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Speciation of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra, and stable Pb in the soil near an exhaust ventilating shaft of a uranium mine

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Abstract

A sequential extraction procedure was applied to investigate the speciation of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra and stable lead in a contaminated agricultural soil near an exhaust ventilating shaft of an uranium mine and in a control soil. Using a radiochemical separation procedure and gamma spectrometry as well as low-level beta counting, we determined the percentages of each of these radionuclides in the "readily exchangeable ions" fraction, in the "bound to carbonates" fraction, and in the "bound to Fe and Mn oxides" fraction. In the contaminated soil samples we observed that the percentages of ^{238}U, ^{226}Ra and ^{210}Pb in each fraction were about ≤ 3–30%, but different for each of these three radionuclides. The largest "readily exchangeable ions" fraction was observed in this soil for ^{210}Pb (19%), the smallest for ^{238}U ($\leq 3\%$). For all radionuclides and for all three fractions the amounts extracted from the contaminated soil were significantly higher than the control soil samples. Possible reasons for this observation are discussed. For both soils the activities of ^{238}U in the "readily exchangeable ions" fraction, and of ^{228}Ra in all three fractions were below our detection limit ($\sim 3\%$). Stable lead was mostly associated with the "bound to Fe and Mn oxides" fraction.

1. Introduction

In our environment, especially in the soil, naturally occurring radionuclides from the uranium and thorium decay series can be found. These terrestrial radionuclides contribute to the external radiation as well as to the internal doses incurred by man. In addition to these

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natural sources, however, a variety of natural radionuclides have been introduced to the biosphere by anthropogenic activities, e.g. as a result of uranium mining. In a recent paper we reported the effect of the exhaust air from a uranium mine on the activity concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra in an agricultural soil near the ventilating shaft (Bunzl et al., 1994). These data revealed that increased concentrations of these radionuclides could be observed up to a distance of about 40 m in the field. The largest effect was observed for ^{210}Pb (increase by one order of magnitude) and the smallest for ^{228}Ra.

Because these radionuclides are generally incorporated in the soil minerals to a considerable extent, only a fraction can take part in short-term geochemical processes, such as vertical migration or root uptake by plants. Thus, to estimate, a possible long-term radiation hazard of radionuclides in the soil, not only their total concentration but also their speciation and availability for ecological processes has to be known.

The speciation of stable heavy metal ions in the soil is frequently studied by using sequential extraction procedures (Tessier et al., 1979). It was thus possible to estimate the fraction of "readily exchangeable ions" (fraction I), of "bound to carbonates" (fraction II), of "bound to iron and manganese oxides" (fraction (III), of "bound to organic matter" (fraction IV), and of "residual ions" (fraction V). While sequential extraction procedures have been frequently applied to investigate the behavior of heavy metals in the soil and sediments, this method has been used to study the speciation of natural radionuclides only in a few cases. Voss et al. (1983) observed that of the various organic solvents used only HOAc removed considerable amounts of ^{210}Pb and ^{226}Ra from the soil. Cooper et al. (1981) found that in soils from Australia significant differences exist between ^{210}Pb and ^{226}Ra in their distribution among the various fractions, with very little ^{226}Ra present in the residual fractions. Very low concentrations of these radionuclides were present in the fraction "bound to carbonates". If iron oxides are present, both radionuclides were associated mainly with the "bound to oxides" fractions. Lima and Penna-Franca (1988) observed that in farm soils from a highly radioactive region in Brazil, about 50% of ^{226}Ra was associated with the residual fraction V, 30% with fraction III, 15% with fraction IV, 5% with fraction II, and 3% with fraction I.

The purpose of the present investigation was to investigate the speciation of ^{238}U, ^{226}Ra, ^{210}Pb and ^{228}Ra in the agricultural soil which was found to be contaminated with these radionuclides due the exhaust air from the uranium mine, and to compare these results with the soil at a distance from the ventilating shaft where anthropogenically introduced radionuclide levels were not detectable.

For comparison we also included stable lead in this study. Stable lead is associated in the soil with fractions III and IV (Zeien and Brümmer, 1991), in fraction V (Cruz et al., 1986), in fraction II (Gibson and Farmer, 1986; Chang et al., 1984) and to some extent in all other fractions.

2. Materials and methods

2.1. Site

The exhaust ventilation shaft of the uranium mine is located in a rural area in Thüringen, Germany, about 4 km south of the small village Ronneburg. This ventilation shaft was

operated since January 1970 by the Wismut AG. Even though the mine was closed down in December 1990, part of the ventilation system is still working. As a result, radon (which emanates from the underground rock material even after the termination of mining) as well as its decay products are still released into the environment via the exhaust air shaft.

The concrete construction which houses the exhaust fan has a vertical 4 m × 4 m rectangular outlet for the air, through which the exhaust air is blown out parallel to the soil surface. On average, 2×10^9 to 5×10^9 m^3 air were released per year. At a distance of about 10 m from the exhaust outlet, and separated by a wire fence, is the corn field from which the soil samples were taken. Representative data on the annual discharge of the above natural radionuclides by the exhaust air during the years of operation of the mine are not available.

2.2. *Soil sampling*

Soil samples were taken at two locations. Location A was about 10 m down wind from the actual air outlet, where we observed previously in a transect survey (Bunzl et al., 1994) considerably increased concentrations of ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra. Because the transect survey, conducted between 10 and 210 m, revealed that at distances exceeding about 50 m from the air outlet the concentrations of these radionuclides were constant, we selected as the location for the unaffected control soil (location B) a point at about 206 m distance.

At each sampling point A and B, 4 samples were taken separately at the corners of a 0.5 m × 0.5 m square from the 0–25 cm layer of the soil. Because the deposition of the contaminants occurred essentially only in earlier years (see above), and the field was plowed and harrowed since that time regularly, the vertical distribution of the deposited radionuclides will be meanwhile rather uniform. Sampling at different depths in the Ap horizon to evaluate the depth profile of the above radionuclides was, therefore, not carried out.

Analysis of the soil at locations A and B showed that their properties were not exactly the same, as would have been desirable. Soil A was a silt loam, pH 4.1 ($CaCl_2$), clay 25%, silt 51%, sand 24%, ion exchange capacity 13.2 meq/100 g; loss on ignition 4.6%. Soil B was also a silt loam, pH 6.4 ($CaCl_2$), clay 17%, silt 67% sand 16%, ion exchange capacity 12 meq/100 g; loss on ignition 3.5%. The carbonate contents of both soils was very low ($< 1\%$).

The soil samples from each sampling point were air dried and passed through a 2 mm sieve.

2.3. *Gamma-ray spectrometry*

The total activity concentrations of the radionuclides in the soil and in the soil extracts were (except for ^{210}Pb in the soil extracts, see below) determined by direct gamma spectrometry. An amount of 105–130 g dry soil was filled into a cylindrical polyethylene vessel (75 mm in diameter, 30 mm height). Similarly, 500 ml of the soil extracts were filled in Marinelli beakers. The vessels were sealed gas-tight using insulating tape and stored for at least two weeks to allow radioactive equilibrium of the ^{226}Ra series. After that time the samples were measured for at least 1200 minutes, using a well shielded low-level gamma-ray spectrometer with a high purity Ge-detector (33.9% rel. efficiency at 1.33 MeV).

Nuclear data for the respective radionuclides of interest were taken from Schötzig and Schrader (1989).

^{226}Ra was determined via the gamma lines of the daughter products ^{214}Pb (295.2 and 351,9 keV) and ^{214}Bi (609.3 keV). For the determination of ^{228}Ra the lines of ^{212}Pb (238.6 keV), ^{208}Tl (583.2 keV) and ^{228}Ac (911.1 keV) were used. To correct for photon attenuation of the low energy gamma-rays of ^{210}Pb (46.5 keV) and of ^{234}Th (63.3 keV and 92.4 + 92.8 keV) the ratio of the attenuation coefficients of the calibration source and the actual soil sample material was determined with point sources of ^{210}Pb, ^{241}Am (59.4 keV), ^{57}Co (122.1 and 136.5 keV) and ^{137}Cs (661.7 keV). This ratio is an estimate of the actual efficiency ratio (Debertin and Helmer, 1988). If relevant, coincidence summing correction was applied, e.g. a factor of 1.13 for the 609.3 keV line of ^{214}Bi. The ^{226}Ra sample activity was calculated by use of the 186.2 keV line of ^{226}Ra and the lines of the daughter products given above. The 186.2 keV line was corrected for the contribution of ^{235}U (185.7 keV) via its 143.8 keV line. Similarly the ^{228}Ra activity was obtained as the mean of the measured activities of ^{212}Pb, ^{208}Tl and ^{228}Ac. ^{238}U was assumed to be in radioactive equilibrium with ^{234}Th and ^{234m}Pa. Its activity was calculated from the 63.3 keV line and the complex line at 93 keV of ^{234}Th and from the 1001 keV line of ^{234m}Pa (Siemon et al., 1991).

02.4. Radiochemical determination of ^{210}Pb

Because concentrations of ^{210}Pb in the soil extracts were too low to be determined by direct gamma-spectrometry, this radionuclide was determined after radiochemical separation (Bunzl et al., 1984) via its beta activity in a low-level beta counter.

2.5. Determination of stable lead

Pb in the soil extracts as well as total Pb in the soil was determined by high resolution ICP-spectrometry. In the latter case Pb was first leached from the soil with aqua regia. Reagent grade chemicals were used throughout. In addition, any contacts of the soil during sampling, storage, or processing the samples with materials which could release Pb were avoided.

2.6. Sequential extraction

The sequential extraction of the radionuclides and of stable lead from the soil samples was performed according to Tessier et al. (1979) as follows:

(i) Readily exchangeable cations (fraction I). 100 g soil were extracted with 800 ml $MgCl_2$ (1M, pH 7.0) at room temperature for 1 hour while stirring from above. Subsequently, the suspension was first passed through a paper filter (Schleicher and Schuell, 589 Black, coarse grade, 9 cm in diameter) and finally through a membrane filter (1.2 μm). The solution phase was used for analysis and the soil phase rinsed with ca. 300 ml distilled water. The rinse water is added to the solution phase.

(ii) Bound to carbonates (fraction II). The above residue is extracted for 5 h at room temperature with 800 ml 1M CH_3COONa, adjusted to pH 5.0 with acetic acid. The subsequent separation of the liquid phase and rinsing of the soil is performed as above.

(iii) Bound to Fe–Mn Oxides (fraction III). The residue from above was extracted with 800 ml 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) acetic acid at 85–95°C for 6 hours with occasional agitation.

Because we were mainly interested in the available fractions of the radionuclides in the soil, the next step in the Tessier procedure, i.e., complete destruction of the organic matter by hydrogen peroxide, was not performed. Note, however, that radionuclides bound to soil organic matter in a readily exchangeable form are already included in fraction I.

2.7. *Estimation of errors*

The errors (coefficients of variation) of the analytical determinations were generally less than 10%. To test the reproducibility of the extraction procedures we repeated the sequential extraction of fractions I, II, and III four times using fresh 100 g aliquots of a large homogenized sample of soil A. The resulting coefficients of variation as tested by analyzing ^{210}Pb in each fraction were smaller than 10%. Quality control over the accuracy of the data was assured by analyzing standard reference samples (e.g. NBS Coal SRM 1632a).

3. Results and discussion

3.1. *^{228}Ra, ^{226}Ra, and ^{210}Pb*

The total activity concentrations of the natural radionuclides ^{238}U, ^{228}Ra, ^{226}Ra, and ^{210}Pb in the soil at the two locations A and B (control) are given in Table 1. If we compare the

Table 1
Activity concentrations (in Bq g^{-1}) of several natural radionuclides and of stable lead (in mg kg^{-1}) in the soil

	^{238}U	^{226}Ra	^{210}Pb	^{228}Ra	Pb
Soil A					
a	0.20	0.13	1.3	0.052	19
b	0.19	0.16	0.96	0.051	17
c	0.48	0.37	2.4	0.050	24
d	0.23	0.14	1.6	0.055	23
Mean	0.28	0.20	1.5	0.052	21
St. dev.	0.14	0.11	0.6	0.002	3.3
Soil B					
a	0.084	0.060	0.071	0.047	19
b	0.077	0.060	0.056	0.048	18
c	0.087	0.056	0.061	0.048	18
d	0.080	0.069	0.070	0.047	20
Mean	0.082	0.061	0.065	0.048	19
St. dev.	0.004	0.006	0.007	0.001	0.95

Soil A is close to the exhaust ventilating shaft of the uranium mine, soil B is from the same field but from a distance