- POSTERS -

RELATIONSHIP BETWEEN CONTENT OF STABLE METALS AND RADIONUCLIDES IN SOILS AROUND THE LARGEST THERMAL POWER PLANT IN SERBIA AND SOIL PARTICLE-SIZE FRACTIONS

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Abstract

Thermoelectric power plants are one of the main polluters of the environment. Power plants Nikola Tesla in Serbia burn lignite containing trace metals and radionuclides to a certain extent. To assess environmental contamination due to power plants operation, concentrations of metals and radionuclides were determined in soil samples of surrounding areas. Concentration of major and trace elements were determined using different spectrometry techniques. Gamma-ray spectrometry was used to determine activity concentrations of natural gamma-emitting radionuclides (^{40}K, ^{226}Ra and ^{232}Th) and ^{137}Cs derived from Chernobyl accident. Soil particle size fractions were determined by the traditional pipette method. To determine the correlation between content of metals and radionuclides in soil and soil particle-size fractions the obtained data were subjected to cluster analysis (CA). Resulting dendrogram identified five clusters. Significant correlations were obtained between Cr, Fe and Co; ^{40}K, silt and clay; ^{232}Th, ^{226}Ra and sand. Weak correlation of Cu, Pb, Cd and ^{137}Cs with other parameters indicated their anthropogenic origin in soil samples. Cesium, clay and Mn were grouped into one cluster which indicated the association of this radionuclide with manganese oxides and clay particles. Results obtained by CA confirmed that multivariate analysis is powerful tool for the assessment of origin of stable metals and radionuclides in areas surrounding thermal power plants.

Introduction

To produce electricity, thermoelectric power plants (TPP) use coal which contains heavy metals and radionuclides to a certain extent depending on coal type. The complex of TPP, Power Plant Nikola Tesla A and Nikola Tesla B, is situated in western Serbia in the municipality of Obrenovac, on the right side of the Sava river 42 km upstream from Belgrade, the Serbian capital city. These two plants of total installed capacity of 2892 MW are the largest one in Serbia (Popovic et al., 2001). They burn lignite of low calorific value and high moisture content, mined and transported to the TPP from the open-pit mines in the Kolubara basin. During the lignite combustion the large amounts of ash, dust, sulfur and nitrogen oxides are produced. In TPP Nikola Tesla, a million tones of ash are produced every year. In the vicinity of TPP there are three open dumps of ash (total area of 900 ha). To prevent the spread into the atmosphere, ashes are mixed with water from the Sava River. Hydraulic transport technology is used in TPP for ash and slag transport to the dumps. Ashes carried by wind can cause damage to surrounding soil surfaces. Recent years, coal ash is used as secondary raw material. All by-products of combustion lead to changes in the environment.

Soil is a heterogeneous system comprised of three phases: solid (mineral particles, organic debris, plant roots), solution (groundwater, rain water, biological excreta, products of biological reactions) and gas (atmospheric, products of biological reactions). Metals and radionuclides can be found in each of those three phases and may pass from one phase to another by changing soil pH, temperature, redox potential, decomposition soil organic matter, leaching and ion exchange process and by microbial activity. Metals in soil originate from parent rock or underlying substrate.

Because of well-known harmful effects of metals and radionuclides to the environment and the man directly, it is necessary to monitor changes in the concentrations of these pollutants. The naturally occurring radioisotopes, ^{40}K, ^{232}Th, ^{238}U and their decay products (^{226}Ra), represents the main external source of irradiation of the human body. Radiocesium, ^{137}Cs, is artificial radionuclide derived after nuclear accident in Chernobyl, Ukraine in 1986.

The aim of this work was the preliminary assessment of extent of pollution of soils around TPP by stable metals and radionuclides. The concentrations of 17 stable elements (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Sr, Pb, Zn, Ti) and 4 radionuclides (^{40}K, ^{232}Th, ^{226}Ra, ^{137}Cs) in soil and soil particle-size fractions were determined. The obtained results were chemometrically treated by the use of cluster analysis (CA).

Experimental part

Soil samples were collected during 2007 with stainless steel spade and fresh samples were packed in plastic bags. After drying at room temperature in laboratory to the constant weight, samples were homogenized and passed through a 2 mm sieve.

Prior to radioactivity measurements samples were kept hermetically sealed for one month. Samples were measured in Marinelli beakers of total volume of 1,000 cm^3. The measurements were performed using HPGe gamma-ray spectrometer ORTEC-AMETEK (25% relative efficiency and 1.65 keV FWHM for ^{60}Co at 1.33 MeV, 8192 channels). The activity of ^{226}Ra was evaluated from area under gamma line at 609.3 keV of ^{214}Bi peak and 351.9 keV of ^{214}Pb, while 911.2 and 969.1 keV gamma-ray lines emitted by ^{228}Ac and 238.6 keV emitted by ^{212}Pb were used to determine ^{232}Th. The activity of ^{40}K was determined using its 1460.8 gamma-ray line.

To determine the metal concentrations samples were digested with HNO_3 and H_2O_2 in a microwave oven (USEPA, 1996). Metal concentrations were measured using a Perkin Elmer PE3100/MHS-1 Atomic Absorption Spectrometer and Perkin Elmer ICP-OES. Quality control was assured by the use of two replicates, standard reference material (Mintana Soil SRM 2711 from the National Institute of Standards and Technology (USA)) and procedural blanks.

The traditional sieve-pipette method was used for particle size analysis (Rowell, 1997). Once the organic matter had been removed by burning in the muffle furnace, the remaining mineral sample was weighed and analysed for the following particle size fractions: coarse sand (0.2–2 mm), fine sand (0.05–0.2 mm), silt (0.002–0.05 mm) and clay (<0.002 mm).

The Statistical Package for the Social Sciences (SPSS 16.0) was used for descriptive and cluster analysis.

Results and discussion

Summary descriptive statistics of obtained data are presented in Table 1. The mean values of specific activities were found to be 600 Bq/kg for ^{40}K, 52 Bq/kg for ^{232}Th, 44 Bq/kg for ^{226}Ra and 33 Bq/kg for ^{137}Cs. These values are higher than those reported for Serbia (Dragovic et al., 2006). Slightly higher mean values were reported for soils in the vicinity of TPP in China: 751 Bq/kg, 60 Bq/kg, 40 Bq/kg for ^{40}K, ^{232}Th, ^{226}Ra, respectively (Lu et al., 2011). The specific activities of radionuclides in soils around the TPP in Hungary were reported to be 330 Bq/kg, 24 Bq/kg, 43 Bq/kg and 14 Bq/kg for ^{40}K, ^{232}Th, ^{226}Ra and ^{137}Cs, respectively (Papp et al., 2002).

Mean values of Cd, Co, Cr, Cu, Mn and Ni in soil were found to be out of the concentration range for uncultivated soils worldwide, i.e. 0.37-0.78 mg/kg, 4.5-12 mg/kg, 12-83 mg/kg, 13-24 mg/kg, 270-525mg/kg and 12-34 mg/kg for these elements, respectively (Ferguson, 1990; Kabata-Pandias and Pandias, 1992). Cadmium concentrations in the soils around TPP were similar to those found in soils around coal-fired power plants in Slovakia (Keegan et al., 2006). Increased concentrations of Cr and Ni were reported in soil in areas round lignite-fired power plants in Western Macedonia, Greece (Tsikritzis et al., 2002). Contamination of soils by Mn was also reported for lignite-fired power plants in Turkey (Tümüklu et al., 2008). The high Ni content for Serbia may attributed to local geochemistry (Dragovic and Mihailovic, 2009).

Particle-size distribution of analysed soil samples (Table 1) shows that most samples fell into the silty loam or silt clay loam class, according to the USDA scheme (Baize 1993).

Table 1. Summary descriptive statistics of obtained results

	Mean	Median	Std. Deviation	Minimum	Maximum	Skewness	Kurtosis
				Bq/kg			
^{40}K	600	590	148	323	886	0.40	-0.77
^{232}Th	52	48	14.5	30	104	1.3	2.4
^{226}Ra	44	35	21.2	25	105	1.8	1.9
^{137}Cs	33	22	41.5	0.6	212	3.1	11
				%			
Sand	25.4	20.4	21.9	3.2	85.3	1.6	1.6
Silt	49.5	54.3	14.4	6.5	66.2	-1.9	1.6
Glay	24.4	25.5	9.71	7.5	46.2	-0.2	-0.5
				mg/kg			
Al	11700	11700	1100	9400	14100	0.04	-0.4
Ca	27600	22100	18800	640	72000	0.6	-0.9
Cd	1.7	1.7	0.35	1	2.6	0.4	0.4
Co	16.7	17.1	2.3	11	21.8	-0.4	0.3
Cr	110	120	23	58	146	-0.7	-0.6
Cu	36	31	38	15	207	4.2	0.7
Fe	65900	69300	22000	20300	120000	-0.04	0.7
K	1240	1250	100	1000	1400	-0.6	0.2
Li	16.4	18.5	7.1	4.1	30.2	0.1	-1.1
Mg	5050	5090	350	4210	5780	-0.2	-0.03
Mn	730	730	170	440	1050	-0.002	-1.11
Na	62.9	61.3	7.7	42.4	78.4	-0.03	0.08
Ni	38.9	37.3	7.5	25.7	60.9	0.8	0.7
Sr	26.8	27	3.2	20.8	34.6	0.08	-0.14
Pb	38.4	35.5	19.6	23	161	5.7	36.1
Zn	62	61	19	24	120	0.4	1.8
Ti	55.3	55.2	10.5	38.5	80.6	0.3	-0.4

The aim of CA is to optimise the heterogeneity between groups as well as the homogeneity within them. Calculation in CA moves forward in an agglomerative way until all objects are joined in a single cluster. Usually the results are presented as a dendrogram, in which the distance within clusters represents the degree of association between the elements. Dendrogram obtained in this paper (Figure 1) identified five clusters and CA indicated that there is significant correlations between Cr, Fe and Co; ^{40}K, silt and clay; ^{232}Th, ^{226}Ra and sand. Weak correlation of Cu, Pb, Cd and ^{137}Cs with other parameters indicated their anthropogenic origin in soil samples.

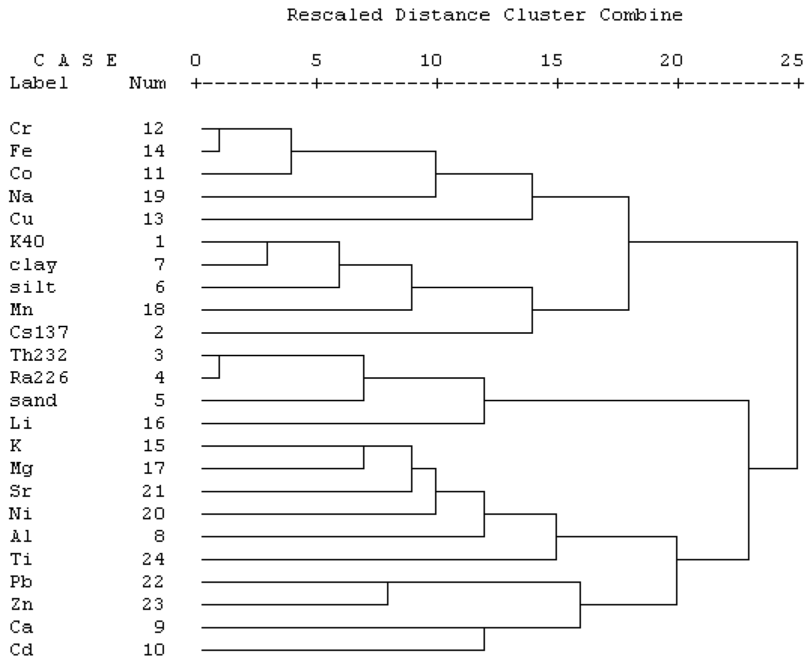

Figure 1. Dendrogram derived from the cluster analysis

Conclusions

The results of this preliminary assessment indicated the environmental pollution around thermoelectric power plant by stable metals and radionuclides. The results obtained in this paper confirmed that cluster analysis is convenient tool to assess the origin of environmental pollutants. The lack of correlation between trace elements and soil particle size fractions indicated their anthropogenic origin. To gain more detailed insight into the extent of environmental pollution around TPP an extended study which will include a larger number of samples is highly needed.

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