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Naturally occurring radioactive materials (NORMs) generated from lignite-fired power plants in Kosovo

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ABSTRACT

The energy production in Kosovo depends primarily on lignite-fired power plants. During coal combustion, huge amounts of fly ash and bottom ash are generated, which may result in enriched natural radionuclides; therefore, these radionuclides need to be investigated to identify the possible processes that may lead to the radiological exposure of workers and the local population. Lignite samples and NORMs of fly ash and bottom ash generated in lignite-fired power plants in Kosovo are analyzed using a gamma-ray spectrometry method for the activity concentration of natural radionuclides. The average activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in lignite are found to be 36 ± 8 Bq kg^{-1}, 9 ± 1 Bq kg^{-1} and 9 ± 3 Bq kg^{-1}, respectively. Indications on the occurrence and geochemical behavior of uranium in the lignite matrix are suggested. The activity concentrations of natural radionuclides in fly ash and bottom ash samples are found to be concentrated from 3 to 5 times that of the feeding lignite. The external gamma-ray absorbed dose rate and the activity concentration index are calculated to assess the radiological hazard arising from ash disposal and recycling in the cement industry.

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1. Introduction

In Kosovo, lignite combustion is the main energy source for the production of electricity. Kosovo has one of the largest lignite deposits in world, with reserves of up to approximately 14.7 billion tons. Approximately 97% of the electricity in Kosovo is produced from the coal-fired power plants (CFPPs) Kosova-A and Kosova-B, with a total installed capacity of 1478 MWe, operating under the Kosovo Electricity Corporation (KEC). Due to degradation and damages the overall available power generation capacity is approximately 910 MWe. The energy deficit from the decommissioning of Kosova-A CFPP, expected to be completed in 2017, will be replaced by the construction of a "new generation" CFPP, known as Kosovo e Re, which will meet the current environmental requirements.

The exploited lignite, principally used for electricity production, generates a large amount of residues as fly ash and bottom ash that are derived from coal combustion. The total amount of ash is estimated to be approximately 55 million tons, according to the Kosovo Environmental Protection Agency (2012). Coal generally contains trace amount of radionuclides with a typical range of activity concentrations of 30–100 Bq kg^{-1}, 10–600 Bq kg^{-1} and 10–200 Bq kg^{-1} (Xhixha et al., 2013), respectively, for ^{40}K, ^{238}U and ^{232}Th. However, some types of coal contain considerably higher amounts of ^{226}Ra, which for lignite is not necessary in equilibrium (Papastefanou, 2010). Moreover, when coal is burned in coal-fired power plants, the remains, such as coal slag and fly ash, become more enriched in naturally occurring radionuclides than the unburned coal. The fly ash and the bottom ash generated from the coal fired thermal power plants are significant sources of exposure to the naturally occurring radionuclides that especially affect the workers and populations in the vicinity of the plant (Papp et al., 2002; Bem et al., 2002). Indeed, according to the new Basic Safety Standard (2014), coal fired power plants are included in the list of sectors involving naturally occurring radioactive materials (NORMs) and shall be investigated to classify their potential for exposure to workers and populations from the radiological

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perspective. Because the generated ashes may either be disposed in landfills or recycled in other applications, such as in cement production (Kovler, 2011), agriculture use as a soil ameliorant (Basu et al., 2009) and other applications, it is very important to study in detail the radiological characteristics of combustion residues.

Previous studies of natural radioactivity in coal fired power plants in Kosovo (Adrović et al., 1997) make an overview of concentrations of natural radionuclides in coal, fly ash and bottom ash streams. In this study, we determined the radioactive concentration in NORMs, such as fly ash and bottom ash that are generated by the Kosova A and B CFPPs with the aim to understand the enrichment mechanisms. The lignite used in the power plants is also examined. Moreover, the radiological hazard was assessed for a better determination of the radiation exposure, both occupationally and publicly, caused by the produced ashes. Since the fly ash and bottom ash are principally used as additives in cement production in Kosovo, their radiological hazards are also evaluated.

2. Materials and method

2.1. Study area

The area of the present study is in central eastern Kosovo, approximately 10 km from Pristina (Fig. 1), which has a population of approximately 0.2 million habitants (approximately 10% of Kosovo's population). The Kosovo-A and Kosovo-B CFPPs are located in the Kosova plain, in northeastern Kosovo, close to one of the main Pliocene lignite reserves that is affected by mining activities. Other important lignite reserves are located in the Dukagjini and Drenica plains, located in southwestern Kosovo. Kosovo's lignite has a low sulfur content and a relatively good concentration of lime (calcium oxide) for absorbing sulfur during the combustion process, with an average combustible sulfur of 0.35% (Morina et al. 2012). The quarried lignite is characterized by an average moisture content of 46%, a calorific value of 7640 kJ kg^{-1} and a fly ash fraction of 16% wt. The feed coal is quarried in the open cast mines of Bardh, Mirash and a new mine in Sibovc, with approximately 8.8 million tons quarried per year (Fig. 1). The average specific coal consumption for the Kosova-A and Kosova-B CFPPs in 2013 is, respectively, approximately 1.705 t MWh^{-1} and 1.230 t MWh^{-1}. In particular, approximately 1.36 million tons of fly ash and 0.25 million tons of bottom ash are generated by the Kosova-A and Kosova-B CFPPs, accounting for approximately 15.5% wt. and 2.8% wt. of the lignite used (Kosovo Energetic Corporation, 2013). These quantities are reasonable considering the ash content in feeding lignite.

2.2. Sampling and sample preparation

The lignite is sampled in the Kosova-A and Kosova-B CFPP coal yards by collecting eight samples of pulverized feeding lignite (Fig. 1). The fly ash and bottom ash residues are sampled from the boilers and the electrostatic precipitators in two different periods over a year by collecting nine samples each. The lignite coal and bottom ash samples are milled and homogenized into fine powders with a particle size of less than 2 mm, whereas the fly ash samples are directly processed because they are already in powder form. To remove the moisture content, all of the samples are dried in a temperature-controlled furnace at 110 °C for at least 24 h (or until constant weight). After cooling in a moisture-free atmosphere, each sample is transferred for measurement to a cylindrical PVC container (with an effective volume of 180 cm^3) and then mass weighted. The hermetically sealed containers are stored for at least 4 weeks to allow ^{226}Ra and its short-lived decay products to reach the secular equilibrium prior to being measured by high-resolution gamma-ray spectrometry (HPGe).

2.3. High-resolution gamma-ray spectrometry measurements

The activity concentrations are measured using the so-called MCA_Rad system described in detail in Xhixha et al. (2013). The MCA_Rad system is self-constructed consisting of two 60% relative efficiency coaxial p-type HPGe gamma-ray detectors, with an energy resolution of approximately 1.9 keV at 1332.5 keV (^{60}Co). The MCA_Rad system is accurately shielded by 10 cm of cooper and 10 cm of lead, leaving a space between the two detectors of a volume of approximately 180 cm^3 that is dedicated to hosting the sample container. The acquisition process is fully automated with a capacity of 24 samples managed without human intervention. The absolute full energy peak efficiency of the MCA_Rad is calibrated

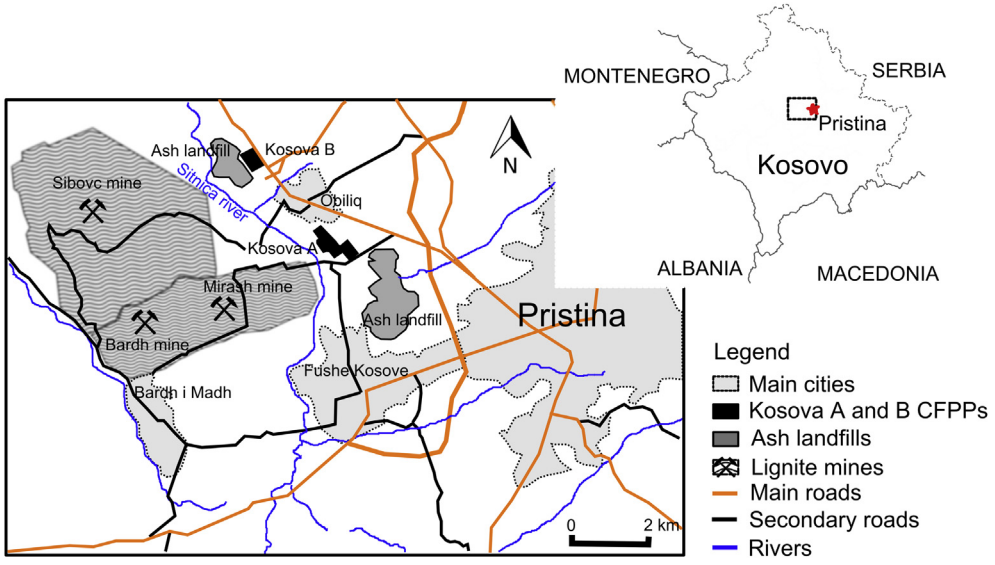


Fig. 1. Locations of Kosova-A and Kosova-B CFPPs, lignite mines and ash dumps that are the subject of investigation in this study.

using certified standard point sources (^{152}Eu and ^{56}Co). The overall uncertainty in the efficiency calibration is estimated to be less than 5%.

The natural activity concentration of ^{226}Ra is determined through 351.9 keV (37.1%) of ^{214}Pb and 609.3 keV (46.1%) of ^{214}Bi. The activity of ^{232}Th is assessed by considering the equilibrium with ^{228}Ra, which is determined using a gamma-ray of 911.1 keV (30.3%) of ^{228}Ac and 583.1 keV (33.2%) of ^{208}Tl. The activity concentration of ^{40}K is determined using the 1460.8 keV gamma-ray.

3. Results and discussion

3.1. Activity concentration

Table 1 shows the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in lignite, varying between 29 and 53 Bq kg^{-1}, 7 and 10 Bq kg^{-1} and 4 and 12 Bq kg^{-1}, respectively. The mean activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in lignite are, respectively, 36 ± 8 Bq kg^{-1}, 9 ± 1 Bq kg^{-1} and 9 ± 3 Bq kg^{-1}. Uranium can be enriched in a lignite matrix principally associated with organic matter, rather than the U minerals that are present, such as coffinite and uraninite. The enrichment occurs under redox weathering processes prevalent in the clay/lignite horizon and can form uranifeous lignite of potential ore grade (Douglas et al., 2011). This indicates that the uranium in the lignite has been introduced after the formation of the lignite leached by groundwater. In the lignite samples from Kosovo, a slight enrichment of uranium (assumed to be in equilibrium with ^{226}Ra) due to geochemical processes can be observed with respect to thorium, where the average ratio of abundances of Th/U (U and Th are converted in abundances expressed in μg g^{-1} dividing by the conversion factors of 12.35 and 4.06 Bq kg^{-1} (μg g^{-1})$^{-1}$, respectively) is found to be 3.0. This compared to world average radioactivity content of the upper continental crust (Th/U ratio value of approximately 3.9) and several studies reported in Table 1, which show a range of the Th/U ratio from 0.2 in Greece (Karangelos et al., 2004) to 2.4 in Italy (Borio et al., 1985). The highest concentrations of ^{226}Ra are observed for the lowest values of the Th/U ratio; this indicates the relatively high mobility of uranium compared to thorium, which is expected to be associated with the accessory mineral having more resistant properties with regards to weathering conditions (Coles et al., 1978). Therefore, the high Th/U ratio in lignite samples from Kosovo may be an indicator of either the low plant uptake of uranium due to the basic origin of host rocks and/or due to the leaching of uranium and inefficient uptake of organic matter in peat formed in acid conditions. Indeed, the activity concentrations of radionuclides in lignite from Kosovo, and especially the activity concentration of ^{226}Ra, are the lowest with respect to other studies (Table 1).

Fly ash and bottom ash samples show higher activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th relative to lignite: in fly ash, respectively, the concentrations are133 ± 16 Bq kg^{-1}, 30 ± 3 Bq kg^{-1} and 30 ± 3 Bq kg^{-1}; whereas in bottom ash, respectively, the concentrations are 195 ± 13 Bq kg^{-1}, 28 ± 3 Bq kg^{-1} and 34 ± 2 Bq kg^{-1} (Table 1). The concentration of radionuclides in ash occurs principally as most of the carbonaceous matter in coal oxidizes during combustion and the radionuclides become concentrated in the residue mass. The mass concentration factor, i.e. the concentration of radionuclides due to the mass reduction, is found to vary from 3 to 5 times that of the feeding lignite for ^{40}K, ^{226}Ra and ^{232}Th in the fly and bottom ash. The mean mass concentration

Table 1
Averages and ranges of activity concentrations (in Bq kg^{-1}) of natural radionuclides in lignite (L), bottom ash (BA) and fly ash (FA) measured in Kosovo and compared with several studies from different countries.

Country	Sample type	^{40}K (Bq kg^{-1})		^{226}Ra (Bq kg^{-1})		^{232}Th (Bq kg^{-1})	
		Mean	Range	Mean	Range	Mean	Range
Kosovo (this study)	L	36 ± 8	29–53	9 ± 1	7–10	9 ± 3	4–12
	BA	195 ± 13	168–211	28 ± 3	22–31	34 ± 2	32–38
	FA	133 ± 16	104–146	30 ± 3	26–35	30 ± 3	27–34
Kosovo Adrović et al., 1997	L	–	14–97	–	3–14	–	2–19
	BA	–	111–243	–	13–63	–	14–31
	FA	–	208–245	–	15–61	–	15–32
Serbia Kisić et al., 2013	L	60	11–101	16[c]	0.5–33	12	3–20
	BA	–	–	–		–	–
	FA	408	311–509	130	91–152	84	71–104
Sebia Janković et al., 2011	L	120	45–243	29	14–52	21	11–32
	BA	241	67–375	65	17–114	39	14–3
	FA	360	174–489	120[c]	45–270	72	29–121
Greece Papastefanou 2010	L	108	59–227	133	44–236	18[a]	9–41
	BA	–	–	–	–	–	
	FA	297	204–382	366	142–605	50[a]	27–68
Greece Karangelos et al., 2004	L	173 ± 14	148–207	346 ± 2	309–395	19 ± 9	19–24
	BA	405 ± 11	334–460	662 ± 9	583–743	44 ± 5	41–47
	FA	454 ± 11	403–516	904 ± 9	794–1028	53 ± 5	50–57
Spain Mora et al., 2009	L	104 ± 15	–	64 ± 3	–	18 ± 3	–
	BA	235 ± 11	–	149 ± 6	–	66 ± 3	–
	FA	306 ± 13	–	191 ± 9	–	74 ± 3	–
Turkey Cevik et al., 2007	L	123 ± 11	–	15 ± 2	–	11 ± 2	–
	BA[b]	376 ± 9	–	50 ± 1	–	25 ± 2	–
	FA	94 ± 28	–	149 ± 2	–	58 ± 4	–
Turkey Cevik et al., 2008	L	435 ± 9	–	81 ± 1	–	39 ± 9	–
	BA[b]	307 ± 12	–	313 ± 5	–	51 ± 9	–
	FA	493 ± 17	–	242 ± 4	–	51 ± 14	–
Italy Borio et al., 1985	L[d]	218 ± 5	–	23 ± 1	–	18 ± 1	–
	BA	1046 ± 13	–	115 ± 2	–	67 ± 3	–
	FA	820 ± 15	–	86 ± 2	–	56 ± 3	–

[a] Reported as ^{228}Ra.
[b] Reported as slag.
[c] Reported as ^{238}U.
[d] Reported as brown coal.

factors in fly ash are found to be slightly lower due to the inverse ash content in lignite. However, the higher variability compared to previous studies in Kosovo (Adrović et al., 1997) implies further investigations to effectively control these residues in case of disposal and reuse. These mass concentrations are more comparable with typical values observed in other studies as they are chiefly related to variations in the quality of the feeding coal and the power plant conditions, whose lower and upper mass concentration factors levels are 1 and 7, respectively. However, in the case of Serbia (Kisić et al., 2013) and Turkey (Cevik et al., 2007), the activity concentrations of ^{226}Ra are found to be concentrated 8 and 10 times, respectively.

To account for the loss of carbon during the combustion process, the radionuclide enrichment factor is calculated after being normalized with respect to ^{40}K, which is assumed to be a tracer for the aluminosilicate portion after coal combustion (Coles et al., 1978). The normalized enrichment factors of radionuclides, (EF_x), relative to the feeding coal is calculated according to the Eq. (1):

$$EF_X = \frac{(A_X/A_{40K})_{\text{ash}}}{(A_X/A_{40K})_{\text{lignite}}} \quad (1)$$

where X denotes the ^{226}Ra and ^{232}Th radionuclides, and A_x are the respective activity concentrations (in Bq kg^{-1}). The results show no enrichment of ^{226}Ra in the fly ash of 0.9 ± 0.3 and depletion in the bottom ash samples of 0.6 ± 0.2, which is within the reported uncertainty. The general behavior of ^{226}Ra is considered to be a non-enriched element; however, several studies observed enrichment in ^{226}Ra as well as ^{238}U in finer fly ash particles (Papastefanou, 2010 and authors therein). Therefore, the depletion of ^{226}Ra in the measured bottom ash sample may be attributed to the formation of volatile compounds of radium and later condensation in finer fly ash particles. The depletion in the bottom ash sample may imply that the uranium associated with silicates, or which is mineralized as coffinite, exists in a lesser content than that associated with the uraninite composing the matrix of the studied lignite samples. It is known that the latter forms volatile compounds (Coles et al., 1978). However, this assumption is only partially supported since the data don't support an enrichment of ^{226}Ra in fly ash within the reported uncertainty. Thorium, a refractory element, is considered to be associated with aluminosilicate minerals as ^{40}K; this assumption seems to be confirmed by the obtained results where the enrichment factor is close to unity within the reported uncertainty of 0.9 ± 0.4 for fly ash and 0.7 ± 0.3 for bottom ash. However, the results may indicate a slight depletion of thorium in the bottom ash samples.

Base on a rough study of the mass balance analysis for Kosovo coal fired power plants (annual energy generation of approximately 1 GW), considering the amounts of lignite and produced fly and bottom ash (discussed above) and the activity concentrations reported in Table 1, we can calculate a loss of total activity through for ^{40}K, ^{226}Ra and ^{232}Th of approximately 30% (150 GBq). Considering other streams of waste that can account for the total activity, like scale generated during the maintenance of coal combustion boilers, a portion can be attributed to gross particulate dispersion in the atmosphere. According to UNSCEAR (1988) the average annual atmospheric particulate discharges of radionuclides for old coal fired power plants (fly ash removal efficiency of 90%) are accounted to be approximately 15 GBq (GW y)$^{-1}$ (calculated for ^{40}K, ^{226}Ra and ^{232}Th). Therefore, the issue of radionuclide escape in atmospheric emissions is of important relevance for environmental and health protection and would be topic of further studies.

3.2. Radiological hazard assessment

The outdoor external gamma-ray absorbed dose rates (D in nGy h^{-1}) at 1 m above ground level, for workers and the local population, due to the presence of radionuclides in lignite coal and ash ponds, can be evaluated assuming uniformly disposed material, according to Eq. (2) (UNSCEAR, 2000):

$$D = 0.0417A_{40K} + 0.462A_{226Ra} + 0.604A_{232Th} \quad (2)$$

where A_{40K}, A_{226Ra}, A_{232Th} are the activity concentrations (in Bq kg^{-1}) of ^{40}K, ^{226}Ra and ^{232}Th, respectively. This evaluation is an attempt to prevent any radiological risk by calculating the worst-case scenario, i.e., the presence of workers or a population above lignite and ash ponds with spatial dimensions much higher than human (i.e., practically close to infinite dimensions). The average outdoor absorbed dose rates (at ±1σ uncertainty) are 11 ± 1 nGy h^{-1} for lignite coal, 37 ± 2 nGy h^{-1} for fly ash and 41 ± 2 nGy h^{-1} for bottom ash. The maximum and minimum absorbed dose rate values are found in lignite and bottom ash ponds, respectively, and are 9 ± 2 and 45 ± 3 nGy h^{-1} (Table 2). However, the absorbed dose rate results are lower than the population-weighted average absorbed dose rate in the outdoor air from terrestrial gamma radiation (60 nGy h^{-1}) (UNSCEAR, 2000).

The radiological hazard for workers and populations living in the proximity of the power plant is evaluated in terms of the annual effective dose rate (AEDR in μSv y^{-1}). The evaluation of the annual effective dose rate is performed adopting an outdoor time occupancy factor equal to 20% and a conversion factor of 0.7 (Sv Gy^{-1}), which accounts for the dose rate's biological effectiveness in causing damage to human tissue (Eq. (3)):

$$AEDR = 10^{-3} D\left[\mu\text{Gy h}^{-1}\right] \times 8760\left[\text{h y}^{-1}\right] \times 0.2 \times 0.7\left[\text{Sv Gy}^{-1}\right] \quad (3)$$

The obtained outdoor annual effective dose rates are 12 ± 1 μSv y^{-1}, 50 ± 1 μSv y^{-1} and 46 ± 3 μSv y^{-1}, respectively, in lignite, bottom ash and fly ash ponds (Table 2). These values are found to be lower than the global annual effective dose value of 70 μSv y^{-1}, as reported by UNSCEAR (2000). The contribution of NORMs in the external gamma-ray exposure to workers and the

Table 2
Average (±1σ) and range of external gamma-ray absorbed dose rates (D in nGy h^{-1}), the annual effective dose rate (AEDR in μSv y^{-1}) and the activity concentration index (ACI) of NORMs generated from lignite-fired power plants in Kosovo.

Sample type		D (nGy h^{-1})	Reference value (UNSCEAR, 2000)	AEDR (μSv y^{-1})	Reference value (UNSCEAR, 2000)	ACI[b]	Reference value (BSS, 2014)
Lignite	mean	11 ± 1	60	13 ± 1	70	–	–
	range	9–14		11–17		–	
Bottom ash	mean	41 ± 2		50 ± 2		0.03 ± 0.002	1[a]
	range	39–45		48–55		–	
Fly ash	mean	37 ± 2		46 ± 3		0.03 ± 0.001	
	range	34–40		42–50			

[a] Maximum ACI value for end-product building materials.
[b] ACI value weighted for the partitioning of fly ash as composite material in concrete and cement according to mass fractions.

local population is calculated to be negligible considering the recommended level of permissible excess of the effective dose rate for the population (1000 μSv y^{-1}).

The fly ash and bottom ash produced by the CFPPs in Kosovo is appropriately used in cement production, whereas no data exist for other applications in Kosovo. According to EN 197-1 (2000), the fly ash is classified as type W (calcareous nature), showing hydraulic properties when used as a cement additive. Another system of coding cement additive materials is used according to ASTM C618:12a (2012), where coal fly ash that exhibits similar hydraulic properties is classified as type C. In Kosovo, approximately 20% of the fly ash and 2% of bottom ash produced annually is recycled in cement production. According to the new Basic Safety Standard (2014), to assess the radiological contribution of fly ash the activity concentration index (ACI) is used. This index is used as a screening tool and applies to end products; in the case of constituents, rather than producing composite building materials, the application of appropriate partitioning factors is recommended. Therefore, considering concrete as an end-product, where the mass fraction of cement used for its production is e.g. 10%, assuming the utilization of fly ash as a cement additive at a proportion of 30%, the partitioning factor (f) used to calculate the radiological contribution of fly ash to the concrete end-product is approximately 0.03 (Eq. (4)):

$$ACI = f \times \left(\frac{A_{40K}}{3000} + \frac{A_{226Ra}}{300} + \frac{A_{232Th}}{200}\right) \quad (4)$$

The estimated average ACI index for concrete, due to the use of fly and bottom ash as cement additives, is found to be 0.01 (±6%). These results show that from the radiological perspective, fly ash and bottom ash are suitable materials to be used as cement additives.

4. Conclusions

Fly ash ($N = 9$) and bottom ash ($N = 9$) NORMs generated from Kosovo CFPPs and the feeding lignite ($N = 8$) are characterized for the activity concentration of ^{40}K, ^{226}Ra and ^{232}Th by means of gamma-ray spectrometry measurements. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th, in lignite samples are found to be lower compared with several available studies. However, considering the higher variability shown in previous studies in Kosovo, we recommend further investigations to effectively control these residues in case of their disposal and reuse. Indications on the possible low plant uptake of uranium from host rocks and/or high leaching in acidic peat environments can be deduced by comparing the high Th/U ratio (equal to 3.0) in lignite from Kosovo with other studies (ranging from 0.2 to 2.4). The natural radionuclides are found in concentrations from 3 to 5 times greater in fly ash and bottom ash samples after lignite combustion. These concentration factors are typical of other studies with a maximum dispersion from 1 to 7, and in the case of ^{226}Ra the concentration factor can reach values as high as 8–10 times. On the one hand, the radionuclide enrichment factor, normalized for potassium, shows no enrichment of ^{226}Ra in fly ash (0.9 ± 0.3) and a decrease in bottom ash (0.6 ± 0.2). On the other hand, ^{232}Th remains invariant within the reported uncertainty in fly ash (0.9 ± 0.4) and bottom ash (0.7 ± 0.3). The depletion of ^{226}Ra in bottom ash may indicate a relatively higher presence of uraninite with respect to coffinite in the lignite matrix because the former is known to form volatile compounds of ^{226}Ra and therefore causes enrichment of the fly ash. However, the invariant activity concentration in fly ash leads us to further study the activity concentrations in atmospheric particulate emissions, since can lead to environmental and health issues. From the radiological perspective, there is no significant excess of the external absorbed dose rate for workers and populations living near lignite, fly ash and bottom ash ponds. Furthermore, fly ash and bottom ash are found to be suitable materials for use as cement additives.

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