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Chemometrics of the distribution and origin of ^{226}Ra, ^{228}Ra, ^{40}K and ^{137}Cs in plants near the West Macedonia Lignite Center (Greece)

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The distribution and origin of ^{40}K, ^{226}Ra, ^{228}Ra and ^{137}Cs has been investigated in trees, mosses and lichens in the basin of the West Macedonia Lignite Centre. In tree leaves ^{137}Cs is negligible, while the ^{226}Ra and ^{228}Ra concentrations are affected by the fly ash particles. Concerning ^{226}Ra and ^{228}Ra values of mosses and lichens, which are systematically larger than those of unpolluted areas, the application of chemometrics proved that they originate mainly from the lignite fly ash.

Introduction

Lignite is the main solid fuel used in Greece. Its calorific value is relative small (~1200 kcal/kg), while the ash content is rather large (about 15%). So, an important amount of ash, estimated to 0.6 to 5.5 tons per GWh, is constantly produced by lignite power plants (LPPs).[1–2]

One of the most important natural coal reserves of Southeast Europe, the Lignite Center of West Macedonia (LCWM), lies in the Northwestern part of Greece. Four LPPs with a total installed power of 4 GW account for approximately 70% of the total electricity produced in Greece.[3] The LPPs are located in a valley with a total area of about 2300 km^2 and an average altitude of 700 m. This basin is surrounded by mountains whose altitude can reach 2190 m (Fig. 1).

At present time, the average production of lignite is $51 \cdot 10^6$ tons/year and as a result $7.14 \cdot 10^6$ tons/year of ash is deposited near the mines and about 21400 tons/year of fly ash is discharged into the atmosphere.[2] The fly ash of LCWM is C class and calcic type,[4] whereas its trace element concentrations are smaller than those found in other countries.[5]

Both organic and mineral parts of the lignite contain natural radionuclides and their decay products, such as ^{40}K and the radioactive series of ^{238}U, ^{235}U and ^{232}Th, in concentrations comparable to the average radioactivity of the earth's crust. However, the fly ash of lignite contains one order of magnitude larger concentrations of the above radionuclides, and represents a potential source of radioactive pollution.[6–9]

Another radioactive pollutant, ^{137}Cs, has been released into the atmosphere due to nuclear tests and the Chernobyl accident. The LCWM basin is one of the areas most highly affected by the Chernobyl fallout in Greece, with a ^{137}Cs deposition estimated[10] at 24 kBq/m^2 in 1986.

As both natural radionuclides from fly ash and radiocesium are finally deposited on the ecosystems, their presence and potential impacts should be carefully investigated. This paper presents the results obtained from the investigation of the total radioactivity of some plant organisms, such as trees, mosses and lichens collected in the LCWM basin.

For a thorough study of the classification of the radionuclides and the investigation of their potential common origin two methods of statistical analysis were used, i.e., cluster analysis, and principal component analysis (PCA).

Experimental

Sampling

According to dispersion models,[11] the fly ash deposition takes place mostly in the center of the LCWM basin, but the airborne particles corresponding to the PM$_{10}$ size fraction can reach as far as the south-west part of the investigated region. Therefore, most of the sampling sites were chosen in the LCWM basin as well as along the axis of the prevailing north - northwest (NNW) to south-southeast (SSE) wind direction.

Fifteen sampling points have been used, i.e., eleven for trees and four for mosses and lichens. The latter were present in sufficient sampling quantity only in four sampling points, all situated very close to the four LPPs. The position of each sampling station was determined by means of the Global Positioning System GPS with a precision of 18 m. Six moss species have been investigated: *Grimmia loevigata, Rhacomitrium canescens, Tortula ruralis*, *Eucalypta streptocarpa, Homalothecium aureum*, *Tortella tortuosa*, five lichens species: *Cladonia rangiformis*, *Parmelia sulcata, Pertusaria sp.*, *Cladonia convoluta*, *Xanthoria parietina* and leaves of the following tree species: *Pinus nigra*, *Pyracantha coccinea*, *Prunus amygdalus* and *Populus nigra*.

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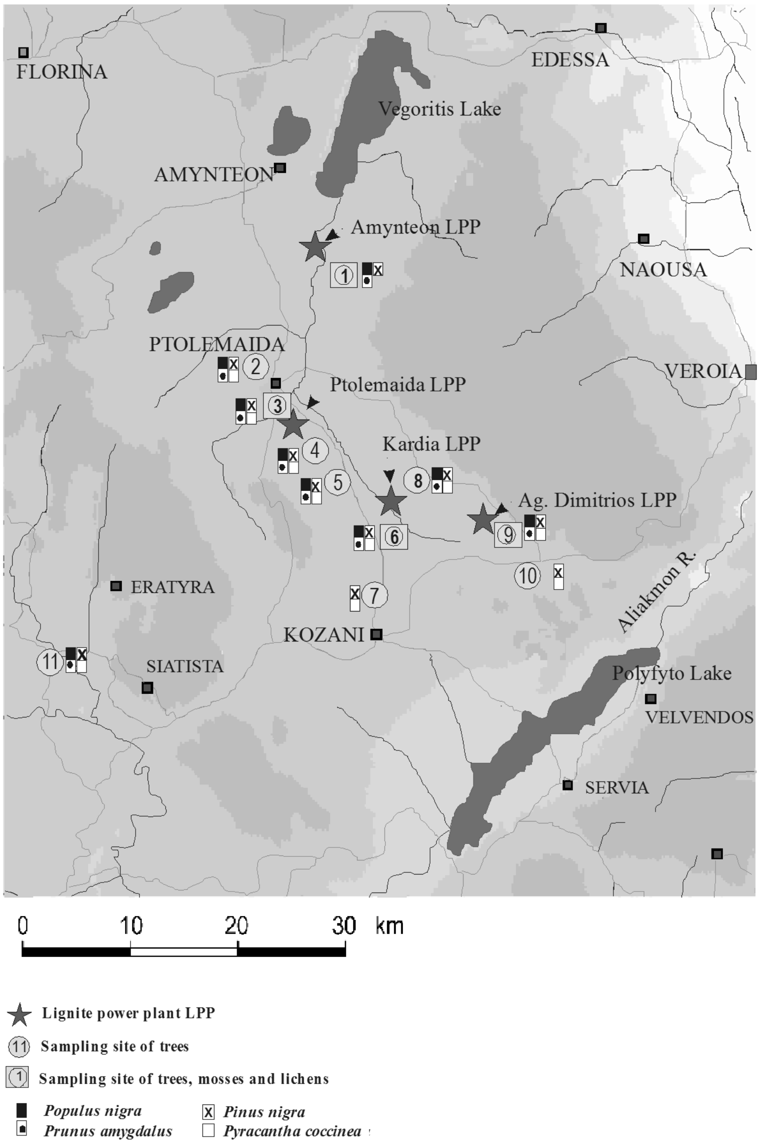

Fig. 1. The general map of LCWM basin with the sampling sites

All samples were collected after a prolonged dry spell (October 1998), washed with distilled water, air-dried, ground and sieved with a 2 mm mesh. Sub-samples of 30–50 g were weighed, sealed into cylindrical plastic boxes (68 mm diameter and 18 mm height) and stored for one month, in order to achieve radioactive equilibrium. Thus, it was possible to determine the concentrations of ^{226}Ra and ^{228}Ra isotopes together with ^{40}K and ^{137}Cs by γ-ray spectrometry.

The total number of the samples was 40 for tree leaves, 23 for lichens and 25 for mosses.

Measurements by γ-ray spectrometry

The radiometric measurements were performed at the TEI Environment Radioactivity Laboratory in Kozani by means of a 73 cm^3 SILENA HPGe detector (10.6% relative efficiency, 1.9 keV resolution for ^{60}Co 1.332 MeV γ-rays) connected on line with a SILENA 8192 multi-channel analyzer (MCA). Gamma-ray spectra were registered for ~40 hours and evaluated by means of SILENA GAMMA 2000 software. Efficiency calibration of the detector was performed by using IAEA-373 reference material.[12] The ^{226}Ra sample specific activity was determined from the weighted mean of two ^{214}Bi (609.3 and 1120.3 keV) and three ^{214}Pb γ-rays (241.98, 295.2 and 351.9 keV). Similarly, ^{228}Ra sample specific activity was calculated by means of 583.1 keV ^{208}Tl and 238.6 keV ^{212}Pb γ-rays. All spectra were corrected for the background by means of the "background subtraction" function of the GAMMA 2000 software.

Cluster and PCA analyses

Cluster (unweighted pair-group average, Euclidean distances) and PCA analyses were also used in order to evaluate statistically the radionuclide concentrations in mosses and lichens. The methods in question were not applied to tree samples because of the small number of data.

For all the analyses reported, a logarithmic transformation was applied to the data,[13] in order to avoid deleting the data series, which had even one zero-value concentration. Values below the analytical detection limit were assigned to half of the detection limit.[14]

Results and discussion

Tree leaves

The ^{137}Cs concentrations are very small, in fact, most of them are under 1 Bq/kg. The average values for the investigated tree species range from 0.3 Bq/kg (*Populus nigra*) to 0.5 Bq/kg (*Pinus nigra*). For the total number of 40 tree samples the mean concentration is 0.4 Bq/kg. These values cannot be attributed to the tree inventory, which was created during the Chernobyl fallout. In fact, when it comes to trees planted before 1986, such as those investigated, the Chernobyl inventory had been decreased to 2–5% within a period of 2 years (i.e., in 1988), due to the small value of the effective time (T_{eff}), which is about 0.7 years for trees lying in the same latitude.[15] It is, therefore, assumed that the specific activities of ^{137}Cs would be negligible and in most cases below the detection limit, which is 0.1 Bq/kg. That does not happen, though, since the mean value is 0.4 Bq/kg.

The systematically larger concentrations of ^{137}Cs in tree leaves must be attributed to: (1) the resuspension of ^{137}Cs from the soil, which can cling to the green parts of the plant.[16] The resuspension is quite intense in the LCWM basin, because of the exploitation works and the morphology of the area (a barren treeless landscape); (2) the uptake through the roots, although it is not so important, due to the alkalinity of the soil in most parts of the study area,[5] and (3) the background of ^{137}Cs, which is due to the world nuclear tests.

With regard to the radionuclides of ^{226}Ra and ^{228}Ra, the first one was detected only in 9 of 40 samples, whereas the ^{228}Ra in none. Having evaluated these data, we can say that the ^{226}Ra concentrations with a mean value of 3.7 Bq/kg and a maximum of 36.4 Bq/kg are not alarming in tree leaves. Still they are larger compared to the UNSCEAR data for leafy vegetation[17] as well as to other values quoted in Reference 18 to 20. Taking into account that (1) the samples containing ^{226}Ra come from sampling sites close to the power plants, (2) the fly ash has one order of magnitude more ^{226}Ra than ^{228}Ra[8] and (3) the transfer factors (TF) in our samples were visibly larger than the TF values from relevant References 18 to 20 (Table 1) we can say that ^{226}Ra can be attributed mostly to the fly ash emissions.

Lichens and mosses

Tables 2 and 3 give the average specific activities of lichens and mosses for each sampling station, accompanied by comparative data.[8,9,21] Both in mosses and lichens the ^{137}Cs specific activities remain large. Given the old age of the samples (more than 12 years), the existence of radiocesium is almost exclusively attributed to the Chernobyl accident. ^{137}Cs concentrations are about three orders of magnitude higher in lichens and mosses than in tree leaves. This fact confirms once more the higher ability of these organisms to accumulate air pollutants including radionuclides.[9,16,22,23]

The ^{134}Cs, with a mean value of 21.4 Bq/kg, originates exclusively from the Chernobyl accident, a finding which is borne out by the value of the ratio ^{134}Cs/^{137}Cs. Indeed, according to our results, this value (Tables 2 and 3) was found to be 0.01 when measured in 1998 (sampling year), whereas in 1986 its value was calculated at 0.54. That year the real ratio ^{134}Cs/^{137}Cs due to Chernobyl fallout was 0.4[1] which is quite close to our data.

The cluster and PCA analyses applied on radionuclide concentrations of mosses and lichens yielded nine diagrams. Only two are presented here, those regarded as most representative. In Fig. 2a the tree-diagram of mosses (grouping per radionuclide) while in Fig. 2b the results of PCA analysis for lichens' data are illustrated. The following comments can be registered:

(1) The tree-diagram of mosses is identical with the tree-diagram of lichens (not illustrated). This is due to the fact that, several years after the Chernobyl accident, the ^{137}Cs concentrations of mosses and lichens are very close[24] despite the fact that lichens have a higher ability of bioaccumulation of radionuclides.[25] With regard to^{137}Cs and ^{40}K, they seem to appear as separate branches because of their large concentrations, in comparison with the other radionuclides.

Table 1. Comparison of the ^{226}Ra concentrations of the trees as well as the transfer factor (TF) values with the bibliographical ones

Tree species	^{226}Ra range, Bq/kg	^{226}Ra mean value, Bq/kg	Transfer factor (TF)	Reference	Notes
Pinus nigra	0.0–14.4	2.2		Present study	^{226}Ra of soil = 23 Bq/kg
Populus nigra	0.0–33.5	1.9			
Prunus amygdalus	0.0–15.5	5.4			
Pyracantha coccinea	0.0–36.4	4.6			
All tree species (40 samples)	0.0–36.4	3.7	0.169 (The calculation of TF is based to Ref. 1)	Present study	^{226}Ra of soil = 23 Bq/kg
Data from bibliography for leafy vegetation					
Pinus pinea		~2	~0.01	18	^{226}Ra of soil = 20 Bq/kg
Cistus ladamiter	1.5–2.5		~0.06	19	^{226}Ra of soil ~40 Bq/kg
Spartina densiflora	1.44–15.2		0.084	20	^{226}Ra of soil = 2–711 Bq/kg

Table 2. Average specific activities (±1SD) of the investigated radionuclides in the lichens (in Bq/kg)

Sampling site	^{40}K	^{137}Cs	^{134}Cs	^{226}Ra	^{228}Ra	Ratio ^{226}Ra/^{228}Ra
Amynteon LPP (#1)	161 ± 92	2061 ± 1031	17.6 ± 8.0	29.5 ± 19.4	12.3 ± 11.3	2.3
Ptolemaida LPP (#3)	147 ± 127	2127 ± 1039	19.3 ± 7.2	30.1 ± 20.6	10.4 ± 12.0	2.4
Kardia LPP (#6)	239 ± 71	3082 ± 387	31.9 ± 4.2	34.2 ± 16.2	19.4 ± 13.6	1.5
Ag. Dimitr. LPP (#9)	185 ± 100	2006 ± 1076	20.1 ± 8.0	19.2 ± 16.2	6.8 ± 10.2	1.6
All samples (23)	181 ± 99	2231 ± 996	21.4 ± 8.5	26.4 ± 17.7	11.0 ± 11.5	2.0
Comparative data from North Greece areas [9,21 mod.]	80–200 ▲	205–2800 ▲	1.7–22 ▲	9.0 ☑	8.0 ☑	
Fly ash of LCWM[8]	264–234			377–430	45–47	

☑ From Thessaloniki area (Capital of North Greece), not affected by fly ash pollution.
▲ From North Greece areas, polluted from Chernobyl accident.

Table 3. Average specific activities (±1SD) of the investigated radionuclides in the mosses (in Bq/kg)

Sampling site	^{40}K	^{137}Cs	^{134}Cs	^{226}Ra	^{228}Ra	Ratio ^{226}Ra/^{228}Ra
Amynteon LPP (#1)	216 ± 88	1676 ± 821	20.9 ± 11.3	46.0 ± 31.0	18.8 ± 18.7	1.7
Ptolemaida LPP (#3)	203 ± 102	1874 ± 743	20.5 ± 8.1	40.0 ± 38.2	25.5 ± 25.7	1.6
Kardia LPP (#6)	167 ± 89	2254 ± 1100	23.8 ± 11.5	61.3 ± 32.5	28.2 ± 23.8	1.9
Ag. Dimitr. LPP (#9)	151 ± 125	2673 ± 1122	29.4 ± 12.9	68.8 ± 21.5	26.9 ± 26.3	1.4
All samples (25)	178 ± 103	2213 ± 1019	24.6 ± 11.4	56.7 ± 30.3	25.3 ± 23.0	1.6
Comparative data from North Greece areas[9,21 mod.]	93–200 ▲	174–913 ▲	1.3–8.4 ▲	9 ☑	18 ☑	
Fly ash of LCWM [8]	264–234			377–430	45–47	

☑ From Thessaloniki area (Capital of North Greece), not affected by fly ash pollution.
▲ From North Greece areas, polluted from Chernobyl accident.

(2) Radionuclides ^{226}Ra and ^{228}Ra do not belong to the same subgroup, as we could expect, taking into account that they have the same concentrations in soil.[1] This is due to the fact that the mean concentrations of ^{226}Ra in mosses and lichens are about 1.6–2.0 times larger than those of ^{228}Ra (Tables 2 and 3). Moreover ^{226}Ra and ^{228}Ra specific activities in mosses and lichens are significantly larger than their respective concentrations quoted in the literature[9,21] for areas such as Thessaloniki, which lies at the same latitude but far from coal fired plants. So the higher values of ^{226}Ra in mosses and lichens can be attributed to the lignite fly ash, whose ^{226}Ra concentrations are considerably higher than the respective ^{228}Ra concentrations.[8]

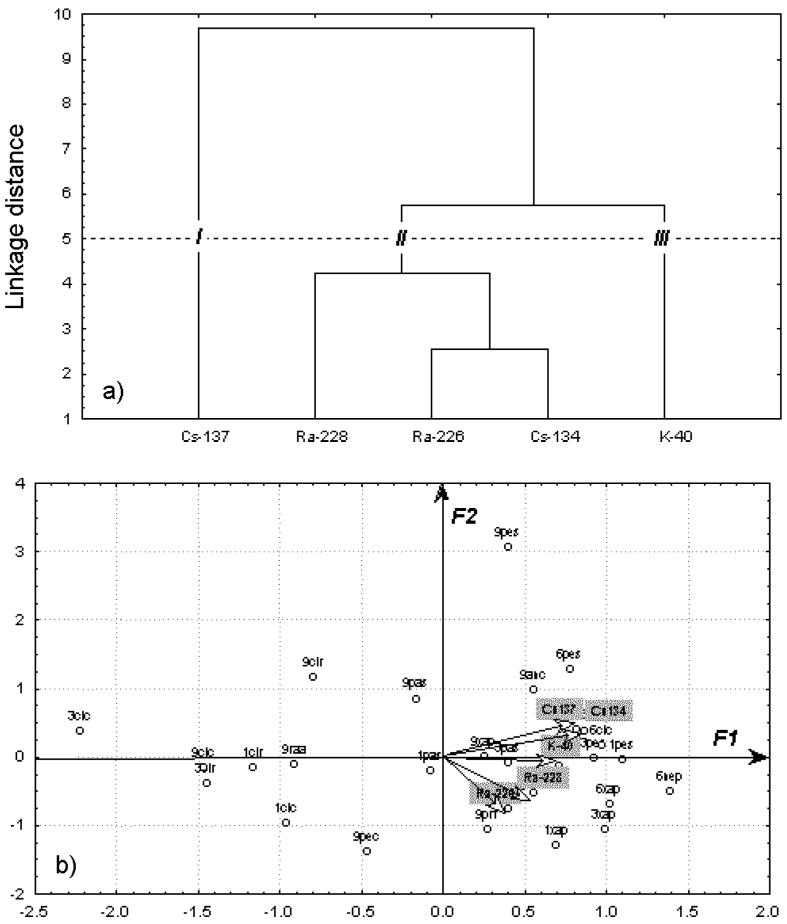

Fig. 2. Cluster and PCA diagrams for 25 moss samples and 23 lichen samples; (a) results of cluster analysis for moss samples, grouping per radionuclide; (b) results of PCA factor analysis for lichen data

(3) The PCA analysis clarifies further the origin of the radionuclides. In the PCA graph for lichens (Fig. 2b) factor F_1 (^{40}K–^{137}Cs–^{134}Cs) and factor F_2 (^{226}Ra–^{228}Ra) definitely stand out. The former can be called "Factor of Chernobyl and resuspension" and the latter "Factor of fly ash". The origin of the radionuclides of F_1 can be traced in the radioactive inventory (^{137}Cs–^{134}Cs) of lichens during the Chernobyl accident as well as in the suspended dust of the soil (^{40}K), while the radionuclides of F_2 come from the fly ash particles. The factor loadings of ^{226}Ra and ^{228}Ra in the factor of fly ash are of special interest: ^{226}Ra has high factor loading value, which is attributed to the fact that the ^{226}Ra concentration in the fly ash is much larger than its concentration in the soil.[1,8] On the other hand, ^{228}Ra, having similar concentrations both in fly ash and soil, has medium and almost similar factor loadings, both in resuspension factor F_1 and fly ash factor F_2. This fact confirms more categorically that ^{226}Ra originates from fly ash and its uptake from the plant organisms through the atmosphere.

Conclusions

The study of natural and artificial radioactivity in plants near the Lignite Center of West Macedonia yielded the followings:

In tree leaves, ^{226}Ra is present in larger quantities than those quoted in literature, which are nevertheless not dangerous. Its origin can be attributed mostly to the fly ash emissions.

In mosses and lichens, ^{137}Cs concentrations were large. Given the old age of the samples and the existence of ^{134}Cs, the origin of radiocesium is almost exclusively attributable to the Chernobyl accident.

Moreover, in mosses and lichens the content in ^{226}Ra is higher than those quoted in the literature. This can be attributed to the suspended particles of the fly ash, whose ^{226}Ra concentrations are considerably large. This assumption is confirmed by the PCA results as well.

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