

MOBILITY OF NATURAL RADIONUCLIDES AND SELECTED MAJOR AND TRACE ELEMENTS ALONG A SOIL TOPOSEQUENCE IN THE CENTRAL SPANISH PYRENEES.

A. Navas^a, Machín J. ^a & Soto. J.^b

^a Estación Experimental de Aula Dei. Consejo Superior de Investigaciones Científicas. Apartado 202. 50.080 Zaragoza. Spain.

^b Dpto. Ciencias Médicas y Quirúrgicas. Universidad de Cantabria. Avda. Cardenal Herrera Oria s/n. 39011 Santander. Spain

ABSTRACT

Natural gamma-emitting radionuclides (^{238}U , ^{226}Ra , ^{232}Th , ^{210}Pb) and selected major and trace elements (Ca, K, Mg, Na, Fe, Al, Mn, Pb, Ba, Zn, Sr, Li, Co, Ni, Cu, Cr, Cd) were determined in a soil toposequence along a mountain slope of the Tertiary Flysch landscapes in the Central Spanish Pyrenees. A variety of basic properties were also measured from the soil profiles. Mean radioisotope activities (Bq kg^{-1}) range from 22 to 33 for ^{238}U ; 25 to 32 for ^{226}Ra ; 23 to 33 for ^{210}Pb and 37 to 46 for ^{232}Th . The radionuclides showed different patterns in their depth distribution, thus ^{238}U and ^{210}Pb had largest differences in concentrations down the soil profiles whereas ^{226}Ra and ^{232}Th exhibited quite uniform depth distributions. ^{238}U was depleted in all upper soil layers and enriched in deeper layers. ^{210}Pb exhibits very different depth profiles along the soil toposequence and accumulated at upper layers in three sites. $^{238}\text{U}/^{226}\text{Ra}$ activity ratios indicate disequilibrium in the ^{238}U decay chain and reflect the leaching of ^{238}U in

contrast with the lack of mobility of ^{226}Ra . The values of $^{232}\text{Th}/^{226}\text{Ra}$ indicate that the initial proportionality in the ^{238}U and ^{232}Th decay chains has not been maintained in this toposequence. The relationships between soil properties and gamma-emitting radionuclides suggested the association of ^{226}Ra and ^{232}Th with Fe and Mn oxides.

Al, Ca, Fe and K were the most abundant, followed by Mn, Ba, Pb, Sr, Li and Zn whereas Co, Cu, Ni and Cr are as trace elements and Cd was not detected. Correlations between elements suggest association with carbonates (Ca, Sr), silicates and clay minerals (Al, K, Na) and with Fe and Mn oxides (Cr, Cu, Ni, Co, Zn). Along the soil toposequence, Ca, Sr, Mg and Na, K, and Al increase at the bottom slope positions, due to highest carbonate contents and abundance of finer soil fractions (clay and silt) respectively. Fe and Mn decrease at the bottom slope because highest contents of Fe and Mn oxides are at upper slope positions. This research is of interest to describe the geochemical cycling of elements in the environment and to assess the processes that affect their mobility in the ecosystems.

Keywords: natural radionuclides; major and trace elements; profile distribution; soil toposequence transfer; Tertiary continental Flysch, Central Spanish Pyrenees.

Short title: Radionuclides and major and trace elements along a soil toposequence.

INTRODUCTION

Soils play a major role in biogeochemical cycles of elements and nuclides. Defining and understanding their distribution in soils is a key issue in many environmental studies (e.g. Salim et al., 1993). Elements are contained within the crystal structure of soil-forming minerals as well as bound to different phases of soil particles by a variety of mechanisms such as adsorption. Moreover, physico-chemical soil properties influence the element mobility and their bioavailability in the terrestrial ecosystems (Kabata-Pendias & Pendias, 2001). The geochemical composition of soils is of primary importance in establishing environmental baselines of both essential and potentially toxic elements (McGrath & Loveland, 1992; Jordan et al., 1997; Wilcke et al., 1998).

Natural radioactivity of soils is largely controlled by the mineral composition of the parent material. To a lesser extent, radionuclides are adsorbed onto soil components (organic matter, clays, carbonates, Fe/Mn oxides) that can take part in biogeochemical processes.

According to Baxter (1991), human exposure to natural radionuclides has increased by two or three orders of magnitude since the 1960s, and radiation from natural sources is a major environmental concern. Because of the risk of radioactive contamination, increasing attention has been given to the abundance and distribution of natural radioisotopes in soils (Kiss et al. 1988; Barisic et al. 1992). Nevertheless data on biogeochemical behaviour of longlived radioisotopes in soils are still scarce (e.g. de Jong et al., 1994).

Natural radioactivity in the soil is mainly due to the decay of radionuclides from the uranium and thorium series. Beck (1972) found that the decay of these isotopes

together with ^{40}K , accounted for 50 to 80% of the gamma radiation flux at the soil surface.

In order to understand the pathway by which radioactivity reaches humans after transference from soils to plants, and through the trophic chain, it is essential to know how the physical and chemical properties of soils are related to the abundance and distribution of radionuclides. Several authors (e.g. Rosholt et al. 1966; Sully et al., 1987) studied the distribution of natural radioisotopes in soil profiles. In Spain, natural radioactivity has been studied at a nation-wide scale survey (Quindós et al., 1994) and Elejalde et al. (1996) analysed the radionuclide content in soils from Biscay. Nevertheless, little information exists on the behaviour of natural gamma-emitting radionuclides in soils of Mediterranean mountainous areas and on biogeochemical processes related to the transfer of radionuclides from soil to plants to animals.

This study determines the depth distribution of the natural radionuclides, ^{238}U , ^{226}Ra , ^{210}Pb , ^{232}Th , as well as 17 major and trace elements along a soil toposequence on a forested slope of the mountainous Flysch region in the Spanish Pyrenees. Other objectives were to assess the relationships between major and trace elements and the natural radioactivity, and the effect that selected soil properties have on the mobility of radionuclides. In addition, this study represents a contribution to the knowledge of the geochemistry of the major soil types in the region. Besides, understanding the processes of radioactivity in soils and pathways to man is of interest because the soils studied are representative toposequences of a very large area in the Intermediate Depression. This Depression extends from east to west for most of region in the south of the Pyrenean range.

THE STUDY AREA

The study area (Figure 1) is located within the Flysch Sector of the Spanish Pyrenees. The Flysch Sector is located within the Intermediate Depression, a structural unit underlain by rocks of Eocene age consisting of thin alternating strata of sandstones and marls that have been extensively folded and faulted. Altitudes in the region range from 800 to 2200m and slopes are covered by thin colluvial materials where slumps and shallow debris flows are frequent. In the Flysch Sector, the lithology is very homogeneous and variation of soil types is due to differences in physiographic and climatic factors. The altitude, slope orientation and gradient are the most important among the topographic factors influencing soil formation whereas solar radiation, rainfall interception/evaporation and infiltration/runoff generation are the most significant climatic factors.

The climate in the study area is sub Mediterranean with Atlantic influence; the average temperature is 10° C and annual rainfall is in the order of 900 mm. The vegetation cover is composed of pine-wood forests along with other deciduous trees and shrubs. The general mineralogy of rocks and soils (Pardini *et al.*, 1991) is estimated as 64 % calcite, 19 % quartz, 9% clays, 5 % feldspar and 3% oxides. Clays (illite-mica, chlorite, kaolinite and smectite) (27 - 41 %) and calcite (33 - 44 %) dominate the soil mineralogy, followed by quartz (18%), oxides (5%) and feldspars (3%).

MATERIALS AND METHODS

A north-facing and densely vegetated slope that is representative of the forest physiography within the Flysch Sector was selected as the study site. The slope gradient is 30 % and altitude ranges from 1245 m at the divide to 1045 m at the bottom slope. Along the 670 m long slope, 5 soil profiles were collected. From the divide to the valley bottom, the sampling sites 1 to 5 were about 175 m apart. A sequence from Kastanozems (sites 1, 2 and 3) to Cambisols (4 and 5) is a characteristic soil toposequence found in the area. Cambisols (Ochrepts) of brown color have a B cambic horizon, characterized by the weathering of parent materials in situ. Kastanozems (Haploxerolls) of dark brown color have an A mollic horizon and can also have a cambic horizon without lithic contact. Soil depth to rock is about 50 cm and horizon differentiation, apart from the organic upper layer, is minimal.

An automatic core driller was used to collect the soil profiles and the cores were extruded and sectioned at 5 cm depth intervals. Each soil sample representing a depth interval of 5 cm was air dried and ground to pass a 2 mm sieve. Total weight of the samples, and of the finer (< 2mm) and coarser fractions, was recorded. Standard techniques were used for analyzing soil properties. pH (1:2.5 soil:water) was measured using an Orion 901 pH-meter and carbonates were measured by calcimetry using a Barahona calcimeter (CSIC, 1976). Organic matter was determined by the Sanerlandt method (Guitian and Carballas, 1976) using a Mettler Toledo titrimeter and electrode. Fe and Mn oxides were measured after extraction with acid ammonium oxalate (Schwertmann, 1964). Granulometric analysis of the sand, silt and clay size fractions were performed using Coulter laser equipment (Gee and Bauder, 1986; Buurman et al., 1997). To eliminate the organic matter, samples were chemically disaggregated with 10

% H₂O₂ heated at 80° C, then stirred and ultrasound was also used to facilitate particle dispersion. The infiltration rate was measured during 180 minutes in four of the studied sites along the slope by using a double-ring infiltrometer.

The methodology for determining natural gamma-emitting radionuclides is described by Quindós et al. (1994). Soil samples were packed in 100 mL PVC cylindrical containers. In order to reach radioactive equilibrium between ²²⁶Ra and ²²²Rn and their progenies, the containers were kept sealed for 2 months. Measurements of radionuclide activities in soil samples were made by a high resolution, low background, hyperpure coaxial gamma-ray detector (EG&G ORTEC HPGe) coupled to an ORTEC amplifier and multichannel analyser. The detector has an efficiency of 20%, a resolution of 1.86 keV and is surrounded with shielding material to reduce the background counting rate. The detector was calibrated using standard samples in the same geometry as the measured samples.

Gamma emission of ²³⁸U, ²²⁶Ra, ²¹⁰Pb and ²³²Th (in Bq kg⁻¹ air-dry soil) was measured in the 5-cm interval soil samples. Counting time was around 30000 s and the analytical precision of the measurements is approximately ± 10%. Considering the appropriate corrections for laboratory background, ²³⁸U was determined from the 63-keV line of ²³⁴Th, the activity of ²²⁶Ra was determined from the 352-keV line of ²¹⁴Pb (Van Cleef, 1994); ²¹⁰Pb activity was determined from the 47 keV photopeak and ²³²Th was estimated from the 911-keV photopeak of ²²⁸Ac.

Samples were homogeneized and quartered and then ground in an agate mortar and analysed for 17 major and trace elements (Fe, Al, Ca, K, Mg, Na, Mn, Pb, Ba, Zn, Sr, Li, Co, Ni, Cu, Cr, and Cd). After total acid digestion with HF in microwave (Milestone 1200 mls), analysis were performed by atomic emission spectrometry using an inductively coupled plasma ICP-OES with solid state detector (Perkin Elmer Optima

3200 DV). Concentrations, obtained after three measurements per element, are expressed in mg/kg.

ANOVA test was used to analyse the fixed effect of soil depth and slope position on soil properties, radionuclides and major and trace elements. The Fisher's LSD test was used to assess differences among the means. The correlation matrix was calculated for the response variables studied. The analyses were carried out using Statgraphics for Windows.

RESULTS AND DISCUSSION

The soils are alkaline, with average organic matter less than 4.5 % and carbonate contents varying from as little as 2% for Kastanozems to 17% for Cambisols. Texture is silt loam and bulk density ranges between 1 and 1.2 g cm⁻³. Table 1 shows the values of measured soil properties down the depth profiles for each sample site along the slope toposequence. pH values are slightly higher in Cambisols, but all Kastanozems present values below 8 within the first 10 cm. In general, the pH increases with depth in all sites although sites 2 and 4 show a slight peak in pH in the middle of the profile. Carbonate contents differ among the profiles, with Kastanozems having lower contents with mean values statistically different from Cambisols. The carbonate distribution with depth shows different patterns, thus in sites 1 and 2 contents remain quite constant below the first 5 cm; site 3 has the largest difference of values between the surface and the deeper soil layers; profile 4 shows a slight peak in the middle of the profile and profile 5 exhibits a constant carbonate increase with depth. All soils exhibit the same decreasing trend with depth in organic matter percentages, thus a sharp decrease occurs within the first 15 cm, whereas below 20 cm average contents remain quite constant between 2.7 - 3.5 %.

Kastanozems have slightly higher organic matter percentages than Cambisols although differences are not statistically significant. Contents in Fe and Mn oxides are statistically different and also higher in Kastanozems than in Cambisols and their depth distribution follow a quite parallel pattern in all soil profiles. Although all the sampled soils are silt loams, some differences exist in their grain size distributions. As expected by the transport of finer soil particles by runoff, the average lowest clay content is found at the upper slope position (site 1) and the contrary is observed at the bottom slope positions (sites 4 and 5). Conversely the lowest average sand content is found at the bottom slope position (site 5). In general, all soils show a slight increase of the clay content with depth whereas the contrary is observed for sand as highest percentages are found at the soil surface and decreasing values occur at deeper layers

The distribution down the depth profiles of natural radionuclides in the sample sites is presented in Figure 2. In the soil depth profiles, ^{238}U is depleted in the upper layers of all soils. Activities between below detection limits (BDL) to 18 Bq kg^{-1} are measured at the upper 5 cm. At deeper layers, a general ^{238}U enrichment was found apart from site 5 where ^{238}U was markedly depleted may be due to the effect of soil particle deposition at upper layers as indicated by the high concentration of ^{210}Pb . ^{226}Ra and ^{232}Th show quite homogeneous depth distribution in all soil profiles. ^{210}Pb has different depth distributions in the soil profiles and together with ^{238}U show the greatest variability within the soil profiles. Decreasing ^{210}Pb activities with depth (from 65 Bq kg^{-1} at the soil surface till BDL at deeper layers) are found in sites 3 and 5. The background levels of natural gamma radionuclides found in these profiles fall within the range for Spanish soils (Quindós et al., 1994) and also agree with values reported by Litaor (1995) and de Jong et al. (1994) in North America.

In the studied profiles, the effect of main soil properties on radioactivity levels has been analysed through correlations and the results are summarised in Table 2. Although it is widely documented that radioisotopes are adsorbed onto clay surfaces or fixed within the lattice structure (e.g. Jasinska et al., 1982; VandenBygaart & Protz, 1995), only the clay content is negatively related with ^{210}Pb . This is due to the general lower clay content at upper layers that coincides with the highest activity of this radionuclide as it accumulates at the soil surface and remains fixed to the finer soil fractions with little mobility. Mn and Fe oxides are positively correlated with ^{232}Th and ^{226}Ra may be in relation to their association with these soil components as indicated by their constant depth distribution paralleled with that of the radionuclides. The organic matter is only significantly correlated with ^{238}U and ^{210}Pb . The negative correlation between organic matter and ^{238}U activities, is due to the fact that decreasing organic matter contents with depth, are coincidental with depletion of ^{238}U at upper soil layers. Conversely, organic matter is directly related with ^{210}Pb because their highest values are found at upper layers and the lowest ones at deeper layers. Carbonates are inversely and significantly correlated with ^{226}Ra , ^{232}Th and ^{210}Pb . Carbonate is a very distinctive soil component in the studied soil profiles and it has a large range of variation among the soil profiles as well as within the depth profile (from 1% till more than 28 %). It appears that highest activities of these radionuclides at upper slope positions in Kastanozems, that in turn have the lowest carbonate contents could be the reason for these negative relationships. The pH is only inversely related with ^{210}Pb may be due to the fact that highest ^{210}Pb activities are found at upper layers where soil pH is lower.

From these results it can be said that ^{226}Ra and ^{232}Th with a similar depth distribution are different from the other two isotopes. They keep quite constant down

the profiles and have very low mobility, besides they are significantly related with Mn and Fe oxides, while in contrast these soil components are not related with ^{238}U and ^{210}Pb . In comparison, ^{238}U and ^{210}Pb have contrasting and variable depth profiles that reflect the relatively higher mobility of ^{238}U , whereas accumulation of ^{210}Pb at upper layers can be caused by sediment deposition as suggested by ^{137}Cs activities (Navas et al., 2005). Moreover both radioisotopes have different relationships with the studied soil properties.

In all soil profiles (Figure 2), ^{238}U shows an important mobility as it is leached from the soil surface down to deeper layers what is may be favoured by slightly higher pH values and lower organic matter contents existing at deeper soil sections. Winde (2001) indicates that even small variations in pH may cause precipitation of some soil components that in turn may affect the behaviour of uranyl complexes. Cowart & Burnett (1994) indicate that ^{238}U may form complex ions and migrate downward in the soil profile, in this study it seems that soil conditions might favour leaching of uranyl complexes downward the soil profiles and their further binding to finer soil particles at deeper layers were they are more abundant. This would agree with findings by other authors that indicate that radioactivity increases as particle size decreases (Megumi et al., 1982; Baeza et al., 1995). In spite that there is a positive trend in the relationship between clay and ^{238}U it appears that a larger data set would be necessary to find a significant correlation between them.

The average radioisotope concentrations (Bq kg^{-1}) lie in the range of BDL to 53 for ^{238}U ; 22 to 36 for ^{226}Ra ; BDL to 65 for ^{210}Pb and 28 to 50 for ^{232}Th . These values fall within the ranges found in the region (Navas et al., 2002). The mean activities of natural radionuclides in the soil profiles of the toposequence along the slope sites are presented in Figure 3. Mean ^{238}U values slightly decrease from the upper

slope position (site 1: 33 Bq kg⁻¹) to the bottom slope (site 5: 22 Bq kg⁻¹) although ²³⁸U means are not statistically different among sites. Mean ²¹⁰Pb activities are also lower in Cambisols. ²¹⁰Pb and ²³⁸U mean activities present similar trends along the slope. Mean lower values of ²²⁶Ra are found at the bottom slope in Cambisols. Mean values of ²³²Th are significantly different among soils and also lower activities are found in Cambisols. Along the soil toposequence ²²⁶Ra and ²³²Th activities have similar patterns.

Although in areas of very homogeneous lithology it is expected to find high correlations among radionuclides (Fairbridge, 1972), our results with data for all sites indicate that only ²³²Th with ²²⁶Ra (r= 0.556) and with ²³⁸U (r= 0.481) are directly and significantly correlated (99 %). Therefore, the only significant correlations are obtained between members of different decay series. The lack of correlation between members of the uranium decay series can be due to differences in mobility and transfer of the radionuclides within the soil profile.

²³⁸U and ²³²Th series commonly occur together in nature, thus in most natural systems there is a relatively constant ²³²Th/²³⁸U mass ratio (Ivanovich, 1994). Activity ratios (AR) between parent/parent or any progeny pairs can be applied to assess maintenance of the initial proportionality between ²³²Th and ²³⁸U decay series. Furthermore ²³⁸U/²²⁶Ra activity ratios can be used to ascertain equilibrium within the same decay series. If secular equilibrium prevails in the ²³⁸U chain, activity ratios of ²³⁸U/²²⁶Ra will be approximately 1, therefore, values other than 1 would indicate disequilibrium. As shown in Figure 3, there is a large variability in the values of activity ratios in the depth profiles. In general, in the upper layers of the studied profiles (0-15 cm), ²³⁸U/²²⁶Ra ratios are lower than 1.0. Apart from site 1 where AR below 1 occur in the first 10 cm, and site 4 that has AR values below 1 for most of the profile (till 30 cm depth). These AR values indicate a general strong disequilibrium in the ²³⁸U chain and

especially at upper and deeper soil layers. This could be due to large differences in mobility of these radionuclides. Differential mobility is widely recognized in the literature as cause of disequilibrium (Baweja et al., 1987; Collerson et al., 1991). Thus in the studied profiles, ^{238}U is intensively leached from the soil surface and it is transferred to deeper soil sections where it accumulates. In comparison, ^{226}Ra has very low mobility and remains quite constant. Therefore in this soil toposequence, the influence of soil properties and of water movement processes that cause ^{238}U leaching appear to greatly disturb the equilibrium of the system.

Along the soil toposequence, mean values of AR are quite homogenous and remain below 1, apart from the upper slope position (site 1) where values exceed 1 by 20%. This deviation is due to both low activities of ^{226}Ra and high mobility of ^{238}U . Because as it has been measured, under the dense forest that covers the upper sites, water infiltrates rapidly and consequently more water is available for leaching and transport of soil components downward the soil profiles.

$^{232}\text{Th}/^{226}\text{Ra}$ activity ratio (i.e. progeny pair $^{228}\text{Ac}/^{214}\text{Pb}$) is applied to assess the maintenance of the proportionality within ^{232}Th and ^{238}U decay series, that according to Evans et al. (1997) in most environmental samples is around 1.1. As can be seen in Figure 3, all soil profiles have $^{232}\text{Th}/^{226}\text{Ra}$ activity ratios higher than 1.1, deviations are slightly higher at the bottom slope site (5), but not significant differences have been found among the profiles. Therefore along the soil toposequence, the original proportionality has not been preserved, suggesting the main effect of soil processes in causing this deviation.

To assess the role of water movement in the soil profiles and its influence on leaching processes and the transfer of radionuclides and elements along the soil toposequence, the infiltration rate was measured at 4 of the soil slope positions. As can

be seen in Figure 4 there is a marked and gradual decrease in the rate of infiltration along the soil toposequence from sites 1 to 4. The rapid infiltration that occurs in sites 1 and 2, that especially in site 1 could be related to very high organic matter contents (12 %) in their upper layers together with the lowest clay percentage (6%), might facilitate the mobility of uranyl complexes that would accumulate at deeper layers. In turn the values of cumulative infiltration would suggest that soil processes related to water movement within the soil profile would most influence the edaphogenesis along this soil toposequence.

Depth distribution of major and trace elements (Figure 5) indicate that Mg, Na and K present quite constant depth distributions in all soil profiles, apart from the profile in site 3 where Mg and K show increasing concentrations with depth. Fe and Al exhibit some variability and especially Al that markedly decreases with depth in site 5 whereas it increases in site 3. Ca exhibits the highest variability within the soil profiles especially at the bottom slope positions. Thus a sharp increase is observed in site 3 where concentration in the upper 20 cm is less than 6000 mg kg^{-1} increasing up to 59000 mg kg^{-1} at the deepest layer. Also a gradual and marked increase occurs in site 5 where Ca ranges from 29000 to 85000 mg kg^{-1} at the upper and deeper layers respectively. These variations are related with the increase of carbonates at the deeper layers of the profiles. Ba, Li, and Zn keep quite constant with depth, as well as Pb apart from a slight decrease observed in deeper layers in site 5. Sr also varies little, apart from increases in deeper layers in sites 3 and 5. In all soil profiles, Mn shows a large variability. Ni, Co, and Cu vary little and in general have quite similar depth distributions whereas Cr shows a larger range of variation.

Concerning the distribution of major and trace elements along the soil toposequence, Al, Ca, Fe and K are in that order the most abundant with median

concentrations in the range of 41306, 32727, 27040 and 12953 mg kg⁻¹ respectively. Median Na and Mg concentrations are 3838 and 3521mg kg⁻¹ respectively. Less abundant are Mn (536 mg kg⁻¹), Ba (187 mg kg⁻¹), Pb (153 mg kg⁻¹), Sr (113 mg kg⁻¹), Li (106 mg kg⁻¹) and Zn (79 mg kg⁻¹). Co and Cu (2 mg kg⁻¹), Ni (3 mg kg⁻¹) and Cr (8 mg kg⁻¹) are trace elements whereas Cd has not been detected. These contents are within the range found in mountain soils of Aragón (Navas and Machín, 2002).

Figure 6 shows that Ca, Mg, Na, K and Sr have a similar trend along the soil toposequence characterized by a marked increase in their mean concentrations at the bottom slope positions (4 and 5), that are significantly different from values at upper slope positions in Kastanozems. Highest carbonate contents in Cambisols (sites 4 and 5) may explain much of Ca, Mg and Sr increases whereas abundance of finer soil fractions would most be the reason for the Na and K increases. Similarly, Al contents increase at bottom slope positions, and although this trend is not as marked this could be related to higher finer fraction (clay and silt) contents at the bottom slope positions. Iron decreases at bottom slope positions and the reason could be the lowest contents of Fe oxides in Cambisols. Manganese contents are also slightly lower in Cambisols and this could be due to the lower contents of Mn oxides at these bottom slope positions. Along the soil toposequence, Ba, Li and Pb do not show significant differences in their mean contents, apart from the highest Pb content at the upper slope position (site 1). Zn varies slightly along the slope and, in general, upper slope positions present higher mean contents. Co, Ni, Cu, and Cr follow a parallel trend along the soil toposequence and the most remarkable feature is their highest and significantly different mean contents in site 3 that could be related to mineral composition.

Results of correlations amongst elements (Table 3) indicate that Ca is positively correlated with Sr, Mg, K, and Na, and negatively with Mn, Zn and Ni. Al is positively

correlated with K, Mg, Na, Pb and Li that could be mainly due to their participation in the composition of clay minerals. Fe is highly positively related with the following minor elements Cr, Zn, Ni, Co. Also Mn is positively related to Zn, Ni, Cr. In turn these trace elements are highly correlated among them, these could indicate their association with Mn and Fe Oxides.

The correlations between radionuclides and major and trace elements confirm that Ca and Sr, that appear mainly related to carbonates in the studied profiles, are negatively correlated with ^{226}Ra ($r = -0.702$, $r = -0.672$, respectively), ^{232}Th ($r = -0.621$, $r = -0.607$, respectively), and ^{210}Pb ($r = -0.615$, $r = -0.623$, respectively). This in turn agrees with the negative correlation of these radionuclides with carbonates. ^{226}Ra and ^{232}Th are positively correlated with Fe ($r = 0.615$, $r = 0.681$, respectively), and less significantly with Mn ($r = 0.570$, $r = 0.493$, respectively), in relation with the association of these radionuclides with Fe and Mn oxides. Moreover the positive correlations of ^{226}Ra and ^{232}Th with Zn ($r = 0.589$, $r = 0.500$, respectively), Cr ($r = 0.546$, $r = 0.578$, respectively), and Ni ($r = 0.610$, $r = 0.628$, respectively), that also appear related with Fe and Mn oxides seem to support this fact.

The relationships between soil properties and major and trace elements (Table 4) confirm the high and positive correlation between Ca and Sr with carbonates and the negative ones with Fe and Mn oxides. Similar relationships although not so strong have been observed for Na, K and Mg. As expected, the contrary is observed for Fe and Mn, as well as for Zn and Ni, that would suggest their associations with Fe and Mn oxides.

An ANOVA test was performed to analyse if soil depth had any effect on the variation of soil properties, radionuclides and major and trace elements. The results indicated that only ^{238}U , ^{210}Pb and on the other hand organic matter, clay, sand and pH were significantly affected by soil depth. The same analysis considering the site along

the soil toposequence as source of variation yielded totally opposite results. Thus ^{226}Ra , ^{232}Th , carbonates, Fe and Mn oxides, silt, sand, pH, as well as all elements apart from Pb, Ba and Li varied significantly in function of the position on the slope. Therefore ^{238}U and ^{210}Pb variations seem to more willingly respond to soil processes (leaching and accumulation of soil particles respectively) than to other reasons such as physiography and soil type (mineral composition and soil properties). However, the latter appear to be the main cause of variation for most of the major and trace elements as well as for ^{226}Ra and ^{232}Th .

CONCLUSIONS

The background levels of radionuclides and major and trace elements determined in this study are potentially useful for research on radioactivity and biogeochemical cycles in the natural environment of the Flysch Sector in the central Spanish Pyrenees. Among the radionuclides very different behaviour has been distinguished. Thus, ^{226}Ra and ^{232}Th have quite constant depth distributions and restricted mobility, whereas ^{238}U and ^{210}Pb present a large variability in their profile distributions.

Along the soil toposequence, the variation of radionuclide activities appears to be influenced by some soil properties such as pH, carbonates and Fe and Mn oxides that differently affect the mobilization of natural radionuclides. The higher mobility of ^{238}U seems to be affected by variations in soil pH and its leaching down the profiles is favoured by high infiltration rates. However, the depth distribution of ^{210}Pb suggests a relation with physical processes such as soil particle movement and deposition.

$^{238}\text{U}/^{226}\text{Ra}$ activity ratios as measure of disequilibrium caused by different mobility of the radioisotopes can be applied to deviate information on intensity of soil processes, such as the difference in leaching intensity that has been observed in the different sites along the soil toposequence.

The correlations found between radionuclides and elements are in agreement with their respective separated relationships with soil properties and helped to explain their behaviour. Variations of most of the major and trace elements as well as of ^{226}Ra and ^{232}Th are significantly affected by the position of the sites reflecting the influence of soil composition and properties. In contrast variations of ^{238}U and ^{210}Pb seems to more willingly respond to soil processes such as leaching and the transport and accumulation of soil particles respectively.

ACKNOWLEDGEMENTS

We thank the EEC project "VAHMPIRE" (EN AA 123431. PL. 1995-1999) and CICYT project "RADIERO" (REN2002-02702) for financial support.

REFERENCES

- Baeza, A., M. del Río, A. Jiménez, C. Miró, and J. Paniagua. 1995. Influence of geology and soil particle size on the surface-area/volume activity ratio for natural radionuclides. *J. Radioanal. Nucl. Ch.* 189:289-299.
- Barisic, D., S. Lulic, and P. Miletic. 1992. Radium and uranium in phosphate fertilizers and their impact on the radioactivity of waters. *Water Res.* 26:607-611.
- Baweja, A. S., S. R. Joshi, and A. Demayo. 1987. Radionuclide content of some Canadian surface waters: a report on the national radionuclides monitoring

- program, 1981-1984. Inland Waters Directorate, Environment Canada, Scientific Series, No. 156.
- Baxter, M. S. 1991. Personal perspectives on radioactivity in the environment. *Sci. Total Environ.* 100:29-42.
- Beck, H. L. 1972. The physics of environmental gamma radiation fields. In : Proceedings 2nd International Symposium on Natural Radiation Environment, Houston, TX, NATL, Springfield, VA, p.101-301.
- Buurman, P., Th. Pape, and C. C. Muggler. 1997. Laser grain-size determination in soil genetic studies: I. Practical problems. *Soil Sci.* 162:211-218.
- Collerson, K. D., D. J. Gregor, D. McNaughton and A. S. Baweja. 1991. Effect of coal dewatering and coal use on the water quality of the East Poplar River, Saskatchewan. A literature review. Inland Waters Directorate, Environment Canada, Scientific Series, No. 177.
- Cowart, J. B., and W. C. Burnett. 1994. The distribution of uranium and thorium decay-series radionuclides in the environment. *J. Environ. Qual.* 23:651-662.
- CSIC 1976. Comisión de métodos analíticos. *An. Edafol. Agrobiol.* 35:813-814.
- de Jong, E., D. F. Acton, and L. M. Kozak. 1994. Naturally occurring gamma-emitting isotopes, radon release and properties of parent materials of Saskatchewan soils. *Can. J. Soil Sci.* 74:47-53.
- Elejalde, C., M. Herranz, F. Romero, and F. Legarda. 1996. Correlations between soil parameters and radionuclide contents in samples from Biscay (Spain). *Water Air Soil Poll.* 89:23-31.
- Evans, C. V., L. S. Morton, and G. Harbottle. 1997. Pedologic assessment of radionuclide distributions: use of a radio-pedogenic index. *Soil Sci. Soc. Am. J.* 61:1440-1449.

- Fairbridge, R. W. 1972. The encyclopedia of geochemistry and environmental sciences. Van Nostrand Reinhold Co., New York. No. 4A. p. 1215-1228.
- Gee, G. W., and J. W. Bauder. 1986. Particle-size analysis. *In* Methods of soil analysis, part 1: physical and mineralogical methods. A. Klute (ed.). 2nd edn., Agronomy. 9:383-411. Soil Sci. Am. Madison, USA,
- Guitian, F., and Carballas, T. 1976. Técnicas de análisis de suelos. Ed. Pico Sacro. Santiago de Compostela. p. 288.
- Ivanovich, M. 1994. Uranium series disequilibrium: Concepts and applications. *Radiochim Acta*. 64:81-94.
- Jasinska, M., T. Niewiadomski, and J. Schwbenthan. 1982 . Correlation between soil parameters and natural radioactivity. *In* Natural radiation environment. K.Vohra, U. C. Mishra, K. C. Pillai and S. Sadasivan (eds). John Wiley and Sons, New York. p. 206-211.
- Jordan, C., J. G. Cruickshank, A. J. Higgins and K. P. Hamill. 1997. The soil geochemical atlas of Northern Ireland. Department of Agriculture for Northern Ireland. Belfast. UK.
- Kabata-Pendias, A., and H. Pendias. 2001. Trace elements in soils and plants. 3rd ed. CRC. Boca Raton, Fla. p. 413.
- Kiss, J. J., E. de Jong, and J. R. Bettany. 1988. The distribution of natural radionuclides in native soils of southern Saskatchewan, Canada. *J. Environ. Qual.* 17:437-445.
- Litaor, M. I. 1995. Uranium isotopes distribution in soils at the Rocky Flats Plant, Colorado. *J. Environ. Qual.* 24:314-323.
- McGrath, S. P. and P. J. Loveland. 1992. The Geochemical Atlas of England and Wales. Chapman and Hall, London. p. 102 .

- Megumi, K., T. Oka, K. Yaskawa, and M. Sakanoue. 1982. Contents of natural radioactive nuclides in relation to their surface area. *J. Geophys. Res.* 87:10857-10860.
- Navas, A., J. Soto, and J. Machín. 2002. ^{238}U , ^{226}Ra , ^{210}Pb , ^{232}Th and ^{40}K activities in soil profiles of the Flysch sector (Central Spanish Pyrenees). *Appl. Radiat. Isotopes.* 57 (4):579-589.
- Navas, A., J. Soto, and J. Machín. 2002. Edaphic and physiographic factors affecting natural gamma emitting radionuclide distribution in soils of the Arnás basin (Central Spanish Pyrenees). *Eur. J. Soil Sci.* 53:629-638.
- Navas, A., and J. Machín. 2002. Spatial distribution of heavy metals and arsenic in soils of Aragón (NE Spain): controlling factors and environmental implications. *Appl. Geochem.* 17:961-973.
- Navas, A., J. Machín and J. Soto. 2005. Assessing soil erosion in a Pyrenean mountain catchment using GIS and fallout ^{137}Cs . *Agr. Ecosystems & Environ.* 105: 493-506.
- Pardini, G., R. Aringhieri, F. Plana, and F. Gallart. 1991. Soil properties relevant to land degradation in abandoned sloping fields in Aisa valley, Central Pyrenees (Spain). *Pirineos*, 137:79-93.
- Quindós, L., P. Fernández, J. Soto, C. Ródenas, and J. Gómez. 1994. Radioactivity in Spanish soils. *Health Phys.* 66:194-200.
- Rosholt, J. N., B. R. Doe, and M. Tatsumoto. 1966. Evolution of the isotopic composition of uranium and thorium in soil profiles. *Geol. Soc. Am. Bull.* 77:987-1004.
- Salim, I., C. Miller, J. Howard. 1993. Proc. Joint CSCE-ASCE Nat. Conf. Environm. Eng., I. Montreal, July 1993.I, p. 821-827.

- Schwertmann, U. 1964. The differentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate. *Z. Pflanzenernähr. Bodenkd.* 105:194-201.
- Sully, M. J., R. G. Flocchini, and D. R. Nielson. 1987. Linear distribution of naturally-occurring radionuclides in a Mollic Xerofluvent. *Soil Sci. Soc. Am. J.* 51:276-281.
- Van Cleef, D. J. 1994. Determination of ^{226}Ra in soil using ^{214}Pb and ^{214}Bi immediately after sampling. *Health Phys.* 67:288-289.
- VandenBygaart, A. J, and R. Protz. 1995 Gamma radioactivity on a chronosequence, Pinery Provincial Park, Ontario. *Can. J. Soil Sci.* 75:73-84.
- Winde, F. 2001. Uranium Contamination of rivers – mechanisms and processes investigated in mining areas of Germany and South Africa. *In Environmental change and sustainability, Abstract Book, Zaragoza, Spain, July 2-6,2001.*
- Wilcke, W., S. Kretzschmar, M. Bundt, G. Saborío, and W. Zech. 1998. Aluminum and heavy metal partitioning in a horizons of soils in Costa Rican coffee plantations. *Soil Sci.* 163(6):463-471.

FIGURES

- 1.- Location of the study area in the Lubierre river basin in the Flysch Sector of the Central Spanish Pyrenees.
- 2.- Concentrations of the natural radionuclides in the 5 cm interval samples of the soil profiles in the sites along the soil toposequence.
- 3.- Mean activities of the natural radionuclides and mean activity ratios in the sites along the soil toposequence.
- 4.- Infiltration rates and cumulative infiltration measured in 4 sites along the soil toposequence.
- 5.- Concentrations of major and trace elements in the 5 cm interval samples of the soil profiles in the sites along the soil toposequence.
- 6.- Mean concentrations of major and trace elements in the sites along the soil toposequence.

TABLES

- 1.- Values of pH and carbonate, organic matter, Fe and Mn oxides and clay, silt and sand contents in the 5 cm interval samples of the soil profiles in the sites along the soil toposequence.
- 2- Pearson correlation coefficients between soil properties and the radionuclide contents in the studied soils.
- 3.- Pearson correlation coefficients between major and trace elements in the studied soils.
- 4.- Pearson correlation coefficients between soil properties and major and trace elements contents in the studied soils.

Table 1.- Values of pH and carbonate, organic matter, Fe and Mn oxides and clay, silt and sand contents in the 5 cm interval samples of the soil profiles in the sites along the soil toposequence.

Site	Depth	pH	CO ₃ ²⁻	OM	Fe oxides	Mn oxides	Clay	Silt	Sand
	cm		%		mg/100g		%		
1	0-5	7.77	3.1	12.0	910	29	6.2	67.8	26.0
	5-10	7.94	10.5	8.2	979	31	8.2	72.2	19.6
	10-15	8.18	11.3	5.6	981	31	8.9	68.2	22.9
	15-20	8.22	13.8	4.0	977	30	12.0	73.2	14.8
	20-25	8.22	14.2	3.6	860	12	11.7	64.9	23.4
	25-30	8.27	11.6	3.2	1002	30	12.6	65.3	22.1
	30-35	8.23	13.4	3.3	1046	32	15.9	74.3	9.8
	35-40	8.26	11.3	3.0	1058	31	16.1	75.5	8.4
	40-45	8.27	12.0	3.0	1044	30	16.0	69.9	14.1
	45-50	8.31	10.1	2.5	1092	32	16.7	77.0	6.3

2	0-5	7.81	0.97	9.2	1162	40	9.2	74.4	16.4
	5-10	7.84	2.0	8.2	1149	38	10.5	71.1	18.4
	10-15	7.96	2.9	6.4	1160	39	11.9	71.8	16.3
	15-20	8.07	2.5	4.1	1180	38	15.3	77.0	7.7
	20-25	8.30	3.2	2.9	1206	39	17.1	74.5	8.4
	25-30	8.24	2.6	3.1	971	29	15.6	75.5	8.9
	30-35	8.28	2.7	2.5	1212	40	15.5	70.7	13.8
	35-40	8.27	2.4	2.8	1192	38	16.4	76.0	7.6
	40-45	8.21	2.4	2.7	1255	40	15.7	75.9	8.4
	45-50	8.22	2.3	2.7	1249	40	18.5	79.0	2.5

3	0-5	7.50	1.0	8.1	1162	41	11.4	69.8	18.8
	5-10	7.85	0.71	5.8	1203	39	11.9	65.5	22.6
	10-15	7.93	0.88	3.9	1224	38	13.3	76.2	10.5
	15-20	7.98	0.93	3.8	1230	38	13.1	74.2	12.7
	20-25	8.05	1.3	3.4	1240	38	14.4	73.7	11.9
	25-30	8.16	2.8	2.9	1215	34	15.1	78.6	6.3
	30-35	8.28	8.5	2.7	1154	29	15.2	76.1	9.0
	35-40	8.38	18.0	2.3	1044	23	18.2	80.5	1.3

	0-5	7.97	12.6	9.6	886	22	9.9	62.4	27.7
	5-10	8.05	12.2	6.4	893	22	10.3	61.9	27.8
	10-15	8.19	16.2	4.8	902	21	11.0	68.5	20.5
	15-20	8.23	8.5	4.1	928	21	13.2	68.0	18.8
4	20-25	8.18	17.5	4.6	905	20	14.4	68.4	17.2
	25-30	8.26	20.3	3.0	883	18	16.6	70.2	13.2
	30-35	8.33	19.2	3.5	862	18	16.4	70.1	13.5
	35-40	8.29	16.8	3.0	922	22	15.2	70.7	14.1
	40-45	8.26	13.7	3.4	1029	28	15.7	70.3	14.0
	45-50	8.23	13.2	3.4	954	25	15.0	69.3	15.7

	0-5	8.07	6.8	7.0	963	32	10.4	81.0	8.6
	5-10	8.12	7.9	4.9	970	32	10.6	75.0	14.4
	10-15	8.24	11.6	3.9	963	30	12.5	74.0	13.5
	15-20	8.27	12.1	2.8	924	27	14.0	76.4	9.6
5	20-25	8.33	14.1	4.7	936	24	15.8	75.5	8.7
	25-30	8.41	21.5	3.2	886	20	18.3	77.7	4.0
	30-35	8.37	24.4	2.2	669	32	17.9	79.2	2.9
	35-40	8.49	25.8	1.7	824	16	18.6	77.6	3.8
	40-45	8.49	28.8	1.8	795	14	20.5	79.4	0.1

Table 2 - Pearson correlation coefficients between soil properties and the radionuclide contents in the studied soils.

		²³⁸ U	²³² Th	²²⁶ Ra	²¹⁰ Pb
		Bq kg⁻¹			
Clay	%	0.382	0.126	-0.012	-0.581
Silt	%	0.167	0.287	-0.046	-0.228
Sand	%	-0.286	-0.252	0.037	0.417
Mn oxides	mg/100 g	0.149	0.645	0.578	0.437
Fe oxides	mg/100 g	0.133	0.637	0.596	0.222
Organic matter	%	-0.568	-0.228	-0.033	0.564
Carbonates	%	-0.046	-0.614	-0.635	-0.563
pH		0.373	-0.156	-0.336	-0.652

Table 3.- Pearson correlation coefficients between major and trace elements in the studied soils.

	Ca	Al	Fe	K	Mg	Na	Mn	Ba	Pb	Sr	Li	Zn	Cr	Ni	Co	Cu
Ca	1															
Al	0.314	1														
Fe	-0.692	0.089	1													
K	0.750	0.740	-0.338	1												
Mg	0.826	0.647	-0.455	0.916	1											
Na	0.649	0.530	-0.260	0.669	0.797	1										
Mn	-0.757	-0.189	0.764	-0.518	-0.589	-0.444	1									
Ba	0.340	0.501	0.055	0.552	0.452	0.429	-0.129	1								
Pb	-0.240	0.811	0.509	0.327	0.150	0.132	0.253	0.346	1							
Sr	0.964	0.336	-0.637	0.802	0.895	0.716	-0.698	0.374	-0.205	1						
Li	0.085	0.699	0.474	0.555	0.411	0.441	0.073	0.502	0.735	0.188	1					
Zn	-0.708	-0.091	0.837	-0.355	-0.414	-0.238	0.712	-0.039	0.348	-0.575	0.372	1				
Cr	-0.488	0.048	0.917	-0.199	-0.285	-0.139	0.668	0.110	0.336	-0.428	0.478	0.735	1			
Ni	-0.583	-0.085	0.916	-0.314	-0.400	-0.215	0.724	0.071	0.310	-0.493	0.448	0.882	0.905	1		
Co	-0.215	-0.108	0.645	-0.041	-0.059	0.024	0.468	0.029	0.021	-0.106	0.410	0.654	0.818	0.786	1	
Cu	-0.040	0.082	0.442	0.040	0.080	0.279	0.256	0.048	0.028	-0.004	0.264	0.252	0.623	0.426	0.566	1

Table 4.- Pearson correlation coefficients between soil properties and major and trace elements contents in the studied soils.

	Ca	Al	Fe	K	Mg	Na	Mn	Ba	Pb	Sr	Li	Zn	Cr	Ni	Co	Cu
	mg kg⁻¹															
Clay %	0.401	0.019	-0.099	0.164	0.166	0.255	-0.266	0.395	-0.122	0.361	0.160	-0.270	-0.027	0.064	-0.003	0.035
Silt %	0.098	0.018	0.156	-0.141	-0.133	-0.041	0.011	0.163	0.026	-0.018	0.030	-0.090	0.193	0.186	-0.045	0.030
Sand %	-0.247	-0.021	-0.062	0.022	0.016	-0.087	0.112	-0.289	0.037	-0.150	-0.092	0.183	-0.119	-0.155	0.032	-0.036
Mn oxides mg/100 g	-0.826	-0.345	0.607	-0.790	-0.776	-0.526	0.695	-0.280	0.144	-0.836	-0.122	0.540	0.434	0.521	0.127	0.036
Fe oxides mg/100 g	-0.629	-0.324	0.527	-0.610	-0.559	-0.315	0.492	-0.082	0.022	-0.601	-0.069	0.517	0.441	0.541	0.279	0.088
Organic matter %	-0.351	-0.221	-0.028	-0.242	-0.217	-0.265	0.206	-0.453	-0.121	-0.313	-0.330	0.199	-0.041	-0.110	-0.025	0.004
Carbonates %	0.945	0.292	-0.731	0.745	0.761	0.544	-0.758	0.347	-0.228	0.905	0.047	-0.755	-0.552	-0.627	-0.291	-0.099
pH	0.661	0.424	-0.323	0.534	0.539	0.483	-0.605	0.513	0.108	0.608	0.275	-0.488	-0.293	-0.269	-0.268	-0.142

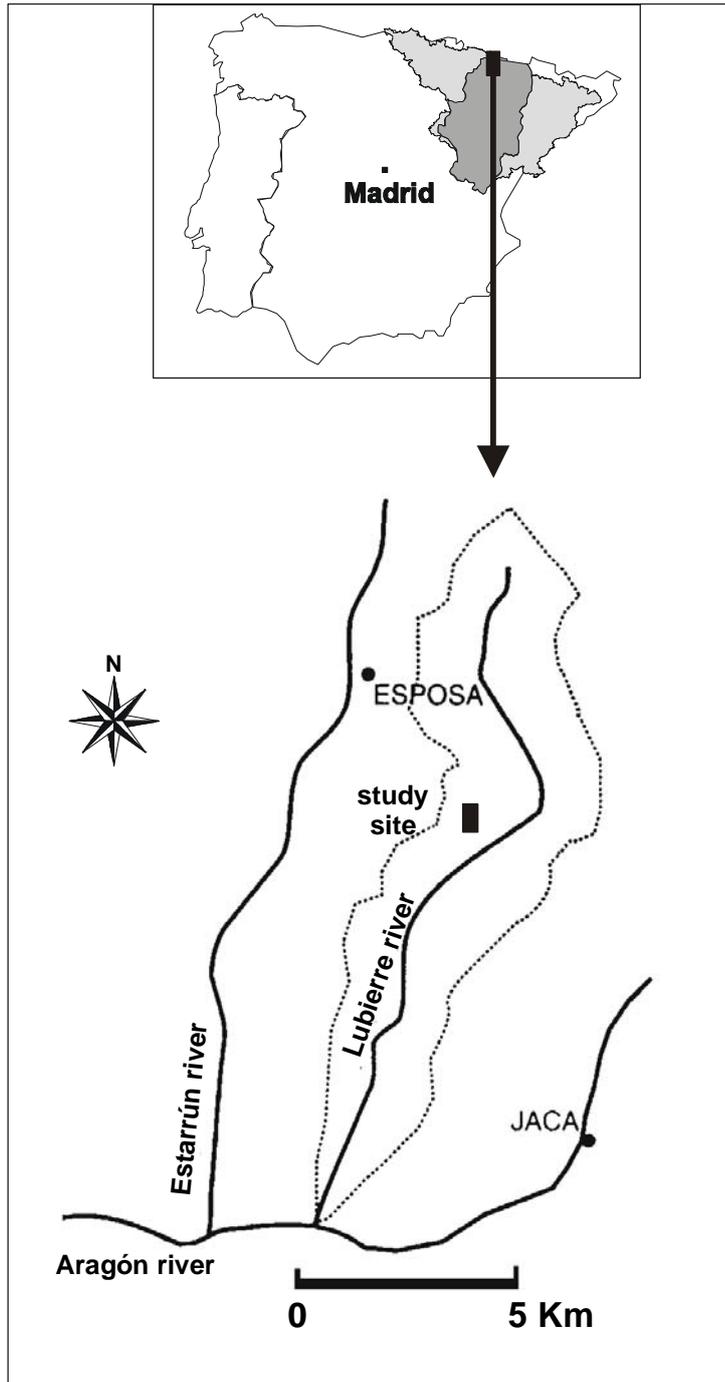


Fig. 1

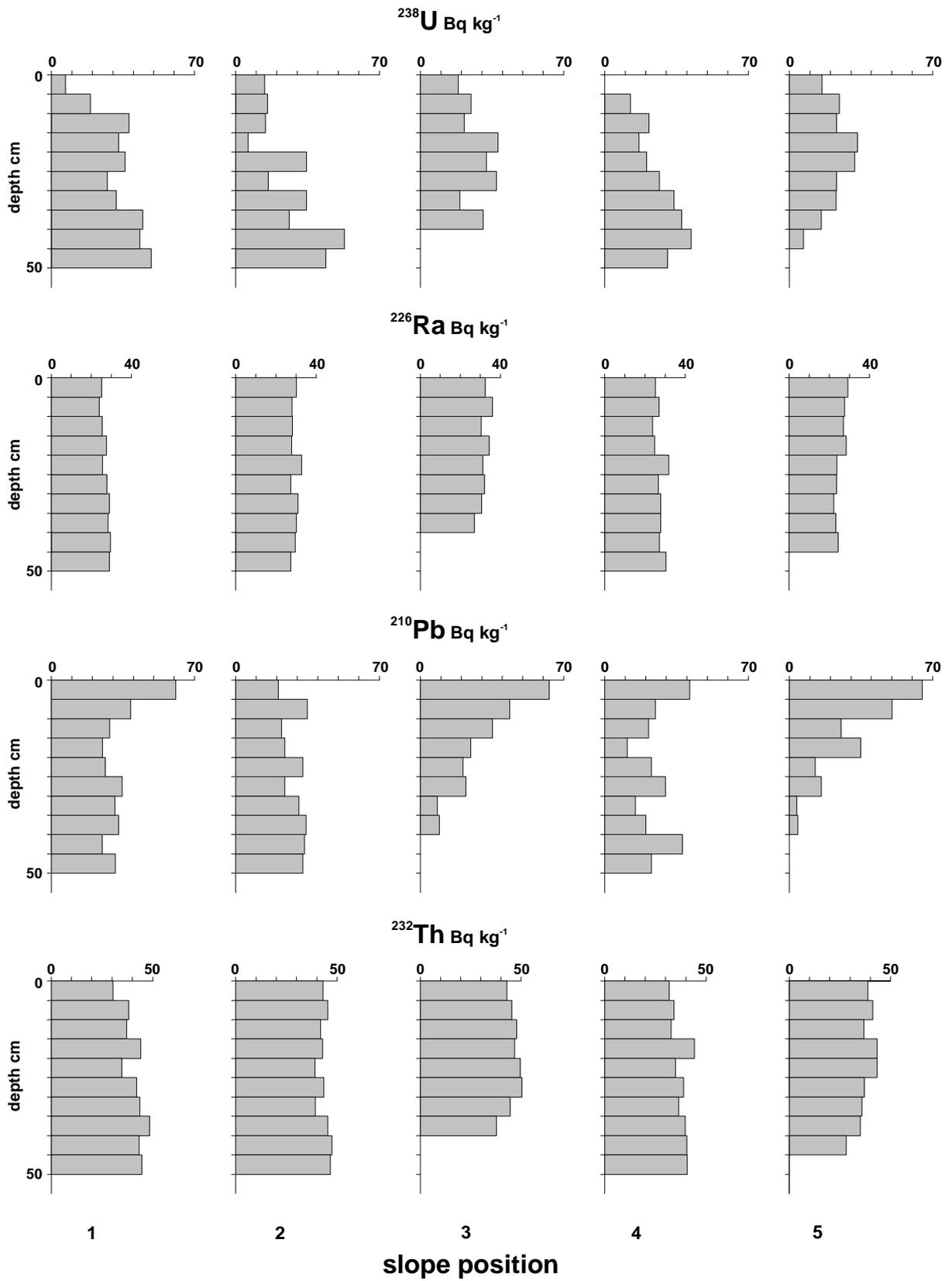


Fig. 2

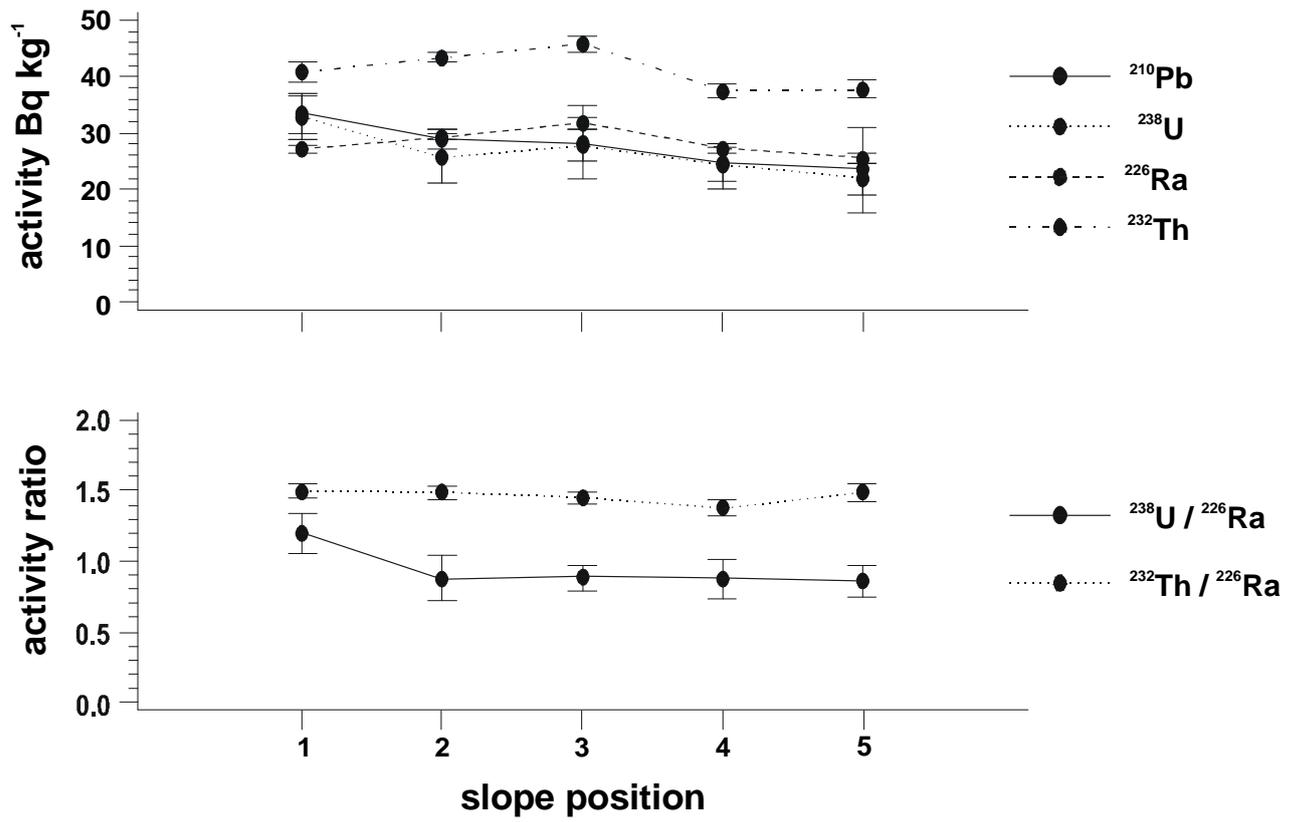


Fig. 3

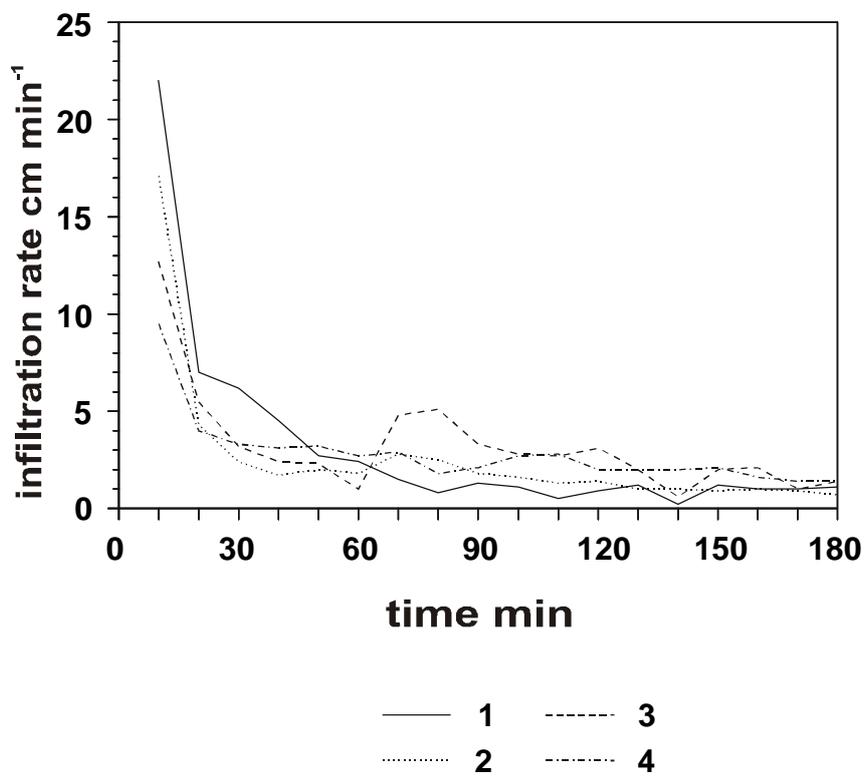


Fig. 4

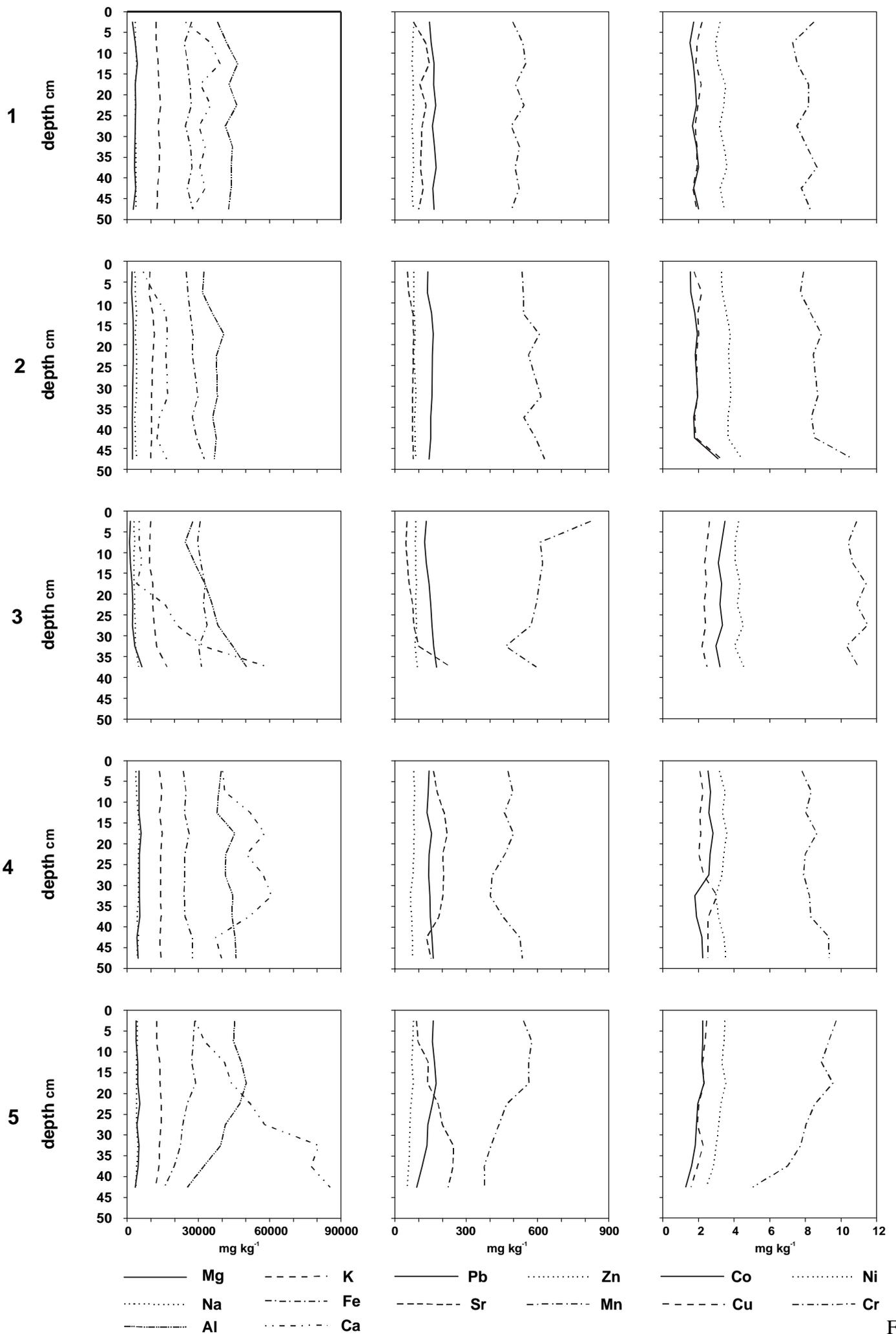


Fig. 5