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Chemometric interpretation of vertical profiles of radionuclides in soils near a Spanish coal-fired power plant

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HIGHLIGHTS

- ▶ Natural radionuclides in soils around a coal fired power plant in Spain was studied.
- ▶ ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{224}Ra, ^{40}K and ^{137}Cs measured by gamma-ray spectrometry.
- ▶ N-way PCA analysis explains 81% of the vertical radionuclide distribution in soil.
- ▶ Evaluation of *K*-parameter, Pb_{uns} and Pb_{neq} shows Pb depositional flux to the soil.
- ▶ Correlation between ^{210}Pb and ^{137}Cs in surface soil confirms depositional fluxes.

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ABSTRACT

The study of the vertical distribution of seven radionuclides in soils around a coal fired power plant in a mountain region in the north of Spain has been performed, in order to know if some deposition and migration of these radionuclides has taken place. Thirteen profiles of 30 cm depth have been selected, and every fraction of 5 cm has been analyzed until of a total of 72 soil samples. The activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{224}Ra, ^{40}K and ^{137}Cs has been measured by gamma-ray spectrometry. The data were analyzed using multivariate statistical techniques, founding the best result when using a simple two-factor model, which can explain the 81.1% of the total variance. Additionally, on the basis of the significant differences found in the concentration of lead in the soil top and deep layers, the evaluation of excess of ^{210}Pb and the *K*-parameter was done. A good correlation between the excess of ^{210}Pb and the concentration of anthropogenic radionuclide ^{137}Cs in surface soil was found. These results confirm the atmospheric deposition of lead as a decay product of exhaled Rn.

1. Introduction

Natural radionuclides are found in coal rocks. The combustion of coal on coal-fired power plants (CFPPs) distributes the radionuclides in solid and gaseous products, most of the radionuclides being accumulated in the ash. These elements are transferred to the fly ash, part of them are released into the atmosphere by the stack, and finally most of them fall into soils and plants by wet or dry deposition. By this reason, CFPP are a source of radioactive contamination for the surrounding area. In this respect, radium and uranium are specially important, given that they can reach humans through several transfer pathways in the biosphere, being the most significant one the ingestion of contaminated water (Stalder et al., 2012) and food (Tagami and Uchida, 2009).

The interest of studying the environmental impact of the industrial coal cycle begun on the sixties, and nowadays many authors have focused their attention on this problem (Cevik et al., 2007; Dai et al., 2007; Wang and Lu, 2007; Psichoudaki and Papaefthymiou, 2008; Papastefanou, 2010) because coal still has a major role in electric generation worldwide, specially in countries like India, China or Brazil. The number of papers on the contents of some radionuclides in soils as a source of contamination have been

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increasing during the last years (Herranz et al., 2011; Baeza et al., 2011; Persson and Holm, 2011; Wang et al., 2011; Sert et al., 2011, 2012). There are some of them analyzing the influence of CFPP on the levels of natural radioactivity in the soils around it (Ugur et al., 2003; Krmar et al., 2009). Although UNSCEAR (1993) estimated rather low values that do not modify significantly the dose received by population, some studies have detected a clear increment of radionuclide contents over natural background in soils around CFPP (Bem et al., 2002; Flues et al., 2002; Papp et al., 2002; Dai et al., 2007). However, the possible contamination of surrounding areas by coal industry highly depends on many local parameters, as soil type, climate conditions, and specially the type of coal. Uraniferous coals (known also as lignites or brown coal) have the activities for uranium series elements one order of magnitude higher than normal coals. By this reason, the highest increments of radioactivity were detected in the top soil around plants burning this type of coal (Flues et al., 2002; Papp et al., 2002; Papastefanou, 2010). In other cases, where no uraniferous coals are used in the CFPP, factors as a very long period of the utilization of coal, the large amount of coal burned, or the low fly-ash retention efficiency in the plant contribute to increase the natural radioactivity background (Papp et al., 2002).

The distribution of radionuclides as a function of depth had been analyzed by different authors, being the profiles of ^{210}Pb and ^{137}Cs in soils one of the subject more investigated in the literature (Bem et al., 1998; Sert et al., 2011, 2012; Persson and Holm, 2011; Herranz et al., 2011). These two profiles are related with fallout mechanisms, and are clearly modified either by anthropogenic effects or by erosion and deposition processes, that could be evaluated attending to the study of caesium and lead profiles (Sánchez-Cabeza et al., 2007). A very recent study of the vertical migration of caesium in Spanish soils has been reported (Herranz et al., 2011). The vertical distribution of some radionuclides is a useful methodology for the analysis of soils, even of agricultural ones (Akyil et al., 2008).

For the analysis of the experimental data, we will use multivariate chemometric tools. One of them, Principal Component Analysis (PCA), allows to build simple linear models which help to identify the most important factors explaining the data variability. Classical 2-PCA can be directly applied to datasets arranged in two dimensions, however, when the dataset has a more complicated multidimensional structure, it becomes essential to apply a multi-way analysis, such as N-way PCA (or N-PCA), to fully explore and extract the hidden structure of data and their relationships. The power of these techniques when applied to environmental data has been fully demonstrated (Stanimirova et al., 2006; Singh et al., 2008; Tsakovski et al., 2009). Most of the studies found in the literature are related with the analysis of heavy metals in soils (Micó et al., 2006; Luo et al., 2007; Dragovic et al., 2008; Pardo et al., 2008; Skrbic and Durisic-Mladenovic, 2010), but it is difficult to found references describing the use of N-PCA for environmental studies involving radionuclides.

In this work, the vertical distribution of radionuclides in soils around the CFPP of Velilla del Rio Carrión, in northern Spain, has been studied. ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{224}Ra, ^{40}K and ^{137}Cs activities have been determined in 72 solid samples. The data have been analyzed using a multivariate statistic. The study was completed using the analysis of some radionuclide ratios, the evaluation of the *K*-parameter and the correlation between ^{137}Cs and the excess of ^{210}Pb. The two main goals of this work are to determine the vertical distribution of the radionuclides ion soils, and them to establish if the CFPP is the cause of a detectable increment of radioactivity in soils over the natural background in the area under study.

2. Methodology

2.1. Study area

The area under study is a mountain region at the central-north of Spain. The weather is continental with temperatures ranging between 4 and 14 °C, and a median rainfall of 1000 mm. The management of the soil is for animal pasture, and the principal industrial activity in the area is coal mining. Geology of the area is marked by calcareous mountains and the presence of coal materials. The local mining activities started at the beginning of last century, reaching their highest productivity during the late sixties. Nowadays, the coal production in the region is about half million tons per year, extracted by both underground and surface mining. The power plant of Velilla del Río Carrión (42°49′N, 4°51′W) is placed next to the Carrión river and was built in 1964 (a new second generator was added in 1984 with a new higher stack). It has a storage capacity of 1 million tons of coal, and consumes on average 800 000 tons year^{-1}.

2.2. Sample collection and measurement

Fig. 1 shows a map of the studied area (a topographical scheme with altitude lines and villages and principal roads have been highlighted) with the location of 13 sampling points. Cylindrical vertical soil samples, Cores, were taken at those points using a stainless steel cylinder sampler of 4.5 cm of diameter and 50 cm of length. The soil sample was divided in portions every 5 cm, up to a total of 6 phases or subsamples (F1–F6). Given that some cores were shorter than 30 cm long, there was impossible to obtain the six phases, by this reason the total number of samples was 72. Every fraction was placed in plastic bags and kept at 4 °C until subsequent analysis. Samples were dried at 110 °C overnight and sieved using a 2 mm grain size mesh; after that, soil samples were placed in Petri dishes of 125 cm^3, sealed and stored for at least three weeks in order to ensure secular equilibrium of ^{226}Ra and ^{214}Pb. The activity concentration of ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{224}Ra, ^{137}Cs and ^{40}K were determined by gamma-ray spectrometry using a Canberra n-type HPGe detector, with 25% relative efficiency, resolution of 1.1 keV at 122 keV and of 2.0 keV at 1.33 MeV. The ^{238}U activity was derived from the (92.4 + 92.8) keV peaks of ^{234}Th. The ^{226}Ra activity was derived from 352 keV peak of ^{214}Pb. The ^{232}Th activity was derived from 911 keV and peak of ^{228}Ac. ^{210}Pb, ^{224}Ra, ^{137}Cs and ^{40}K activities were calculated from their photopeaks at 46.5, 240.9, 661 and 1460.8 keV, respectively. Self-absorption correction was applied (García-Talavera and Peña, 2004). Uncertainty (with $k = 1$) were determined attending to statistical uncertainty of peak areas provided by Canberra Genie-2000 software, uncertainty values calculated from internal procedures for mass and efficiency and literature data for gamma emissions parameters, always according to ISO 11929 (2007) accepted rules. Limit of detection were estimated less than 1 Bq kg^{-1} for all radionuclides.

2.3. Multivariate analysis

The resulting dataset has three modes or dimensions: 7 radionuclides (nrad) measured in cores collected at 13 sampling points (nsamp) along six different depths (ndepth). The dataset can be arranged into a three-dimensional array (parallelepiped matrix) $\underline{\mathbf{X}}$ of dimensions (nsamp × nrad × ndepth), whose complexity requires multivariate data analysis tools, such Principal Component Analysis (PCA), to provide a more comprehensive interpretation and to formulate general conclusions about the underlying model in $\underline{\mathbf{X}}$.