene bags. Soil samples were sieved to < 2 mm through a stainless steel sieve and approximately 200 g of each sample were transported to Germany. The pH value was measured in 0.01 M $CaCl_2$ (Hanna Instruments HI 8817). $CaCO_3$ contents were determined by the SCHEIBLER volumetric method. Organic matter contents were determined using dry combustion at 420 °C. The major and minor element contents were measured by WD-XFA using powder pressure technique and Philips PW 1404/10. For qualitative mineralogical detection the samples were analyzed by XRD powder compounds using Philips PW X-ray Diffractometer. For both about 20 g of each sample were ground to < 50 µm with a vibratory disc mill and an agate grinding set. A 6 g powder compound for XFA measurement of each pulverized sample were mixed with 1.5 g C-wax and pressed by 20 t in an aluminum capsule with a diameter of 40 mm. After that the compounds were measured. The data for pH values were based on two replicates with standard deviation always < 10 % of the mean. The data for organic matter, $CaCO_3$ content and minor and major elements were based on one replicate.

4 Results and discussion

4.1 Characteristics of lignite ash

New ash (NADD) has a pH value of 12.5 and $CaCO_3$ content of 1.1 % (Tab. 4). Old ash (OADD) has a geometric mean of pH value of 8.2 (SD 0.7) and an arithmetic mean of $CaCO_3$ content of 26.6 % (SD 10.8). New ash from settling ponds (NAWD) has a geometric mean of pH of 9.5 (SD 1.1) and an arithmetic mean of $CaCO_3$ content of 12.6 % (SD 2.7). Ash from old settling ponds (OAWD) has a geometric mean of pH value of 8.5 (SD 0.4) and a arithmetic mean of $CaCO_3$ content of 15.8 % (SD 2.2). The average CaO content (WD-RFA) of all samples (without slag) is 23 % (SD 3.3). Calcium in new ash exists mainly as calcium oxide ("quicklime") and reacts under atmospheric conditions with an intermediate step of $Ca(OH)_2$ ("hydrated lime") to $CaCO_3$ ("lime") [5].

For this study minor element concentrations in ash ranges for Mo, (Pb), Th, U, (Zn) and Br between 0.1 and 10 mg/kg, for As, Co, Cr, Cu, (Ni), Pb, V and Zn between 10 and 100 mg/kg, for Ba, (Cr), Ni, Sr and Cl between 100 and 1000 mg/kg and for F as well as Mn between 1000 and 10000 mg/kg (Tab. 5). Cd and Hg were not detected [4], [5].

Two ash samples were analyzed to evaluate the mineralogical composition of old disposed and new ash. The main minerals in sample P 10 II Cm (NAWD) are calcit, ettringite, minor minerals are quartz and gypsum as well as traces of gehlenite and gismondin. Old ash from sample P 6 Cm (OADD) contains mainly calcite and aragonite, as minor components gypsum and quartz as well as traces of gehlenite.

Spolic Technosols (calcaric) are found in loose ash as well as spolic Technosols (calcaric) with takyric properties at the soil surface are found in loosely solidified ash.

Table 4: Chemical and physical characteristics of sampled ashes

Site	Horizon	Depth cm	pH	$CaCO_3$	LOI	H_2O	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	Σ^a
										%							
NADD																	
CB	ash	-	12.5	1.1	1.0	40.3	15.80	4.46	5.67	1.88	22.01	0.54	0.33	0.25	0.10	6.81	58.3
NAWD																	
P10	I Cm	0-10	8.7	12.3	10.4	20.9	20.27	6.25	5.61	2.51	20.29	0.46	0.53	0.28	0.12	6.49	63.3
P10	II Cm	10-20	11.1	16.1	12.5	21.7	16.21	4.36	4.95	2.08	25.37	0.32	0.20	0.19	0.13	4.50	58.7
P10	III Cm	20-40	8.9	9.5	9.3	27.6	18.05	5.81	4.78	2.56	20.51	0.38	0.39	0.27	0.11	5.63	59.0
OADD																	
P6	Ah	0-40	7.8	37.3	11.4	5.7	19.35	3.55	4.63	2.56	31.33	0.26	0.21	0.20	0.15	3.73	66.5
P6	Cm	40-70	7.7	36.5	13.5	3.1	19.51	3.60	4.40	2.98	29.70	0.54	0.25	0.19	0.14	5.56	67.4
P8	Cm	0-5	8.9	-	9.5	-	22.19	6.23	4.59	3.31	20.84	4.07	1.43	0.30	0.11	6.55	70.1
P15	Ah	0-10	8.0	26.6	8.3	18.5	21.12	5.89	4.94	2.11	23.69	0.31	0.42	0.29	0.13	2.20	61.2
P15	Ah	10-30	7.6	25.6	9.0	25.9	17.34	5.11	4.19	1.63	21.30	0.26	0.38	0.24	0.11	2.83	53.8
P15	C	30-35	9.5	7.3	12.5	29.3	15.02	4.05	3.46	1.86	24.22	0.11	0.06	0.18	0.10	5.65	55.1

OAWD																	
P1	Ah	0-17	8.0	13.0	20.6	16.0	21.60	6.79	3.89	1.94	16.94	0.31	0.37	0.28	0.09	5.17	57.8
P1	Ah	17-27	8.0	18.3	11.8	14.3	25.17	7.69	4.92	2.46	19.56	0.39	0.45	0.31	0.11	4.39	65.9
P1	Bw	27-30	7.8	-	10.9	-	21.53	7.03	6.60	4.19	23.03	0.28	0.27	0.30	0.15	1.35	65.3
P1	Cm	30-32	8.5	16.6	13.2	20.4	15.64	4.87	4.44	3.37	23.03	0.16	0.10	0.23	0.12	6.47	59.1
P2	I Cm	0-10	8.9	14.1	12.0	14.3	22.25	7.29	6.12	3.24	22.28	0.41	0.32	0.31	0.13	4.62	67.5
P2	II Cm	10-20	8.8	12.9	12.0	28.0	17.38	5.53	5.17	2.10	18.35	0.26	0.34	0.25	0.11	4.40	54.3
P2	III Cm	20-30	8.9	17.9	14.2	17.6	17.62	5.11	5.03	2.57	23.54	0.30	0.28	0.22	0.12	5.09	60.3
P2	IV Cm	30-32	9.0	-	13.9	-	19.52	5.19	4.75	2.88	27.39	0.33	0.19	0.23	0.13	5.82	66.9

Table 5: Contents of minor elements of sampled ashes

Site	As	Ba	Br	Cl	Co	Cu	Cr	F	Mn	Mo	Ni	Pb	Sr	Th	U	V	Zn	Zr
									mg/kg									
									NADD									
CB	30	452	7.0	b.d.l.	9	24	94	1873	994	2.90	123	9	332	3.4	0.50	61	26	72
									NAWD									
P10	41	417	2.5	115	15	18	110	2069	1316	1.40	133	19	295	6.2	2.10	67	34	68
P10	27	395	0.6	b.d.l.	4	18	70	2166	1246	2.70	99	6	252	6.9	0.25	38	12	53
P10	33	460	2.3	68	11	22	92	2240	1002	1.60	114	15	309	6.7	1.70	65	30	74
									OADD									
P6	24	510	2.9	b.d.l.	12	17	58	2700	1352	1.90	100	9	486	5.9	4.10	38	4	66
P6	31	489	2.3	b.d.l.	9	16	70	2784	1290	2.10	101	3	418	4.9	0.25	46	8	61
P8	27	447	46.1	869	11	22	117	1917	938	4.40	140	8	361	5.8	2.90	56	27	77
P15	17	518	2.6	b.d.l.	12	23	98	2364	1098	2.40	105	14	349	8.3	0.25	64	32	80
P15	22	447	2.1	b.d.l.	5	17	72	2202	960	1.30	90	14	310	2.1	1.60	52	25	69
P15	19	404	1.6	b.d.l.	6	7	56	2160	986	2.10	64	8	246	5.7	2.70	42	15	57
									OAWD									
P1	19	369	1.3	9	10	25	103	2423	512	1.30	87	8	265	4.5	0.25	58	25	70
P1	19	461	2.1	137	8	30	121	2299	732	0.15	110	11	313	4.7	0.25	67	30	77
P1	42	657	2.3	b.d.l.	14	34	130	2918	1434	0.40	168	26	382	6.3	6.20	81	44	66
P1	32	475	0.5	2295	8	28	79	2598	1199	0.30	97	14	273	6.9	1.30	52	20	55
P2	16	524	1.0	4	14	29	112	2766	1077	0.70	136	17	327	8.2	2.20	75	36	76
P2	22	447	b.d.l.	453	9	26	95	2317	995	2.40	111	16	268	6.8	2.00	62	27	66
P2	32	491	1.8	b.d.l.	12	21	101	2209	1229	1.50	121	18	333	5.3	2.00	53	24	60
P2	32	531	1.2	18	13	17	83	2645	1258	2.4	113	15	381	4.9	0.25	53	25	62

m: mean, s: standard deviation, v: coefficient of variation, n: umber, LOI Loss of ignition (organic matter content – 420°C), a □ Sum of major and minor element contents

4.2 Characteristics of soils

Soils in the vicinity of Kosova A and B are mainly distributed in a mosaic of Vertisols of clay texture and Cambisols of silt or sand texture. Azonic soils in this area are Regosols and Fluvisols. The soils pH ranged from neutral to alkaline with pH values from 6.9 to 8.2 and a mean pH value of 7.6. The mean carbonate content in these soils was 1.1 % (Tab. 6). The geological host rocks are Holocene fluviatic sediments and Pliocene sediments [11]. The soils that developed in Pliocene sediments from weathered ultrabasic rocks are naturally enriched with higher contents of Cr, F and Ni [11], [13], [16], [17]. The minor element concentrations range for Ag, Mo and Br between 0.1 and 10 mg/kg, for P, S, As, Co, Cu, Pb, Sr, Th, V and Zn between 10 and 100 mg/kg, for Ba, Cr and Ni between 100 and 1000 mg/kg and for F and Mn between 1000 and 10000 mg/kg for the analyzed soil samples (Tab. 7).

Table 6: Chemical and physical characteristics of sampled soils

	pH	$CaCO_3$	LOI	H_2O	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	Σ^a
								%							
m	7.6	1.1	9.3	32.6	35.8	9.5	5.1	1.0	1.9	0.3	1.2	0.6	0.1	0.1	56.1
s	0.3	1.0	2.1	10.1	9.0	1.7	0.6	0.3	1.0	0.1	0.3	0.1	0.0	0.0	11.7
v	4	95	22	31	25	17	12	29	53	35	29	22	39	55	21
n	21	21	21	18	21	21	21	21	21	21	21	21	21	21	21

Table 7: Contents of minor elements of sampled soils

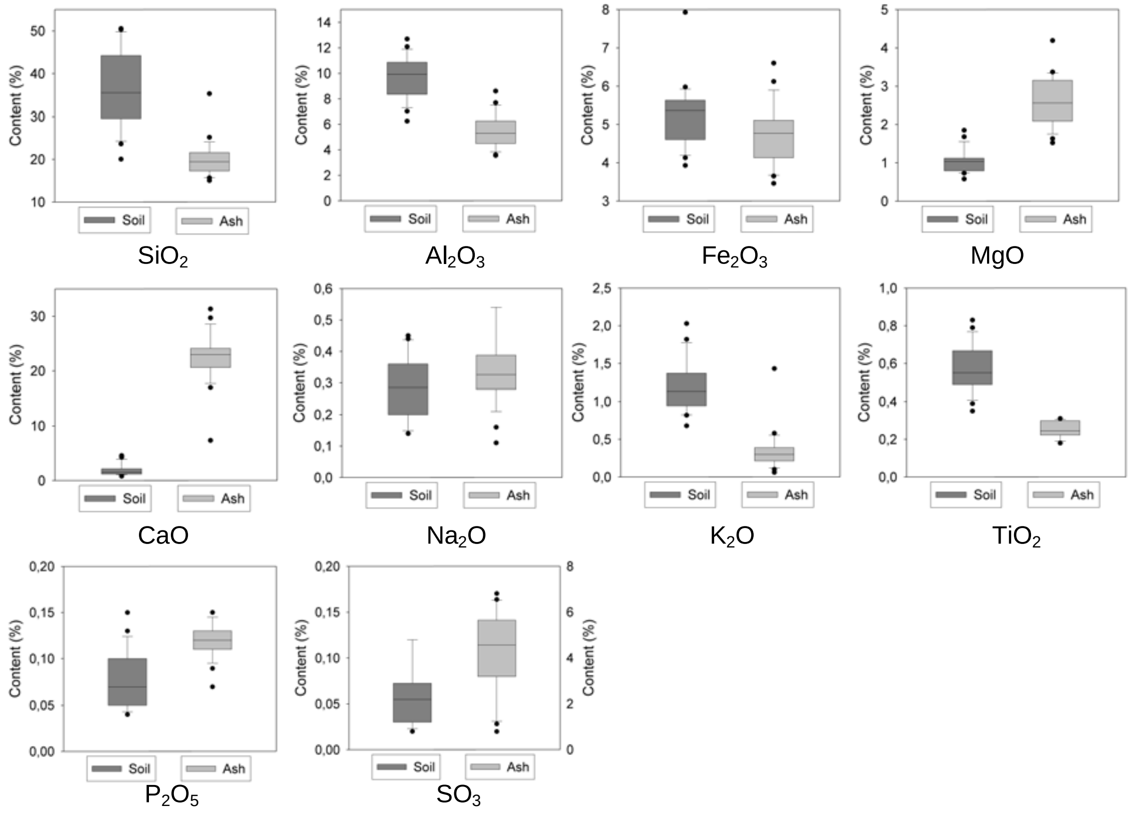
	As	Ba	Br	Co	Cu	Cr	F	Mn	Mo	Ni	Pb	Rb	Sr	Th	U	V	Zn	Zr
									mg/kg									
m	19.3	357	8.8	18.9	29.7	240	2146	1145	1.1	134	78.5	70.7	68.5	10.6	1.9	90.0	90.2	142
s	18.5	49	2.5	4.1	9.4	62	427	301	0.7	37	83.7	9.9	13.2	1.6	1.2	12.3	70.3	31
v	96	14	19	22	32	26	20	26	70	27	107	14	19	15	67	14	77.9	22
n	21	21	21	21	21	21	21	21	21	21	21	21	21	21	20	21	21	21

The origin of Cu, Cr, F and Ni are geological. Chrome, fluorine and nickel are components of the minerals in the surrounding rocks and their primary or secondary decomposition products [9], [29]. Primary minerals are in serpentinite, peridotite and biotitical slate. Other authors have described that soils formed from serpentinite can contain very high contents in Cr and Ni and also secondary minerals such as bentonite, which belongs to the smectite group [29]. The amount of $CaCO_3$, Pb and Zn vary greatly and for Cu, Cr, F, Ni and CaO the variability is very low.

Sample P 36 (Vertisol) contains mainly quartz and subordinated calcite, muskovite, montmorillonite and plagioclase (albite) and traces of chlorite. The main minerals of sample P 20 (Vertisol) are quartz and feldspar (mainly albite and some orthoclase), minor minerals are montmorillonite, illite and of traces chlorite.

4.3 Mineralogical and chemical comparison

The comparison of results with ash from other regions shows that the ash from Kosova A contains more Cr, Ni, Cl, F and S than lignite ash from Germany [9], [21]. The data also show that the ash samples show lower contents of Cr, K, Ni, Pb and Zn compared to surrounding top soils (Fig 3 and Fig. 4). The contents of Ca, Mg, Na, P and S are higher in ash samples compared to soil samples (Fig. 3).

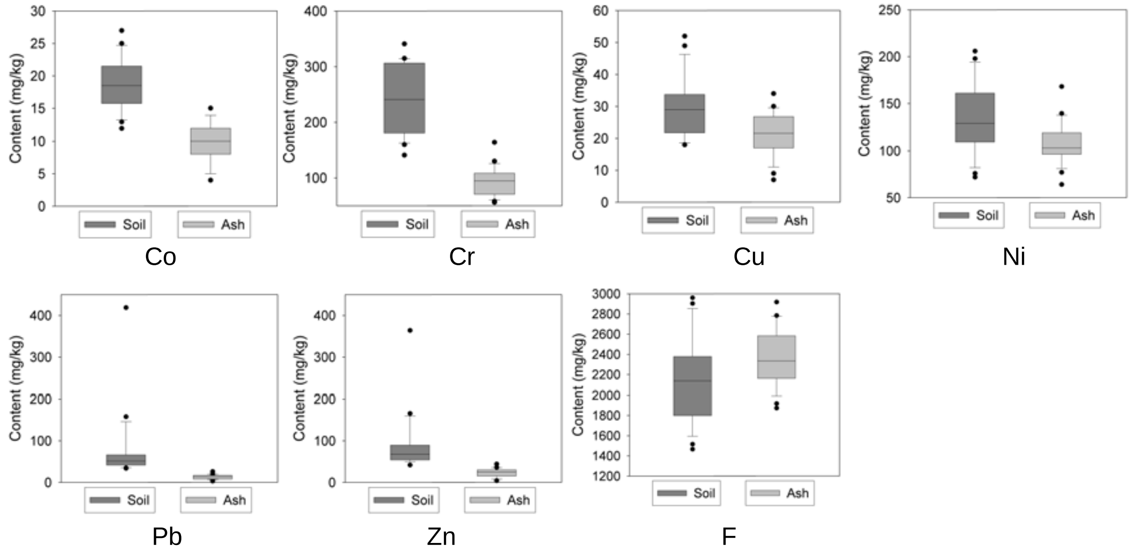


SiO_2 Al_2O_3 Fe_2O_3 MgO

CaO Na_2O K_2O TiO_2

P_2O_5 SO_3

Figure 3: Major element contents in soil and ash



Co Cr Cu Ni

Pb Zn F

Figure 5: Minor element contents in soil and ash

The mineralogical composition differs substantially from mineralogical ash composition of other regions. The ash of Kosova A contains very high contents of carbonates and sulfates (Tab. 8).

Table 8: Mineral components of ash and soil

Minerals	SA[a]	Co[a]	K[b]
mullite	+++	+++	-
amorphous Al-Fe silicates	+++	+++	-
amorphous Ca-Al-Fe silicates	++	++	-
lime, calcite, aragonite	++	-	+++
quarz	+	++	+
portlandite	+	+	+
felsspar	+	+	-
hematite	+	+	+
magnesite	+	+	+
pyrite	+	+	-
anatase	+	+	-
gypsium	-	-	+++
gehlenite	-	-	++
gismondin	-	-	+

SA South Africa, Co Columbia
[a] Nathan et al. (1999) [24]
[b] Korporata Energjetike e Kosovas (2004) and own data [30]

4.4 Environmental impacts

In strikingly high concentrations the elements Cr, Ni and F are present in the ash and soil samples. Contents of Pb, Cd, Cu and Zn are not high in ash, but for Cl very high contents have been found. Due to the high content of lime ($CaCO_3$) ash is a natural pH buffer [24], only after the entire wash out of CaO and its derivatives $Ca(OH)_2$ and $CaCO_3$ the pH sinks, but not under 7.5. For ash from Kosova A a minimum pH of 7.6 for OADD and 7.8 for OAWD was analyzed (Tab. 4). The high pH value prevents leaching of trace metals and flurine, but not of chlorine [31]. Other authors have described that lignite ash can permanently absorb trace metals [32]. In the surrounding soils Cl could not be detected and Cd, Cu, Pb and Zn were at low levels [4].

5 Conclusion

The ash disposal sites from the power plant Kosova A near Prishina are a major source of pollution due to emissions of dust enriched with carbonates and sulfates. Low graded of Cd, Cu, Pb and Zn, but for Cl very high contents have been found. Due to the high contents of lime ($CaCO_3$) ash is a natural pH buffer and prevents leaching of trace metals and flurine, but not of chlorine. Ash and soils contain high concentrations of Cr, Ni and F. These elements are governed by the base lithology where rocks such as serpentinites and biotite enriches schists exist. In soils Cl was not detected whereas Cd, Cu, Pb and Zn were analyzed for low levels of enrichment.

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